EFFECT OF FILLERS ON DEGRADATION OF POLYSTYRENE (NANO)COMPOSITES

Bc. Barbora Hanulíková

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Ústav inženýrství polymerů

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děkan

Roman
doc. Ing. Roman Čermák, Ph.D.
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ABSTRAKT

Polymerní nanokompozity jsou v dnešní době oblíbenou a často studovanou skupinou materiálů. Během posledních let jejich výzkumu bylo zjištěno, že nanoplniva jsou při dostatečné disperzi v matrici schopná poskytnout vynikající mechanické a bariérové vlastnosti, a zároveň neovlivnit hmotnost nebo vzhled produktu, protože jsou účinná ve velmi malém množství. Tato diplomová práce se zabývá nanokompozity s matricí z polystyrenu a houževnatého polystyrenu a sledováním jejich chování během umělého stárnutí a zkušebního biodegradačního experimentu. Hlavním cílem tohoto výzkumu bylo zjistit, zda jsou nanoplniva schopná zrychlit nebo zpomalit degradační procesy matric. Nanokompozity byly hodnoceny pomocí Fourierovy transformační infračervené spektroskopie a karbonylového indexu, a jejich vzhled pomocí optické spektroskopie a měření indexu žlutosti, barevných souřadnic povrchu a propustnosti světla. Určitý potenciál pro snížení míry fotodegradace mohou, podle všech získaných výsledků, v některých případech mít vrstevnatá jílová nanoplniva, což by mohlo vést k jejich uplatnění v nové oblasti aplikací.

Klíčová slova: Polystyren, Houževnatý polystyren, Nanokompozit, Nanoplnivo, Fotodegradace, Biodegradace

ABSTRACT

Polymer nanocomposites are popular and often studied group of materials nowadays. During last years of their research, it was found that nanofillers, if their dispersion in the polymer matrix is on proper level, are able to provide excellent mechanical or barrier properties and at the same time do not influence the weight of product or its appearance, because they are useful in very low loadings. This thesis proposes the use of several types of nanofillers for preparation of polystyrene and high impact polystyrene nanocomposites and to observe their behaviour during artificial weathering and initial biodegradation experiment. The main purpose of this investigation was to find, if nanofillers are able to accelerate or slow degradation processes of matrices. Nanocomposites were evaluated by Fourier transform infrared spectroscopy and carbonyl index, and their appearance by optical spectroscopy and measurement of yellowness index, surface colour coordinates and light transmission. According to all obtained results, layered clay nanocomposites, in some cases, may have the potential for reduction of photodegradation rate, which could provide new opportunities for their applications.

Keywords: Polystyrene, High impact polystyrene, Nanocomposite, Nanofiller, Photodegradation, Biodegradation

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I hereby declare that the print version of my Master's thesis and the electronic version of my thesis deposited in the IS/STAG system are identical.

Zlín, 11. 5. 2012

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CONTENTS

INTRODUCTION

In the last decades, there has been a significant interest in the production of plastics and their applications. This has led to an increase of public awareness and a beginning of massive use of plastics. The need of modification of their properties has become an important part of their development and many types of additives have been introduced to eliminate their disadvantages [1, 2]. One of these negative properties is poor resistance of some plastics, especially polystyrene (PS), to outdoor environment. This problem was described in details and the research in this field has concentrated on a deep examination of stabilizers, pigments, PS copolymers or material surface changes [3, 4, 5]. However, little data has been collected in the area of nanofillers, PS and ultraviolet light interaction [6].

Hence the main purpose of the experiment reported here was to evaluate and compare an influence of different types of nanofillers on polystyrene degradation caused by UV light. Four sets of samples were subjected to thorough investigation and a wide spectrum of results was obtained. Although this thesis was primary focused on photodegradation, there was also another goal in the research, which implies the possibility to apply biodegradation for volume reduction of PS waste. This second interest is based on the natural origin of nanofillers and an assumption, that they could support biological disintegration of PS by their own decay.

I. THEORY

1 STYRENE POLYMERS

Polystyrene (PS) and other styrene polymers belong to the most manufactured plastics. They are on the fourth rank on the scale of the amount of a plastic production per year. Expressed in numbers, today's world consumes 265 million tonnes of plastics every year. The consumption of European countries is 21.5 % of this total amount, which can be quantified at 57 million tonnes annually. The position of PS in this statistics is shown in *Figure 1*, together with several other plastics including polyethylenes (PE-LD, PE-HD, PE-LLD), polypropylene (PP), polyvinylchloride (PVC), polyethylene terephtalate (PET) and polyurethane (PUR) [7].

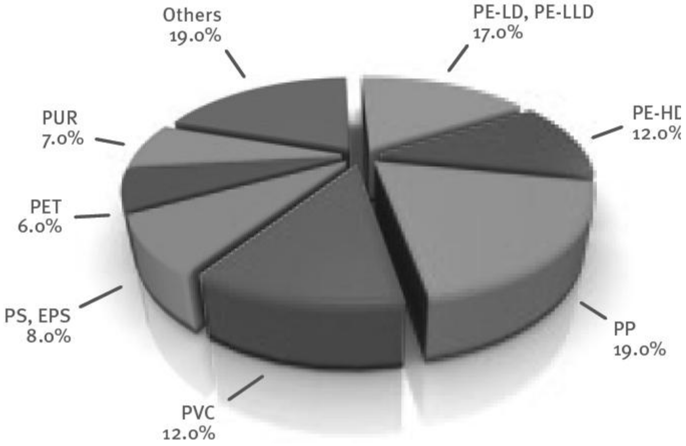


Figure 1 - Plastics in the European Union + Norway and Switzerland (46.4 mil. tonnes) [7]

The popularity of PS, which has been in use for almost 80 years, arises from its properties and acceptable price. These two facts will be discussed later in this chapter, but now it is convenient to review briefly history of this plastic. The first factory for the production of polystyrene resin was opened in Germany in 1930 by BASF and the first injection moulded products were manufactured in the same country three years later. The volume of the production was many times lower in a comparison with present days, but the interest in this material spread also to the USA, where Dow Chemical Company started its own production. This development of PS was interrupted by World War II, because the aim of the main manufacturers was changed. At that time, the priority was to search for new material which would substitute natural rubber. The development of styrene plastics continued after the war period, but its character was slightly different. Polystyrene as a material had already been discovered and there was also some experience with it and its properties, such as brittleness. Thus there was a need to focus on an improvement and elimination of its disadvantages. This situation led to the creation of high impact polystyrene (HIPS) and styrene copolymers, such as acrylonitrile-butadiene-styrene (ABS), styrene-acrylonitrile (SAN) [8].

The history of the first chemical reaction the result of which was polystyrene goes even deeper to the history. It was in 1839, when Eduard Simon made a reaction product and called it styrol oxide. He did not know about the real nature of PS and a polymerisation and he thought that it was a result of oxidation. A breakthrough work was done in 1920s by Herman Staudinger, who understood the macromolecular nature of these materials. This was the year when discovery of many other polymers started [8, 9, 10].

Beside the aforementioned, a family of styrene polymers consists of expanded polystyrene (EPS), acrylonitrile-styrene-acrylic copolymer (ASA), styrene-butadiene (SB) or styrene-butadiene-styrene (SBS) copolymer and many others. EPS is processed to the form of foam and used mainly in packaging and construction insulating applications, while terpolymers (ABS and SAN) and block copolymers (ASA, SB, SBS and others) can be used for more demanding applications, for example in automotive industry [11, 12].

1.1 General purpose polystyrene

General purpose polystyrene is a term describing an amorphous atactic homopolymer with crystal clear appearance. It can be abbreviated to GPPS or simply PS and is also called standard polystyrene. This designation has a reason, because there are also semicrystalline types of this material, namely syndiotactic polystyrene (sPS) and isotactic PS (iPS). All of them originate from the same monomer with systematic name ethenylbenzene, but which is usually called styrene or vinyl benzene. During polymerisation reaction, these low-weight molecules join each other and create a long-chain macromolecular structure of polystyrene. The structure formula of styrene and PS can be seen in *Figure 2,* where is also depicted the way of notation of such long-chain molecules [13].

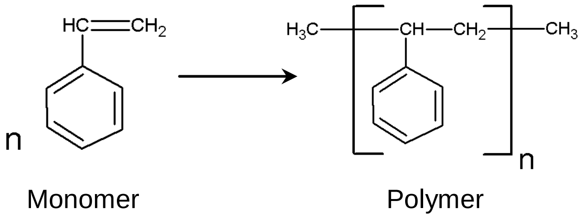


Figure 2 - Structure of styrene and polystyrene

1.1.1 Structure and properties

Structure and properties of all polymers are very closely related. Every little change in molecular structure can be observed as some variation in their properties and, vice versa, some details of polymeric structure can be concluded from their properties. Despite the fact that this statement is also relevant to thermosets and elastomers, next parts of this thesis will be limited to thermoplastics. From this point of view, the degree of crystallinity and molecular weight are the most important factors and when they are considered, a specific behaviour of the material can be deduced.

In the amorphous state, macromolecular chains are organized randomly and they do not evince any signs of spatial arrangement. Their typical behaviour during heating is called glass transition, appears at certain temperature (glass transition temperature *Tg*) and can be described as follows. When temperature increases, statistical segments of chains are not frozen anymore, because the thermal motion starts to prevail over intermolecular forces that hold chains together. The polymer approaches rubbery (leathery) state and begins to be softer, i. e. leaves glassy state and is not further brittle. Materials with a high *Tg* are therefore very brittle at room temperature. This is also the case of PS, the glass transition temperature of which is about 100 °C, but softening temperature is even lower – about 80 °C. This is the reason why PS can be used only at temperatures below 75 °C. Further heating causes that the material reaches the flow temperature (*Tf*) at 200°C, it means intermolecular forces are finally surpassed and viscous melting with non-newtonian characteristics is created [9].

On the other hand, the structure of sPS or iPS behaves in a different way. As the crystalline phase is a highly organized structure it can be made only of highly organized macromolecular chains. It means that atomic groups which create the polymer have to be arranged regularly along the backbone chain. This arrangement is called tacticity and enables chains to fold to the form of lamellas with a certain thickness. Lamellas can also grow and create spherulite – the highest level of the polymer crystalline structure. Since there are strong intermolecular forces, crystalline polymers are more thermally resistant and they do not go through the rubbery (leathery) state. When melting temperature (*Tm*) is approached, they melt at once and become a viscous melt. All signs of organized structure disappear and there is no difference between amorphous and crystalline state. *Tm* of sPS is around 275 °C and iPS 225 °C [8, 14].

Both of these phases, amorphous and crystalline, cannot exist separately, therefore there is no 100% amorphous, or crystalline polymer. However, in case of PS the degree of crystallization is negligible. Hence, its properties are: transparent, brittle and rigid appearance with excellent dimensional stability and minimal water absorption. The surface of PS products is smooth and glossy. The course of its mechanical behaviour is close to Hooke's law, i. e. the dependence of the tensile strength on the tensile strain is almost linear. It can be said that all deformations are reversible until the terminal tensile strength and strain is reached, so it is not surprising that the elongation is very small and the modulus rather high [8, 12].

The properties depend significantly on molecular weight. For PS the weight average molecular weight (*Mw*) is between 100 000—400 000 g-mol^{-1}, but it can be prepared with *Mw* much higher – about 1 000 000 g.mol^{-1}. PS fractions with a higher *Mw* have higher *Tg* (or *Tm*), higher viscosity of the melt, better strength and lower solubility. They are also more chemically resistant. Generally, PS is resilient to water, oils, alcohols and diluted inorganic acids, but it can be attacked by carbonyls or aromatic hydrocarbons [11].

A typical property of PS, which has to be mentioned, is its low heat conductivity, which is the reason of very large use in insulating applications, e.g. in civil engineering. The major disadvantage, which is also characteristic for polystyrene, is its flammability. It can be ignited very easily and in burning black soot and smoke are evolved [8]. PS can be identified by all the features listed *Table 1*.

Table 1 - Properties of standard polystyrene [9, 11, 12]

Property	Unit	Value
Density	$g.cm^{-3}$	1.05
Molecular weight	$g.mol^{-1}$	100 000—400 000
Glass transition temperature	°C	85–95
Heat deflection temperature	°C	65–93
Modulus	MPa	3200
Tensile strength	MPa	31–45
Elongation at break	%	2–3
Impact strength	$J.m^{-1}$	59
El. resistance	Ω	10^{14}

Polystyrene and UV radiation

PS and styrene polymers are susceptible to degradation reactions caused by an exposure to daylight. It is connected with UV light and sensitivity of some components, usually impurities, which are present in the material. They are at the beginning of a sequence of changes, which have a character of chain reactions and lead to the formation of new structures in the molecule. One consequence of this is yellowing of material surface that devaluates product appearance [15]. An example of such deterioration is shown in *Figure 3*, where the closure of heating after 6 year of indoor (behind window glass) exposure is depicted. Since this is the crucial part of the Master's thesis, more information about this problem can be found in the whole Chapter 2.

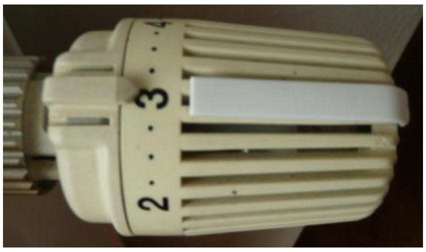


Figure 3 - Heating closure

1.1.2 Polymerisation reactions

Polystyrene is a very variable material in terms of polymerisation. It can be prepared by radical and ionic (anionic and cationic) reactions, as well as by the stereoregular polymerisation. PS is usually prepared by radical polymerisation in suspension, but other methods – mass, solution and emulsion polymerisation – can be also used. Using of stereoregular reactions with Ziegler-Natta or metallocene catalysts is typical for semicrystalline types [9].

Preparation of styrene monomer

Styrene is a colourless liquid with molecular weight 104 $kg.mol^{-1}$. It has a typical odour reminding a smell of aromatic compounds or natural gas. It has the boiling point at 145 °C and is soluble in alcohol and ether, but insoluble in water. Furthermore, it is a solvent for polystyrene and several synthetic rubbers. Styrene is commercially produced from benzene and ethylene, which react together to form ethylbenzene. As the catalyst in this reaction aluminium chloride is used; this reaction is called Friedel-Crafts synthesis. Next steps involve dehydrogenation of ethylbenzene at 630 °C and formation of styrene. Another possibility is oxidation of ethylbenzene on phenylethanol and following dehydration [16]. Individual steps are displayed in *Figure 4*.

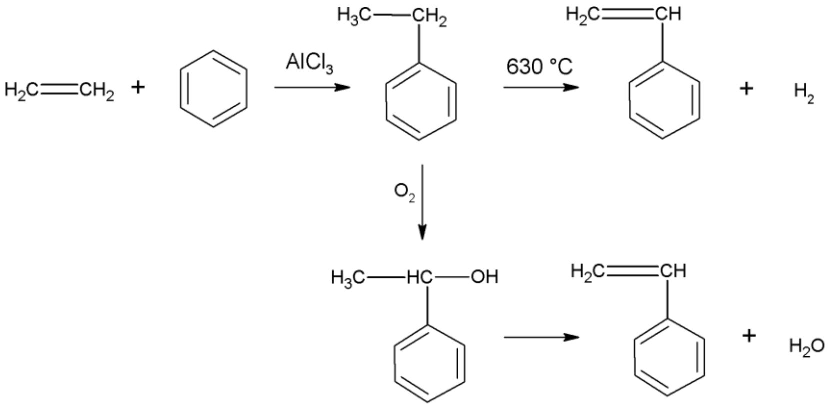


Figure 4 - Reaction steps of styrene preparation

Suspension polymerisation

This is the often used method for commercial mass production of PS. It combines acceptable processing conditions with good quality of the product. In the process, styrene monomer is put into an inert substance (usually water), with which it is immiscible. The suspension is formed and stirred during the whole polymerisation. This creates droplets of styrene in a size of 10^{-3}—1 mm and whose size is dependent on the rate of stirring; the faster the stirring, the smaller droplets are obtained. Another component of the reaction mixture is an initiator, dibenzoyl peroxide in this case. It must be miscible with and solved only in styrene. The mixture also contains a suspension stabilizer, which prevents droplets from merging. Calcium chloride ($CaCl_2$) plus sodium phosphate and polyvinyl alcohol are often used for this purpose. Polymerisation occurs inside the droplets and polystyrene is prepared in the form of powder. The time of the reaction is between 6 and 7 hours at 125 °C. The prepared powder is put into hydrochloric acid and $CaCl_2$ is washed out. Water is removed by filtration and PS is dried and ready for pelletizing [8, 11, 14].

Other polymerisation methods

The purest reaction product is obtained when mass polymerisation is used. There are no other chemicals, such as solvent or water, but the monomer and initiator. The viscosity, as well as the temperature of the reaction mixture, increases during this exothermic reaction. The main disadvantage of this method, however, is the complicated way of heat removal, because the mixture cannot be stirred. The created polymer has a shape of the reaction vessel and there is no need of additional operations (e. g. filtration, washing, drying) [14].

Other methods – solution and emulsion polymerisation – solve the problem with increasing temperature, but have their own disadvantages. Solution polymerisation does not have difficulties with the heat removal, because there is surplus of a solvent that enables sufficient stirring. On the other hand, the quality of prepared PS is much worse due to its lower molecular weight caused by transfer reactions between polymer chains and solvent molecules. At the end of the process, the product has to be separated from solvent and dried [14].

Another method is the emulsion polymerisation, which is used for the production of polystyrene latex. It is not suitable for other purposes, because of a large amount of emulsifiers that gets into polystyrene structure and influences its appearance and insulating properties. For these reasons emulsion polymerisation is only used for production of paints [8].

1.1.3 Processing methods

Processing of polystyrene does not differ from other thermoplastics manufacturing. The main point is heating with consequent melting, forming and shape fixation by cooling below the flow temperature. Standard polystyrene is mainly processed by injection moulding, extrusion and thermoforming. This is possible due to good flow properties of PS. It can be prepared with various values of melt flow index (*MFI*), i. e. low values for extrusion and higher values for injection moulding. *MFI* range is from units to hundreds of grams per 10 minutes. Processing additives, such as plasticizers (e. g. mineral oils) are usually added for flow facilitation. Beside these, colorants, antioxidants, stabilizers, flame retardants or fillers are added if needed [8].

Common temperature of melting during injection moulding is 180—280 °C and the mould temperature is between 5 and 80 °C. It is important to choose proper processing conditions (temperature and pressure) to avoid unwanted difficulties, which can be high frozen stresses, deformations or surface defects. Suitable conditions must be set for every PS type individually at the beginning of the mass production [12].

The process of extrusion provides foils, sheets, tubes and plates, which can be finished and used as final products or they serve as semi-products for thermoforming. Finishing operations are necessary for all processes even for injection moulding. In spite of the fact that the product has the precise shape of the mould, there is still excessive material from the mould channels, which must be cut off. Extrudates are cut into proper lengths and thermoformed articles are treated similarly as the injection moulded ones. The end of processing lines belongs to surface modifications, such as printing, and dimension checking. After that the final products are packed and distributed to customers or transported to warehouses [12].

1.2 High impact polystyrene

Some of commercial applications are more mechanical demanding than PS can withstand. Thus, there is a need to modify some of its properties, especially impact strength and reduce its brittleness.

1.2.1 Production methods

HIPS can be theoretically made by several methods which should lead to required result, but only two of them – copolymerisation and blending with an elastomer – are commonly practised. From other techniques adding plasticizer, production of PS with higher *Mw* or orientation of macromolecules can be mentioned, but their disadvantages are a very low softening point, insufficient improvement and limitation to sheets, respectively [8].

To summarize, materials for a preparation of HIPS are monomers of standard polystyrene and elastomer (when copolymerisation method is used) or more precisely rubbers (when blending method is used). There is large number of rubbers, from which to choose, but butadiene rubber (BR) and styrene-butadiene rubber (SBR) are the ones commonly used in practice [8].

Polymerisation of styrene with elastomer

High impact polystyrene is mainly prepared by polymerisation method. It has a similar course as the polymerisation of standard polystyrene. Its mechanism is also radical but the difference lies in the presence of styrene-butadiene copolymer solved in styrene monomer. The polymerisation occurs in bulk, so it is mass polymerisation, and can be set as continuous process. There are usually three reactor zones and monomer proceeds from the first to the third one with increasing degree of conversion. At the beginning it is important to set the proper rate of stirring to obtain elastomer particles of the right size, which is the range from 1 to 5 µm. Such HIPS is not crystal-clear any more and if higher brilliance is demanded, the particle size must be smaller than 1 µm, which, on the other hand, does not provide sufficient impact strength improvement. The result of this polymerisation actually is block copolymer with polystyrene and polybutadiene blocks and with a small amount of the grafted structures. Thus, there is clear dependence of gloss and impact strength on the size of butadiene blocks. If the fine product is expected the compromise between them must be taken depending on purpose of HIPS application [17].

Another way is to realize the copolymerisation first in mass and then in suspension environment. The reaction starts at 100 °C in bulk and after 4 hours and 30% conversion, water is added and suspension (latex) is created. The polymerisation continues another 5 and 3 hours in two stages – at 110 °C and 135 °C, respectively [11].

Blending of polystyrene and rubber

This is a very simple way of the preparation of HIPS, because it comprises basically only compounding of PS and BR. The real process consists of several steps. First, ingredients are put together to an internal mixer or an extruder and then PS granules or pellets are melted and BR is added. Very important is the course of a blending, where sufficient degree of rubber particles dispersion must be achieved. It can be controlled by temperature or time of compounding. Finally, the prepared HIPS is cooled and able to undergo common processing methods, such as injection moulding, extrusion, thermoforming or compression moulding [8].

1.2.2 Morphology and properties

Mechanical properties of HIPS are highly dependent on the size of elastomeric particles and their distribution. Toughened PS (another name for HIPS) is a two phase system, where PS acts as a rigid homogenous phase, in which polybutadiene soft discrete particles are dispersed. The modification is successful if the material performs high impact resistance and no cracks are created under the stress. To meet these requirements, the size of rubber particles must be lower than 50 µm. There should not be any empty spaces in PS matrix, because they can act as stress concentration points and be the location where cracks are created and begin to spread [8, 17]. A great importance is also attributed to the degree of a compatibility of the particular components. If they are too compatible, the rubber component cannot work as the impact modifier, since the blend on molecular level of mixing is created. On the other hand, too incompatible components do not provide sufficient phase interconnection and they stay separated. In this case, they concentrate mechanical stresses and again they do not assure better mechanical behaviour [8].

Since HIPS is a modification of PS it is appropriate to compare their properties, especially mechanical characteristics. *Table 2* shows some property values adopted from datasheets of Krasten® PS and HIPS. It is obvious that impact strength of HIPS is many times higher than the original value. This fact and the nature of rubber modifier, on the other hand, decrease modulus, tensile strength and hardness and also increase elongation at break. The density is also little lower [18, 19].

Table 2 - PS and HIPS properties [18, 19]

Property	**Unit**	**PS**			**HIPS**		
		Krasten 137	Krasten 152	Krasten 172	Krasten 336 M	Krasten 552 M	Krasten 662 E
Density	$g.cm^{-3}$	1.05	1.05	1.05	1.04	1.04	1.04
Hardness	MPa	150	150	150	80	70	60
Tensile modulus	MPa	3 100	3 200	3 200	2 300	2 100	1 750
Tensile strength at break	MPa	43	50	56	23	22	22
Elongation at break	%	2	2	3	35	40	50
Charpy impact unnotched	$J.cm^{-1}$	1.8	2.6	2.6	5.0	No break	No break
Heat deflection temperature	°C	75	80	85	70	72	75

1.3 Applications of PS and HIPS

It is not necessary to go far to find several objects made of polystyrene. This is caused by the fact that this material combines both a low price and excellent utility properties. According to Plastics Europe [7] and Polystyrene Packaging Council [20] the vast majority of PS is used for packaging applications. They are predominantly represented by cups and boxes for food and consumable goods. Namely, they are boxes and foil packages for meat, dairy products and eggs, cups for beverages from vending machines, or CDs and DVDs boxes. A large amount of products from this application area is made of EPS, especially packages for hot drinks and meals. Usage of EPS also exceeds to the electronics industry. It can be found inside boxes for electronics, where it serves as insulation from external shocks during transportation. Another region where EPS plates are commonly applied is civil engineering, namely the walls of buildings, where expanded PS ensures thermal insulation. These last mentioned industrial areas are also rich in PS and especially HIPS applications. From these housings for computers, televisions and for all electronic and IT equipment, housings for household appliances, such as refrigerators, dishwashers or ovens and last but not least parts of lamps, showers and bath systems can be enumerated. The actual situation in Europe from 2009 is expressed in *Figure 5*, where PS and other plastics are compared by their consumption in five main areas [7, 11, 12, 20, 21].

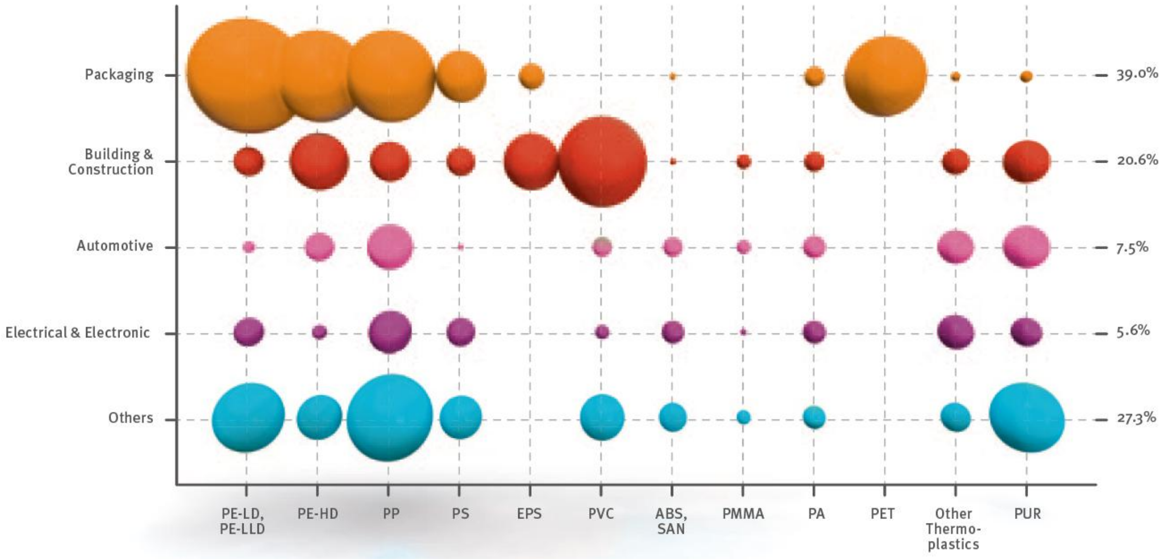


Figure 5 - European plastics and their demand in 2009 (EU + N and CH) [7]

Producers and suppliers

The most traditional company in the Czech Republic concerned with production of polystyrene (brand name Krasten®) was Kaučuk a. s. in Kralupy nad Vltavou. This was true until 2007, when Kaučuk was taken over by Poland company Firma Chemiczna Dwory S.A.. Since then they are members of one group SYNTHOS and Kaučuk is called SYNTHOS Kralupy a. s. Their material portfolio stayed unchanged, so the tradition can continue [22].

The polystyrene industry is widespread and the whole world is influenced by the global PS market. There are several producers of PS, HIPS and their copolymers. Probably the best known manufacturer is Dow® Chemical Company. They have a rich history and experiences with styrene, PS and EPS production and their following processing. In present days they are concerned only with expandable polystyrene STYROFOAM^{TM}, which is recognizable by its typical blue colour [23]. In 2010, Styron^{TM} was founded and took over PS and HIPS production from Dow® under the trade names STYRON^{TM}, STYRON-A-TECH^{TM} and STYRON-C-TECH^{TM} [24]. EPS is also supplied by European company Ineos Styrenics [25], North American Nova Chemicals® under name DYLITE® [26] or Styrotech Corporation with location on Philippines and specialization in food packaging [27]. All types of styrene polymers are produced also by Italian company called Eni with commercial names Edistir® (PS, HIPS), Extir® (EPS), Sinkral® (ABS) and Kostil® (SAN) [28].

2 MATERIAL WEATHERING AND PHOTODEGRADATION

Majority of people do not have the knowledge from the polymer area, but everybody knows that plastic articles can undergo some changes (e. g. yellowing, embrittlement, surface deterioration) during their use or exposure to sun. The length of a product service life is one of the most important details that customers want to know before they purchase it. This is the reason why weathering assessments have been developed and used abundantly. Photodegradation is then the main result of the polymer weathering or a consequence of a similar process polymer aging. This term will be specified later, but briefly it is a change in material properties due to an influence of ambient conditions. Most of imperfections caused by weathering have already been solved by development of stabilizers or by replacement of one material for another in some applications. However, some defects can be still observed in some undemanding applications of commodity plastics and it would be convenient, from the point of view of both expense and waste removal, to find such additives that would provide satisfactory resistance for the time of service life and then help with waste volume reduction. .

2.1 Polymer weathering

As indicated above, weathering is an interaction of the polymer and physical factors that occur in its surrounding. This general can be specified as deterioration of polymer surface, such as changes in colour, roughness (cracking, crazing), even composition and others during its exposure to outdoor factors (e. g sunlight, temperature, water) [29, 30].

2.1.1 Main weather(ing) factors

Weathering is a complex process consisting of several permanently changing variables. They are: UV radiation, temperature, moisture or water and atmosphere composition including pollutants. These are changing within the day and night cycle, season or location on the planet and climate. This diversity makes impossible to test and evaluate their influence on materials according to established standards, because it is not possible to take into account the interference of all these factors at once. For this purpose three main elements – UV light, temperature and water – were detached and several methods of their testing with detailed conditions were developed [29, 31].

Ultraviolet light and sun

The biggest energy source – the sun – stands above all these influences and beyond the fact that weathering even exists. From astronomical point of view, the sun is a star consisting of hydrogen and helium atoms in a form of gas in proportion 3:1 with trace amounts of other elements [32]. The energy emitted to the Earth is created in a thermonuclear reaction, during which a helium atom is created from four atoms of hydrogen. Since four hydrogen nuclei are heavier than one of helium, the excess energy releases. Such energy consists of the spectrum of wavelengths and UV region is represented by only 9 %. The rest is divided between visible (45 %) and infrared (46 %) regions [31].

As all types of light also the ultraviolet is described by unique range of wavelengths, which is 120—400 nm and is divided into three subregions, similarly to visible light colours which differ in wavelengths. UV-A is a linking region between visible and UV light and it lies between 400—315 nm. Another one is UV-B light (315—290 nm) that is partly captured by the ozone layer. The intensity of UV-B depends on the conditions in the atmosphere and is expressed by UV index (usually reported in weather forecasts). It can influence the macromolecules of synthetic polymers, in this case, molecules of polystyrene. Thus, this part of UV light is the most problematic in the field of polymer damage. The third type of UV light is designated UV-C and its wavelength is 290—120 nm. It does not reach the Earth's surface and is completely absorbed by the ozone layer. There is also extreme UV in the region of 120—10 nm and several others, in which the main groups (A, B, C) are involved, e. g. near UV, middle UV and far UV light [29, 33].

The percentage of UV light that reaches the Earth's surface is only one third of the amount produced by the reaction on the sun. Nevertheless, it is powerful enough to break bonds in the polymer chains and starts their degradation and changes in colour. As will be discussed later, UV light usually causes splitting of hydrogen atoms and creation of radicals that can react with the oxygen in an environment of the air or water and cause oxidation of the polymer surface [29].

Temperature

The temperature that actually affects material, as another factor, cannot be expressed by a simple value read from a thermometer. It depends on the temperature of ambient air, intensity of infrared radiation from sun, air movement (wind) and properties of the polymer, such as colour of surface and thermal coefficients. It also differs with the latitude and longitude as can be seen in *Figure 6*. For instance, the average temperature in summer months in the Czech Republic was 16 °C in 2010, but in the winter of the same year it was only 0.4 °C. These are only averages and when real temperatures are considered (e. g. +30 °C in summer and -15 °C in winter) polymers have to resist a wide range of temperatures and various conditions. These fluctuations in the temperature can affect polymer chains, especially when polymer structure goes through the glass transition. Every new or different position of a macromolecule and its freezing causes an increase of the stress inside the material structure and its subsequent cracking [31, 34, 35].

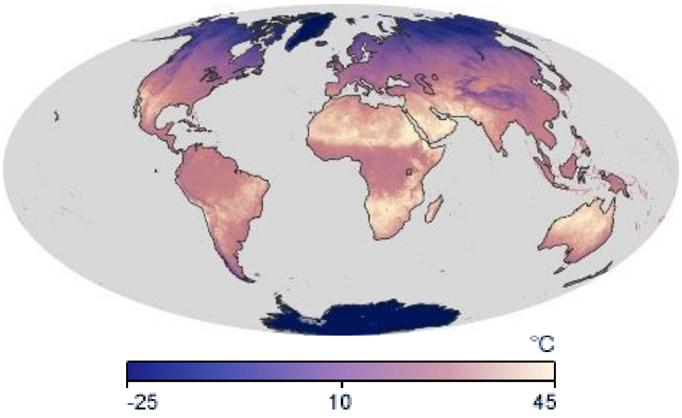


Figure 6 - Temperature distribution around the world [34]

What is extremely significant for weathering is the interaction of all the above factors. A polymer degrades in different rates when exposed to only UV light and UV light together with a higher temperature. This fact is very clearly explained in *Figure 7*, which is taken from the research of Czekajewski et al. from 1994. It describes the rate of degradation expressed through oxygen uptake during irradiation time. The temperature of the sample was kept at 100 °C and UV light was applied twice as shown in graph. The conclusion is that combination of UV radiation and the temperature distinctly increase the degradation rate [31, 36].

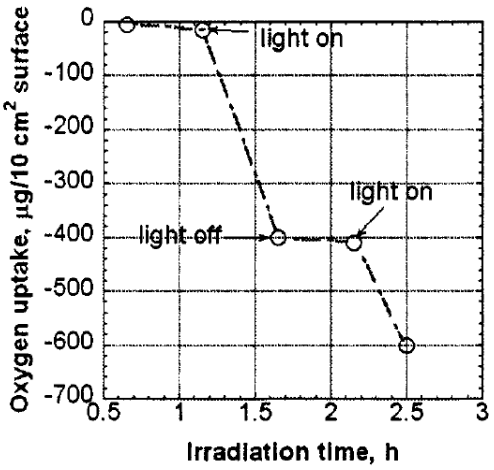


Figure 7 - Influence of UV light and temperature on polymer degradation [36]

Humidity and rain

Since two thirds of our planet are covered with water, it is another important factor that influences both all living organisms and nonliving things such as plastics. Water can be destructive for some polar, soluble or hydrolysable polymers, but for the materials as polystyrene it does not cause undesired changes. Its real danger is in the presence of oxygen in the molecule, which can cause the polymer oxidation. Again its effect is multiplied by the action of UV light similarly as in a case of temperature. It should be noted that during weathering, the water is represented by air moisture and rain and therefore by the geographical location. This implies the necessity of weathering tests carried out in very humid conditions for products with planned usage in tropics, which means that water does not have as significant influence for central Europe latitudes as for equatorial areas [29].

2.1.2 Weathering test methods

In the previous chapter three main elements of the weather were briefly introduced and now the methods of their combinations and the ways of polymer testing will be discussed. Common to all these methods is examination of several samples at once and comparison with each other and with a reference sample. The data have to be collected several times during exposure and are usually expressed in graphical form. The most common assessment methods are Fourier transform infrared spectroscopy (FT-IR), yellowness index (*YI*), surface optical microscopy and rentgenography, because they provide information about changes in colour, surface and composition of samples (see Chapter 2.4).

Natural environment

The weathering in natural or outdoor conditions is a long time process. For good relevance of the measured data the exposure should take several months, at least 6 months. There are few locations on the planet called weathering sites, which have been chosen for their unique or severe weather conditions. The well-known sites are in Arizona, Florida and Japan. Arizona provides extremely hot and dry climate, while Miami on Florida wet and rainy weather. Apart from these reasons testing locations are chosen by the population density. The explanation is very rational, because people use plastics, where they live. Thus, it does not have any sense to weather polymer materials on abandoned deserts or highest mountain peaks, if products made of them never get to such places. The choice of a particular site has to be well considered by a manufacturer according to the polymer application and requirements of his customer [31].

For these specific weathering locations, standards describing exact procedures of sample preparation to exposure, time of exposure or additional humidification have been set and are used at these sites, which are large areas with a lot of weathering racks (*Figure 8*). They are called weathering stations and usually are run by a company or organisation (e. g. Atlas Material Testing Technology) which carries out tests for customers from around the world [37].

Figure 8 - Weathering site in Arizona, USA [38]

There are two groups of these test methods that are designed as static weathering and accelerated outdoor weathering. The static weathering is characterised by the test performance in real time without any external help and is further divided into direct and indirect weathering. The samples are placed in the holder and the whole rack is positioned with an inclination of 45° to the south. During indirect testing the samples are additionally covered with window glass, which imitates the conditions in internal spaces of cars and buildings. And accelerated outdoor weathering multiplies the intensity of UV radiation and can be equipped with water spraying. It is represented by Equatorial Mount with Mirrors for Acceleration (EMMA) and Equatorial Mount with Mirrors for Acceleration Plus Water (EMMAQUA) methods. The apparatus is composed of reflecting mirrors that are able to increase eightfold the intensity of sunlight. The emplacement of the samples is similar to the static method. The equipment also includes a blower that prevents specimens from overheating. The exposure time ranges from 6 to 12 months, which corresponds to 2.5—5 year of real time testing. The difference between EMMA and EMMAQUA is simply in the presence of water [29, 37].

Artificial environment

To shorten exposure times, artificial weathering methods have been developed. They are located in laboratories and provided by a special device which consists in a light source that emits energy of certain wavelengths. These devices eliminate variability of outdoor conditions and give uniform and fast experimental data that can be fully compared with results obtained in other laboratories. A better result interpretation is assured by precise instruments and set weathering conditions. Weathering devices can imitate sunlight, rain and temperature of the samples as they would have in natural environment, but prevent any contamination that can cause the impossibility of experimental evaluation. Another advantage is the use of small size samples and possibility of testing several specimens at the same time. The major difficulty of this method is to choose a proper temperature and other conditions of weathering to achieve the most accurate results [31].

The choice of appropriate radiation source is also a very demanding feature of these test methods. It must consider the wavelength and intensity of daylight in summer and winter and its range produced by different light sources, if the results are to be compared to natural weathering. Very often light source is xenon light, which produces the spectrum of radiation very close to sunlight as can be seen in *Figure 9*. At present there are companies that produce fully equipped weathering devices and the test only requires selection of suitable filters to obtain the required wavelength. These machines are called weather-o-meters or Xenotests after their commercial names [29].

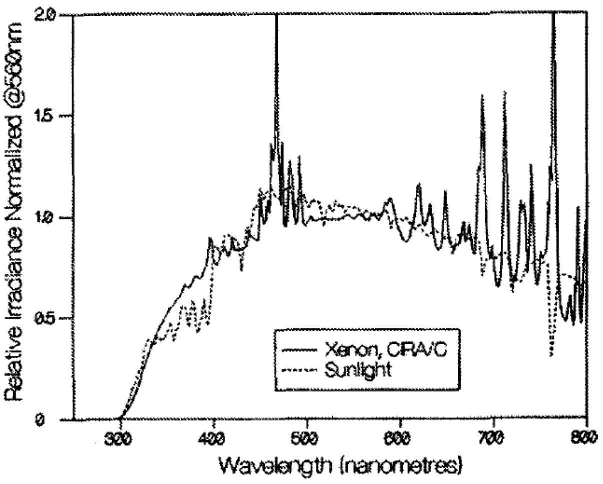


Figure 9 - Comparison of xenon arc and sunlight [37]

2.2 Process of photodegradation

Degradation is closely related to absorbed energy and the energy is dependent on frequency *f* (or wavelength *λ*) of the radiation. This relation was formulated at the begging of the 20th century, when Max Planck introduced an equation (1) [31], later called Planck's law, describing the relations between these quantities.

$$E = h \cdot f = h \cdot \frac{c}{\lambda} \tag{1}$$

where h is Planck's constant (h = 6,63.10^{-34} J.s) and c is a velocity of a light (c = 3.10^{8} m.s^{-1}).

The energy of the light with certain wavelength can be easily calculated and related to 1 mol of a substance by multiplying the Avogadro's number (N_A = 6.022.10^{23} mol^{-1}). For example 290 nm is the edge value of UV light that is definitely not absorbed by ozone layer and its energy according to equation (1) is 413 kJ.mol^{-1}. Now it can be compared with the strength of C–H bond and C–C bond, which most frequently occur in polymer chains. Their values are 420—560 kJ.mol^{-1} and 300—720 kJ.mol^{-1}, respectively. It is clear that radiation at 290 nm is too weak to break C–H bond and the destruction of C–C bond is therefore strongly influenced by the substituent. Another fact is that with increasing value of wavelength, the energy of radiation decreases. Hence, UV light and generally the sunlight can never reach the energy of the C–H bond [31].

The question arises how it is possible to cause degradation involving abstraction of hydrogen without breaking bonds in polymer chains. In this case, more information is needed for description of the process. It is not only the fact that the photon provides its energy to the molecule and if the energy is high enough, the bond breaks. Every molecule has its own mechanism by which it deals with an excessive energy in the structure. A chemical compound, which the polymer is, undergoes a molecular transition if it is irradiated. Transitions on electronic levels, i. e. movements of electrons from bonding to non-bonding positions, need very high dosage of energy, which is unreachable for UV light. However, there are also vibrational, rotational and translational molecular movements that are dependent on the structure of each molecule and less energy is required for their initiation. Hence, it is the structure of the polymer, which decides if the harmless dissipation or drastic chemical reaction with bond breaking occurs [39].

Grotthus-Draper principle or the first law of photochemistry says: "Absorption of radiation by any component of the system is the first necessary event leading to photochemical reaction" [39]. The second law of photochemistry then describes the initiation step that moves the molecule to an excited state. Only the photons with sufficient level of the energy are absorbed by the molecule and push it to the excited state. Full text of this law is: "If a molecule absorbs radiation, then one molecule is excited for each quantum of radiation absorbed" [39].

Real reactions observed during photodegradation can be classified into four groups according to their chemical character. They are dissociation, isomerization, ionization and reaction with other molecules or atoms. All of them are then specified as photodissociation, photooxidation, photoelimination or creation of hydroperoxides and their reactions and many others. Very often degradation ways are those led by photooxidation mechanism and inclusion of the oxygen to the reaction. This is the reason why water is so dangerous in the weathering of materials [31].

2.2.1 Polystyrene degradation

Despite the fact that PS and its phenyl group do not absorb energy from the sunlight, it is very sensitive to this factor and goes through photodegradation in very large extent. The initiation is carried out by an abstraction of the hydrogen atom and formation of the radical. It is believed that the very first radical is created from some impurities, which are sensitive to photons and which are always present in material. They cause the hydrogen rapture and then this polystyryl radical reacts with a molecule of the oxygen and creates a PS peroxy radical (F*igure 10*). The next step is its reaction with another polystyrene chain and formation of new PS radical (the same as in the first step) and hydroperoxide (*Figure 11*). Hydroperoxides are very reactive compounds and decompose into alkoxy and hydroxyl radical very easily – this step is shown in *Figure 12* [39].

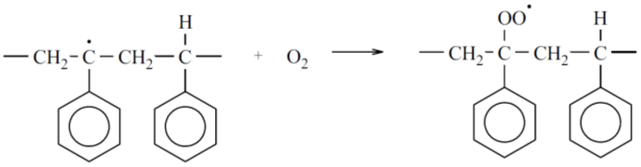


Figure 10 - Initial radical and reaction with O_2 [39]

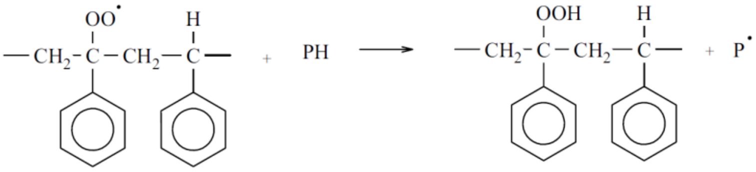


Figure 11 - Formation of hydroperoxide [39]

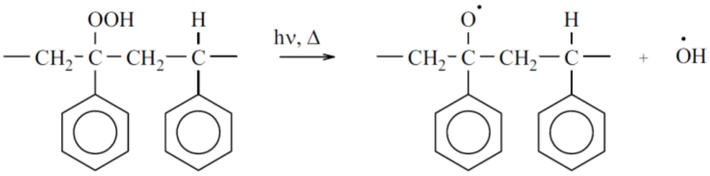


Figure 12 - Decomposition of hydroperoxide [39]

Photolytic reactions

There are three types of alkoxy radical reaction and one of them lead to the creation of another radical from PS chain. First, hydroxyl group OH can be formed by abstraction of hydrogen from another chain. Second, alkoxy radical can be decomposed into ketone and PS radical. This radical continues in hydrogen abstraction from PS and the whole cycle is constantly repeated. Third, alkoxy radical decomposes, but no radicals are created, only benzene and ketone. All of three reactions are depicted in *Figure 13* [31].

Photolytic reactions are characterized by the end products of benzene and hydrogen and their own way of double bonds creation in the PS chain, which probably causes yellowing of the material. The reaction is shown in *Figure 14* [31].

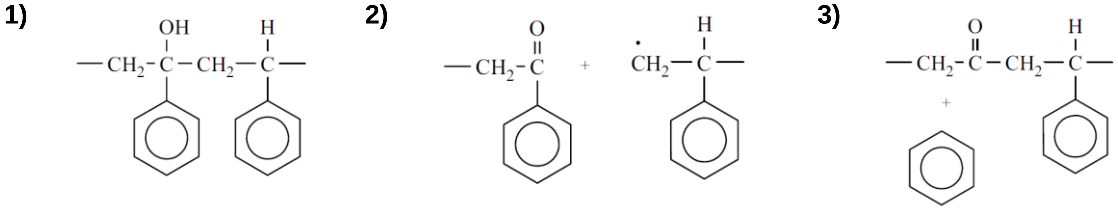


Figure 13 - Three types of products from alkoxy radical [31]

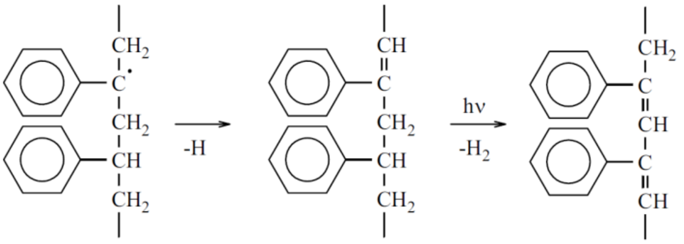


Figure 14 - Formation of double bonds by photolysis [31]

Photooxidation reactions

This is the second type of reactions that occur during PS photodegradation. They vary from the previous ones by different end products, which in this case are mainly water (*Figure 15)* and carbon dioxide. The origin of the yellowing is also different and consists of a complex of steps which begins with PS macroradical and ends up with quinomethan derivatives [39].

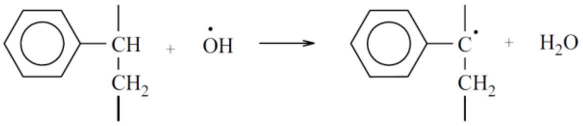


Figure 15 - Photooxidative reaction [39]

Beside the already mentioned reactions, PS and alkoxy radical can recombine and create intermolecular crosslinks [31, 39].

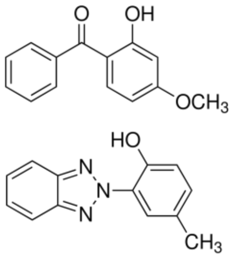
Photooxidative and photolytic reactions or creation of crosslinks occur in PS during photodegradation, but they can appear in different extent. Poland research gives an example of this claim. In 2008, they studied the differences between photodegradation of pure PS and poly(styrene-maleic anhydride) copolymer (PS-MAH). While PS-MAH was more susceptible to chromophore production and its structure was changed by creation of crosslinks, pure PS underwent photooxidation in a large extent [40].

The rate of photodegradation is another important fact, which was the object of some researches. Studies showed that the rate depends not only on the intensity of UV irradiation, but on composition of plastic as well. Waldman and Paoli observed the behaviour of the PP/PS blend. They prepared several samples with different volume fractions of the polymers and also with compatibiliser, because these polymers are naturally immiscible. Although PP undergoes degradation in different way than PS, their blend was more susceptible to photodegradation then both pure polymers. Researchers explain this fact by possible energy transfer between PS and PP.

This excessive energy helped to create many tertiary carbons (in PP), which are very labile and easily degraded. Hence, this study indicates an importance of the knowledge of blend structure and composition. Moreover, the compatibiliser amplifies photodegradation effects, because it creates better conditions for the blend existence and at the same time for sharing of negative effects leading to blend destruction [5].

2.3 Process of UV stabilization

Stabilization of polymers against UV degradation can be realized primarily by addition of UV stabilizers or UV absorbers, but it can also be supported by antioxidants or pigments that are able to reduce the amount of oxidation products and shield the polymer from UV light, respectively. This is enabled by the fact that stabilization can be realized by several different mechanisms. The most effective are those based on the absorption or quenching of reactive radicals. The absorption is very often way of the prevention of contact of UV light with the polymer. It is assured by UV absorbers, which are able to hold a significant part of radiation and thus protect the polymer. It is not possible to prepare a UV absorber that would have 100% efficiency, because also the polymer always absorbs energy. The amount of radiation absorbed by the polymer depends on the concentration of chromophores. Chromophores are organic groups that are very sensitive to UV light, absorb it very easily and attract radiation more dangerous to the polymer. It can be, for example, carbonyl group. The concentration of chromophores is not constant during the whole photodegradation process, but it changes with their formation during the degradation steps. The effectiveness of absorbers is then dependent on their chemical structure. An important property of these compounds is their ability to cope with adopted energy and prevent their own degradation. In fact, absorbers are able to dissipate the energy by tautomeric conversion. They usually are in the keto form in their ground state, but after energy acceptance they are excited and turn to the enol form and then back with the energy release. The most often used groups of them are benzotriazoles and benzophenones. Representative examples of both groups are displayed in *Figure 16* with their systematic names [31, 39].



2-hydroxy-4-methoxybenzophenone

2-(2H-benzotriazol-2-yl)-p-cresol

Figure 16 - Chemical structure of UV absorbers [39, 41, 42]

The second mechanism of stabilization is completely different. It is performed by hindered amines, which are known as HALS, which means Hindered Amines Light Stabilizer. Their function is based on reactions with the radical, which are formed during polymer degradation. HALS also create radicals, but these are stable, do not react with the polymer chain and do not remove the hydrogen atom that could begin the chain degradation. In addition, they are able to react with radicals

(e. g. alkyl, hydroxyl) that are already present in the polymer and deactivate them. They have a complex structure, which assures these unique properties. The evidence about their efficiency is given by research of Italian scientists from 2004. They studied PS films with three types of hindered amines and compared their results with a pure PS. As can be seen in *Figure 17*, HALS rapidly decreased the UV degradation rate, which is expressed by lower values of the carbonyl index (axis y) during the photodegradation period [3].

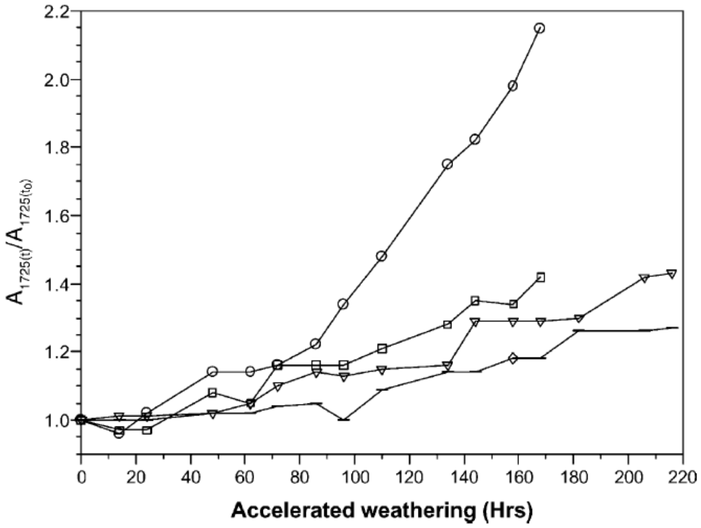


Figure 17 - Influence of HALS on photodegradation (pure PS – circle mark) [3]

Thus, HALS are very popular group of stabilizers, because they provide high effectiveness and do not influence other polymer properties. One of them, which is used for PS stabilization, is shown in *Figure 18* [39]. There is countless number of HALS, which are commonly used and, on the other hand, those that are still being developed and studied. Some of well-known commercial names are Chimassorb® and Tinuvin® (from former Ciba, now BASF) [43, 44], Uvinul® produced also by BASF [45] or Eversorb delivered by Everlight Chemicals [46].

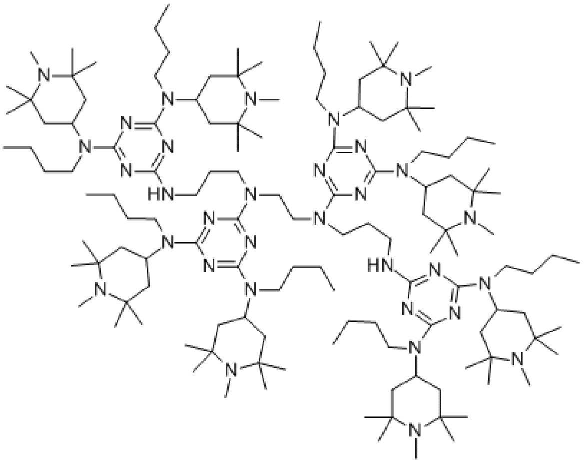


Figure 18 - Structure of HALS (Chimassorb® 119) [43]

These two described groups are only the tip of the UV stabilizators pyramid and new chemicals with stabilization abilities are being discovered. One of such new and promising compound was described and published last year by Yousif et al. They added 2-N-sylicylidene-5-(substituted)-1,3,4-thiadiazole to PS and performed standard photodegradation tests. They examined five modifications of this compound, which differed according to used substitute group. The best stabilization effect was evinced by compound with P-nitro-phenyl as substituent. However, all PS samples with these additives, independently on the substitute group, were better protected to UV light [47].

Stabilization systems are usually composed of more components, which help and support the main function of UV absorbers or HALS. The auxiliary chemicals are mainly pigments (the darker the pigment the more UV radiation absorbed) with screening properties and antioxidants that are able to quench oxygen atom and reduce the risk of oxidation. These complex systems are mixed with the polymer before its processing. They are added in amounts of tenths of percent. Addition of 2 % of stabilizers is considered almost maximum. Another possibility for achieving demanded stabilization effects is creation of a coloured surface layer or a modification of surface, e. g. metal plating completely isolates the polymer from the environment [29, 31].

2.4 Photodegradation evaluation methods

Changes in the material occur during the whole photodegradation process. Therefore, it is necessary to collect data from samples in chosen intervals and compare the results from samples with one another other and with the reference sample. The reference sample is usually pure material without any stabilization system or without other additives, whose influence is tested.

There are several traditional methods which are used for an assessment of chemical, surface and colour changes of the samples. They are Fourier transform infrared spectroscopy and optical methods, such as yellowness index and change of colourfulness, and eye evaluation with taking the photographs. Each of these experimental techniques will be described individually and the best ways of their result explanation will be introduced. Since each experimental work needs to be well justified and presented, the choice of the proper evaluation method is very important and one of the essential part of research work.

2.4.1 Fourier transform infrared spectroscopy

Spectroscopic methods are very often used for identification of changes in a structure of materials. They are rather simple and quick to measure and give good results which are well understandable and comparable with results obtained in laboratories around the world. They are based on the interaction or influence of electromagnetic waves and motions of atoms and molecules of any compound. These motions can be of different types – vibrational, rotational and moreover symmetrical or unsymmetrical. They originate from forces between atoms which create a bond. Each atom in molecule or group of atoms oscillates with characteristic frequency and is able to absorb radiation of various wavelengths. In the case of IR spectroscopy, absorbed radiation has wavelength in the area of 0.8—100 μm, but typical interval for identification of changes in organic (polymeric) systems is 2.5—50 μm [48].

Devices designed for purposes of FT-IR spectroscopy are called spectrophotometers. Their main part is Michelson interferometer that consists of the source, fixed mirror, moveable mirror, beam splitter (element that is able to transmit one half of incoming radiation to moveable mirror and reflect the rest of it to fixed mirror) and detector. The beam of IR radiation reflects from the both mirrors and goes back to beam splitter and then to detector. The half of beam (50 %) returns back to the source. Divided beams interfere in dependence on the position of moveable mirror. After taking this path through mirrors, the beam goes through the sample, which is put in front of the detector [48].

The sample always reduces the intensity of beam and so called interferogram is obtained. It is a graph, where intensity vs distance of moveable mirror is plotted according to equation (2) [49]. This result is not very clear for assessment of the structure of sample. Therefore, a mathematical Fourier transformation must be done to obtain demanded results in the form of relation between absorbance or transmittance and wavenumber $\bar{\nu}$ [cm^{-1}], which can be seen in equations (3), (4) and (5) [49]. While absorbance *A* is related with intensity of the radiation *I*, wavenumber can be calculated from its frequency *f* or wavelength *λ*.

$$I(x) = 0{,}5 \cdot I(f) \cdot cos(2\pi \cdot f \cdot x) \tag{2}$$

where, *I(x)* is intensity of signal going to the detector, *I(f)* is intensity of the source with frequency *f* and *x* is retardance – optical path differences of beams caused by mirror moving.

$$\bar{\nu} = \frac{f}{c} = \frac{1}{\lambda} \tag{3}$$

$$T = \frac{I}{I_0}\ ,\ A = log\frac{1}{T} = log\frac{I_0}{I} \qquad (4), (5)$$

where *I* is intensity transmitted by sample, I_0 is intensity of incident beam, *c* is velocity of light and *λ* is wavelength.

The above description corresponds to the spectrometer with transmission arrangement of a measuring, but method of an attenuation of the total reflection (ATR) is also often used. ATR works on principle of the different refractive indices of the sample and material of the prism (part of device) and record the dependence of reflectivity on wavenumber. It is convenient, because it is not so demanding for a preparation of a specimen [49].

Although the description of recording of one IR spectrum seems to be very difficult, modern spectrophotometers are equipped with software, which manage to do all necessary steps at once during few seconds and provide the result right in the form of graph A vs $\bar{\nu}$. An example of such spectrum is depicted in *Figure 19*. There are several strong peaks and some wide bands (a peaks that are not so sharp) corresponding to certain wavenumber. As has been stated before, each molecular group absorbs radiation of different wavenumber and according to this fact, particular groups can be identified. Some well-known peaks and their wavenumbers are listed in *Table 3*. F*igure 19* also shows how the spectrum of PS can be changed during photodegradation process. There are typical growing peaks at about 1725 cm^{-1}, which is a characteristic position for carbonyl group [31, 50].

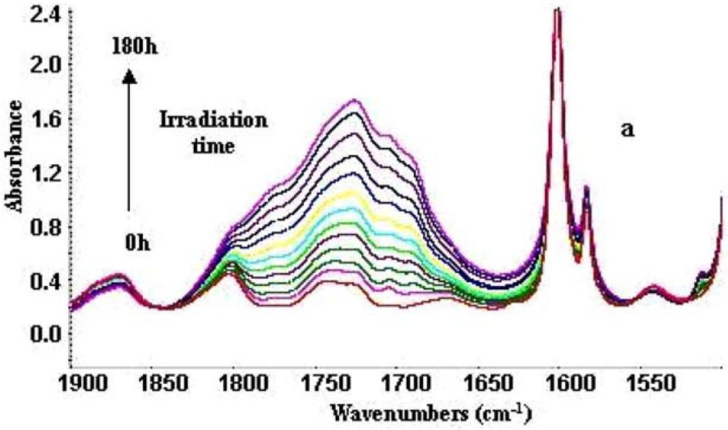


Figure 19 - Growing peak at carbonyl area of IR spectrum of pure PS [50]

Table 3 - Wavenumbers of characteristic groups in PS and HIPS IR spectrum [31]

PS		HIPS	
acetophenone	± 1700 cm^{-1}	**carbonyl**	**± 1717 (1725) cm^{-1}**
benzophenone	± 1662 cm^{-1}	hydroxyl	± 3450 cm^{-1}
carbonyl	**± 1730 cm^{-1}**	polybutadiene	± 966 cm^{-1}
ester	± 1240 cm^{-1}	cis-polybutadiene	± 727 cm^{-1}
hydroperoxide	± 3555 cm^{-1}	trans-polybutadiene	± 911 cm^{-1}

From the above facts follows that the FTIR spectrum can be used for identification of unknown material by comparison of measured and existing spectrum registered in databases or by description of peaks and their assignment to proper molecular groups. Besides, spectrum is good tool for assessment of photodegradation rate by calculation of the carbonyl index (*CI*), which is the ratio of absorbances *A* in the area of the carbonyl group wavenumber after and before degradation A_0. The equation (11) [6] shows the mathematical expression of this relation.

$$CI = \frac{A}{A_0} \tag{11}$$

A research team in Japan used ATR FT-IR method for an exploration of the depth profile of UV degradation of polymer materials. They studied several polymers including PS and found that PS is influenced by UV degradation to 2 μm from the surface and that extremely degraded layer extents to 0.6 μm [51].

2.4.2 Colorimetry

Colorimetric measurements are also performed on spectrophotometer. A source of daylight (with different specification in dependence on used standards) is used as an initial radiation beam going through sample. Such devices are able to determine the percent of the transmission of a sample and trichromatic coordinates for finding a colour and calculation of various indices and properties related with the colour of specimen surface. Their main principle is similar to IR spectroscopy – the light beam is led through or reflected from the surface of measured sample which absorbs and reflects specific wavelengths depending on the functional groups content and its structure. Results are obtained in the various forms (coordinates, indices, etc) according to an equipment of the used software.

Yellowness index

Yellowness index (*YI*) is popular way for expression of changes in the colour of material during photodegradation process. As the yellowness is related with degradation of polymers, *YI* serves as a rate of such degradation and helps to recognize quickly if the tested material undergoes some changes or not. From the occurrence of the yellowness, the alterations in the polymer structure can be concluded, because such variations in colour are usually caused by formation of double bonds in originally saturated structure, e. g. main chain in PS [52].

There are several standards describing methods for the *YI* measurement, for instance E313 ASTM or D1925 ASTM. Both of them are based on the values of trichromatic components (X, Y, Z) of measured material. These components define coordinates of the one specific colour in the spectrum by Commision Internationale de l”Eclairage (CIE). An example of the *YI* calculation according to E313 is given below by equation (6) [53].

$$YI\ E313 = \frac{100 \cdot (C_X \cdot X - C_Z \cdot Z)}{Y} \tag{6}$$

where C_X ans C_Z are coefficients dependent on a type of the lighting and observer (2°or 10°) and can be found in tables.

There are nine types of lightings designed as A, C, D65, D50, D55, D75, F02, F07 and F11. A represents white light of a wolfram bulb, C is average daylight of the north sky with correlated colour temperature at 6770 K, D series is daylight with temperature of the colour 6500 K, 5000 K etc. and F series represents fluorescent lightings [53]. For experimental part of this work, E313 ASTM method with D65 and 10° was chosen and *YI* value was directly received from the spectrometer software.

For better result evaluation after period of photodegradation, it is convenient to express percentage change of yellowness index (*ΔYI*), because majority of samples (polymers, composites, nanocomposites) have their own colour right at the beginning of tests. Equation (7), which was designed for Master’s thesis experiment, can be used for this purpose.

$$\Delta YI = \left(\frac{YI}{YI_0} \cdot 100 \right) - 100 \qquad (7)$$

where YI is yellowness index after and YI_0 before photodegradation.

Colour change

Change in a polymer colour, which occurs during photodegradation, expresses similar properties as has been described in *YI* part. Tristimulus components according to CIE or CIELAB can be received again from the spectrometer measurement. CIELAB is also a scale of colour spectrum with the difference that measurement and calculations work with L*, a* and b* instead X, Y, and Z components. CIELAB is possible to convert to CIE and vice versa with formulas given in standard ASTM E308 [53].

Coordinates L*, a*, b* describe colour by a different theory then CIE. As is shown in *Figure 20a*, L* is lightness and ranges from 0 (black) to 100 (white), a* constitutes position on an axis from green (minus) to red (plus), while b* position on an axis from blue (minus) to yellow (plus). The main difference between L*a*b* and XYZ (*Figure 20b*) is in expression of the lightness. It has its own axis in CIELAB space and is detached from the colour axes, while in CIE space it depends on the tristimulus values XYZ and is part of them. A distinction between these two scales is also evident from both parts of *Figure 20* [53, 54].

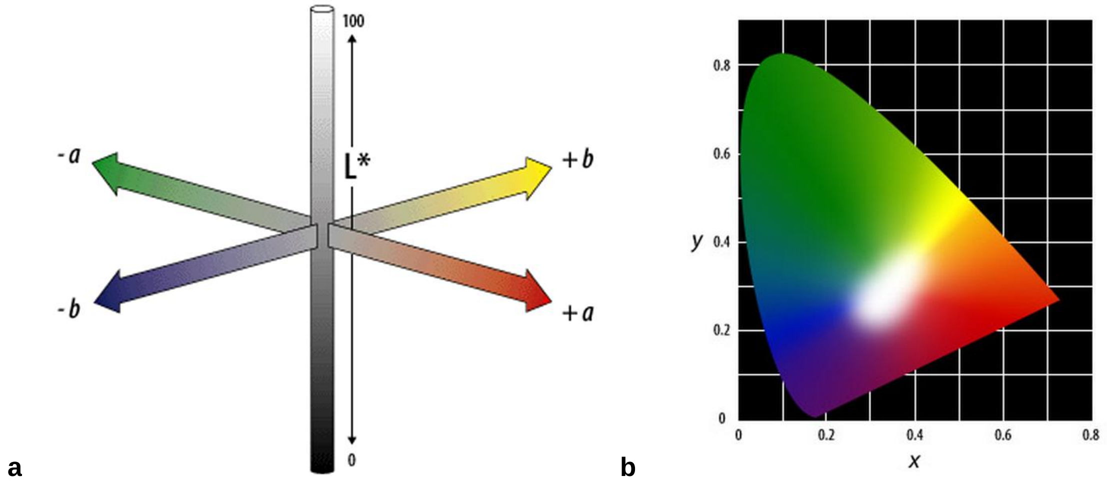


*Figure 20 - 1976 CIE L*a*b* Space [54]*

The CIELAB coordinates can be used for determination of colour saturation, shade of colour or, according to German standard, redness and yellowness (equations (7), (8), (9) and (10) [53], respectively).

$$C^* = \sqrt{a^{*2} + b^{*2}} \qquad (7)$$

$$h^0 = \arctan \frac{b^*}{a^*} \qquad (8)$$

$$e = \cos(16^\circ) \cdot a^* + \sin(16^\circ) \cdot b^* \qquad (9)$$

$$f = -0.7 \left[-\sin(6^\circ) \cdot a^* + \cos(6^\circ) \cdot b^* \right] \tag{10}$$

These quantities are not the only ones, which can be calculated from colour coordinates, but they are useful in an assessment of plastics in solid state. Beside these, opacity, haze of liquids, gloss of paints and many more is possible to evaluate by this spectroscopic method.

3 BIODEGRADATION

Biodegradation is a natural way of an organic compounds removal by the engagement of microorganisms, such as bacteria or fungi and an integration of their products to the basic cycles in the nature, the cycles of carbon, nitrogen and sulphur [55, 56]. The degradation mechanism is led by the metabolism of microorganism, i. e. it is from a completely different area of degradations than photodegradation. However, there is some connection between them, which lies in efforts to eliminate UV light or temperature effects on the material, but at the same time to create possibilities of a faster and more effective biological decay. Another thing that must be considered is the fact that UV degradation can facilitate biodegradation, but it is overshadowed by high demands which must be met during the material and article production [57]. It is not surprising that during the decades of plastics development, improvement and removal of their disadvantages, producers have made these materials almost indestructible. Innumerable number of additives, primarily stabilizers but also flame retardants, fillers, colorants and many others are used to make such simple products as disposable dishes, vending machines cups and tonnes of packaging bags, foils or boxes. These resistant articles are accumulated on dumps and also in the nature, where make up a white pollution (a pollution caused by plastic waste in cities and nature) [58, 59]. The movement for environmental protection of present days is a very efficient tool which forces governments to make steps for the reduction of every possible pollutant. Hence, engineers and technologists try to choose the most environmentally friendly solution of plastics removal and the biodegradation would be one of the best choices.

3.1 Biodegradable material

About twenty years ago, when the interest in biodegradation began to be serious, there was a need to define what can be considered as biodegradable material. In fact every material, no matter how well stabilized, degrades in some time, which can be years or hundreds of years. In 1992 four requirements were established to describe biodegradable material as material that undergoes a specific way of disposal, namely composting, sewage treatment, denitrification and anaerobic sludge treatment and the rate of degradation of each component must be consistent. Further, the process of disintegration must be harmless and end products must consist of carbon dioxide or methane, water and minerals [57].

Biodegradable material should have some important characteristics, which are suitable for enzymatic performance. The process of polymer biodegradation occurs in two steps. Firstly, it is necessary to shorten long macromolecular chains to oligomeric or lower level. Chain cleavage is catalysed by extracellular enzymes outside the microorganism cells. For this purpose, it is very convenient for the polymer to be hydrophilic and hydrolysable. Immediately after chain scission, small pieces of polymer are moved into cells and mineralised by other enzymes with energy for the microorganism metabolism as a product. This second step also provides already mentioned CO_2, water and salts together with a biomass formation. Other properties, which are helpful for this purposes are low degree of crystallinity and presence of ester and amide bonds with nitrogen substituent in the chain. Other plastics are attacked by enzymes very hardly [57, 58].

From synthetic polymers some polyesters can be classified as biodegradable, e. g. polylactide, polyglycolide, poly(ε-caprolactone), polyethylene succinate and polybutylene succinate. All of these polyesters are aliphatic, because aromatic types have excellent mechanical properties, but no prerequisites for the biodegradation [58]. Therefore copolymers of aliphatic and aromatic polyesters, which are at least partly biodegradable, were developed and produced by BASF under commercial name Ecoflex® [60] or by DuPont as Biomax® [61].

Polystyrene is a hydrophobic, high molecular weight, amorphous, water and chemically resistant polymer with no suitable substituent chemical groups. Compared with requirements on biodegradable material, only one match – amorphous state – can be found. However, other properties are more significant and very different that PS can be considered as non biodegradable. Nevertheless, there are several microorganisms that can cause PS deterioration, even thought in a very small extent (tenths of percents). They are *Aspergillus niger, Aureobasidium pullulans, Candida albicans, Escherichia coli, Penicillium funiculosum, Pseudomonas putida, Salmonella choleraesuis* and others [55, 62].

3.2 Biodegradation environments

The Earth offers two main environments that are suitable for biodegradation, since they contain appropriate conditions for the bacteria and fungi growth. They are water and soil in all their forms. Water is essential for bacteria, while soil is suitable for fungi because they need, beside water, solid surface to attach and grow. A combination of both of them is advantageous for a good biodegradation course: for instance, 50—60% humidity in soil is optimal for microorganism interactions. Another criterion for division of these environments is the presence of oxygen, which affects the character of end products. In aerobic biodegradation CO_2 is formed, while CH_4 indicates anaerobic process [57].

3.2.1 Soil environment

Agriculture, composting and pollution are three ways, how plastics can get to the contact with soil and have several common features; biodegradation takes place on the soil surface and is influenced by physical factors, such as temperature, UV light, humidity and by living animals that can unintentionally eat and digest some parts of plastics. The second part of the degradation is located underground and is led by microorganisms and plants. The whole process is described in *Figure 21*, where the interactions are introduced [63].

One of the three above indicated contacts of plastics with the environment – pollution – can be classified as a non-deliberate way. It is found along motorways, in parks, or on pavements as used plastic products. In this case, it is not always guaranteed that plastics get in soil, so it must be removed by the traditional way – cleaning [63].

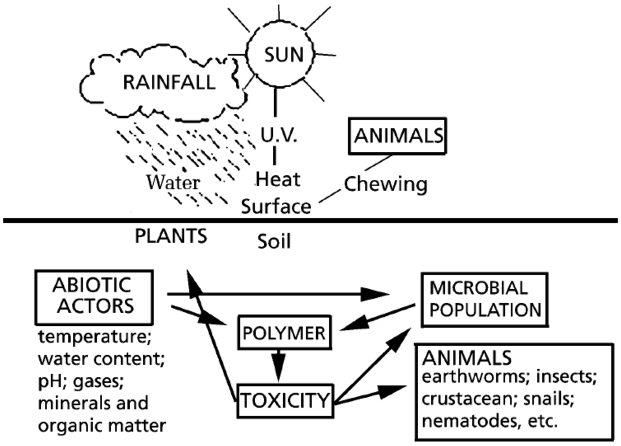


Figure 21 - Scheme of soil biodegradation [63]

Agriculture, on the other hand, uses a conscious deposition of various types of a foil and other plastic products on and in the soil. They are often used to facilitate growth of plants and prevent growth of weeds, and after several weeks, they are completely destructed and disintegrated. Such articles as mulch foils are usually made of polyethylene and starch blends or pure starch. Starch as biopolymer undergoes biological decay very easily and it is convenient to be used in a large extent for this purpose, because the requirements on mechanical properties are not so high [63].

The last type of soil biodegradation, which is fully standardized, is composting. Compost is a mixture of organic waste and soil with a lot of microorganisms and soil animals, such as earthworms or beetles. They cooperate together on a conversion of the waste into nutritious soil of the highest quality. For composting purposes blends of synthetic materials and biopolymers are used. The biodegradation is then described as a disintegration of these materials during one composting cycle so that no pieces bigger than 2 mm are finally present. This compost can be used as usual for fertilization, but the rest of synthetic polymers still remains [63].

3.2.2 Water environment

Water, a liquid environment of the Earth consists of sweet water, marine water and water coming from the activity of the mankind, i. e. waste water from industrial areas, agriculture and households. There are also several factors that characterize these liquids, e. g. temperature, *pH*, content of microorganisms or minerals. However, none of them can provide conditions which would be able to cause biodegradation of the most common plastics. It is applicable only for polyesters as already discussed in Chapter 3.1 [64].

3.3 Biodegradation and waste disposal

Relation between biodegradation and waste disposal is based on though of a full material decay in contact with the environment (water, soil and their combination). This is possible only with biopolymers, such as starch or cellulose and some synthetic polyesters, but concerning polystyrene, the only way may be the reduction of the waste volume. It cannot be expected that PS will be fully “absorbed” into the natural cycle, but there are some signs of possible deterioration

[55]. Figure 22 shows the composition of plastic municipal waste. As can be seen, PS occupies 6 % of the total amount, which is not negligible and this is the reason for the research of PS biodegradation [65]. Another significant factor is that – as soon as PS is biodegraded (disintegrated into small pieces) it will be possible to do the same with other plastics, which will lead to a massive reduction of the volume of polymer waste.

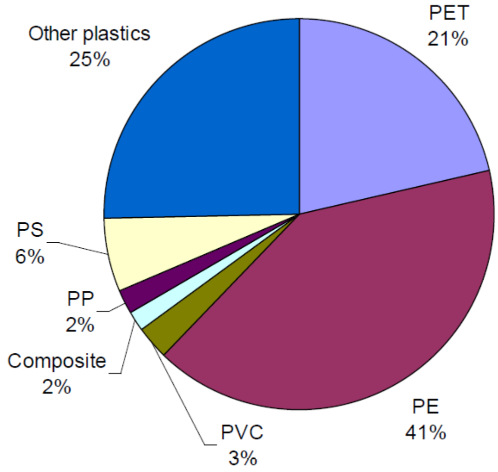


Figure 22 - Municipal solid plastic waste [65]

3.4 Biodegradation testing methods

Many of experimental methods for testing of material resistance in natural conditions, such as water or soil, are not as complex as tests used for evaluation of UV degradation and demands on laboratory equipment are also lower. All biodegradation experimental methods are described by many standards for the unification of results. However, tests usually take several months, thus some changes in conditions are admissible, e. g. small temperature or humidity fluctuations are irrelevant. Often used methods include composting, during which CO_2 or CH_4 formation (in anaerobic environment) or O_2 consumption (respiration test) is controlled. Common soil is also a good material for biodegradation assessment and mass loss is sufficient evaluation method, as will be presented in a following paragraph [57, 66].

Soil Burial Test

Burial test is very easy to prepare and maintain for the long time period. It can be performed either in laboratories, or directly in the outdoor soil. A preparation of polymer samples involves their weighing and considering of the best way of the sample marking to make them well recognizable after biodegradation period. This is important, because the main principle of test is to bury samples in the suitable soil (e.g. the soil from a garden) and leaving them there for several months. There is a need to keep the humidity of the soil on 50—60 %, because this is the favourable interval for the growth of microorganisms. Soil organisms are also influenced by *pH*. This parameter depends on type of soil and must be taken into account, because too acid or too alkali environment slows the microorganisms activity. Temperature conditions should be kept at 20—25 °C and the whole system with samples is necessary to saturate with oxygen to ensure aerobic environment. After expiration of experimental time, samples have to be removed, washed carefully and dried for relevant results of following weighing [66]. A susceptibility of polymer to biodegradation can be expressed by determination of microorganism activity, i. e. to explore to what extent microorganisms settled the polymer. This can be realized by microscopic observation of the surface [57].

4 ADDITIVES

Polymers in their pure form have properties due to which they are not always processable effortlessly and suitable for the manufacture, especially of some demanding products. This is the reason why a wide range of ingredients are used to ensure good flow and processing properties and to improve mechanical and thermal behaviour of the material as well as to make them more resistant to various factors and chemicals. These ingredients are generally called additives. These includes pigments, thermal and UV stabilizers, antioxidants, oils, various types of fillers, antistatic agents, crosslinking agents, blowing agents, plasticizers and many others. They are commonly added to polymers and majority of products cannot be manufactured without them.

Additives are a very variable group and some of them are used in large (e. g. fillers), others in small (e. g. stabilizers, pigments) amounts. For PS and polymers derived from it, additives reducing the burning (for better health and property protection) and UV degradation are among the most important because they can assure a fine appearance of products for a long time without any loss of properties caused by negative influence of UV radiation [1]. More information about them has already been provided in Chapter 2.3. Now, attention will be paid to fillers and especially nanofillers, because they are used in the experimental part of this Master's thesis.

4.1 Fillers

An original reason for addition of fillers to polymer matrices was a reduction of polymer products price. This idea is also often considered in present days, since economical and profit aspects are on the first place of each product manufacture. Their other and important functions, such as influence on and improvement of the polymer properties, were discovered as the development in the filler area continued and deepened during last decades [67]. Price lowering fillers are called inactive or diluent fillers because they are present in the polymer matrix primarily for the purpose of polymer save. On the other hand, fillers that significantly influence some property are called active and those, which are able to predominantly improve mechanical properties, are reinforcing [1].

Fillers can be of both organic and inorganic nature, in all possible shapes and very different sizes. This gives engineers a spectrum of opportunities how to design a product of required properties. One of the basic filler divisions is into fibres and particles. The particles shape is either close to sphere, flake and plate, or does not have any regular geometric character. Fillers size can be from centimetres (long fibres), through millimetres to nanometres (nanofillers) and their density is equally diverse from hundredths to tens of grams per cubic centimetres. Another feature is so called aspect ratio, the ratio of the length and the diameter. According to this, fibres (more than 1 000) can be recognized from spheres (1 for regular sphere or cube) [67]. Last of the most important properties of fillers is the area of the particle surface, because it influences the filler activity. There is a relation between the surface and the particle size. The smaller the particle size the larger the surface area of the filler. This is the reason why nanofillers began to be studied and used. Another essential requirement on all composites is, in general, good particle dispersion of fillers in the polymer matrix, which ensures homogeneity and required improvement of properties.

However, particles can aggregate and create initiation sites of cracks in composites. This negative behaviour is directly connected with particle size of fillers, i. e. the smaller the particle size, the more demanding processes of composite preparation because of the more difficult keeping particles detached. For every type of filler, an important aspect is good compatibility with the polymer matrix. If the bond between the filler and the polymer is weak, filler can release from the matrix and it cannot provide satisfactory effect and mechanical properties can be even worse. To support compatibility, special additives – compatibilizers (e. g. silanes) – are used [68, 69].

Calcium carbonate

Calcium carbonate is one of the most used fillers. Polymer sciences have rich experiences with its use, initially for reduction of polymer products price and later also for mechanical properties improvement and preparation of quality composites. Its advantage among other fillers is white colour, i. e. composites stay colourable. In the nature, calcium carbonate is formed by long time process of sedimentation, primarily of shells of marine organisms. Therefore, it can be found in minerals and rocks (e. g. chalk, limestone, travertine, dolomite). For purposes of polymer filler, $CaCO_3$ is prepared from other crystalline forms – calcite or aragonite. All of these modifications differ in admixtures and history of their formation (e. g. temperature and pressure). There are three types of technological processes used to $CaCO_3$ filler preparation, however, 90 % is prepared by dry or wet milling. Very fine grades with particle size below 1 μm are obtained by precipitation process during which a lime is formed and then $CaCO_3$ is again precipitated [67]. Calcium carbonate and several examples of other PS fillers with their properties are listed in *Table 5*.

Table 4 - Fillers used in PS matrix [69]

Filler	Chemical formula	Density [$g.cm^{-3}$]	Particle shape	Particle size [μm]	Spec. surf. area [$m^2.g^{-1}$]
Calcium carbonate	$CaCO_3$	2.7—2.9	irregular	0.15—30	2—24
Glass beads	SiO_2	2.2—2.5 (solid)	spheres	7—30	0.4—0.8
Kaolin	$Al_2O_3.2SiO_2.2H_2O$	2.2—2.6	plates	0.2—7.3	8—65
Magnesium hydroxide	$Mg(OH)_2$	2.4	hexagonal crystals	0.5—7.7	7—30
Talc	$Mg_3Si_4O_{10}(OH)_2$	2.7—2.8	plates	0.8—35	2.6—35

4.2 Nanofillers and nanocomposites

As written above, common fillers improve, beside others, mechanical properties of the polymeric material, but they must be added in a certain amount. For instance, some profiles reinforced with glass fibres are filled in tens of percent. They consist of almost pure glass with only little polymer resin (e. g. epoxide), which works as a binder. These composites have been used for many years, but at the turn of 20th and 21st century nanocomposites made their breakthrough. Their boom was caused by fact that they significantly enhance mechanical and other properties of the material in the very low loading (maximum about 5 wt%). This low filling does not influence such properties of polymer matrix as weight, which is very important, especially for applications in automotive or aircraft industry. At the same time, modulus, strength, heat resistance or degradation abilities of biodegradable polymers are sharply increased and flammability or gas permeability are reduced [70, 71, 72].

Nanocomposites are usually composed of a thermoplastic or reactoplastic matrix (polyolefines, polyvinyles, polyamide, polyesters) and layered silicate nanofiller (NF), whose representatives are montmorillonite or hectonite. They had been known before 1990's (the very first experiments with clay minerals date back to the half of the 20th century), but their research only brought valuable results in the mentioned decade [73]. The first applicable results are from Toyota engineers who studied composite of nylon 6 and montmorillonite with a conclusion that only a very small amount of the filler leads to significant improvement of mechanical properties and they later showed that nanocomposite can be prepared by mixing the polymer melt with mineral clay without the need of an organic solvent usage [74, 75].

4.2.1 Structure of nanocomposites

Only the composites with filler particle size in the range of nanometres in at least one direction can be regarded as nanocomposites. Phyllosilicates, a type of clays, are often used as nanofillers. They have layered structure, which creates tetrahedral and octahedral geometries. For example, phyllosilicate designed as 2:1 consist of tetrahedron with oxygen or hydroxyl atoms in the vertices and a silicone atom in the middle. Tetrahedrons are joined through shared oxygen atoms and some edges. Between two tetrahedral layers there is a layer of the octahedrons of either aluminium, or magnesium hydroxides [76]. This complex structure is shown in *Figure 23 a* and *b.* Thus, one main layer is made up with tetra-octa-tetrahedrons and its thickness is about 1 nm. Between these layers, there is a gap that is filled with cations (Al^{3+} or Mg^{2+}), which can be replaced by other cations (Fe^{2+}, Li^{+}). This gap is called gallery and can be seen in *Figure 23a*. By exchanging the gallery members (e. g. application of the alkylammonium), more polymer-friendly phyllosilicates are prepared. The reason for this replacement is that clays are naturally hydrophilic and an interaction with nonpolar polymer matrices is very poor. Such modified silicates are called organoclays and their characteristic features are lower surface energy and easier "mixing" with polymer which help to achieve good NF dispersion in matrix [77, 78].

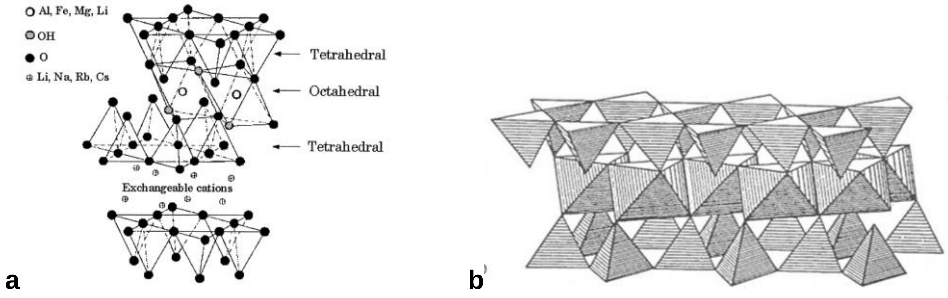


Figure 23 - Structure of phyllosilicate [77, 79]

"Mixing" in previous paragraph means separation of silicate layers and diffusion of polymer chains between them, i. e. intercalation. According to the degree of intercalation and dispersion of nanofiller, three types of nanocomposite structure can be recognized. The first is phase separated structure (*Figure 24a*). It is characterized by deficient layer separation and therefore poor dispersion of nanofiller layers. In this case, the filler particles have larger dimensions than nanometres and they behave as common filler. Another is intercalated structure, where polymer chains create regular interlayers as shown in *Figure 24b* and nanofiller layers are better dispersed. If the layer separation continues exfoliated structure is obtained, where no signs of the original arrangement can be recognized and individual silicate layers are irregularly spread in the entire matrix (*Figure 24c)*. The latter two are the required states, because nanocomposite properties reach the maximum [78]. Therefore, it is very important to pay attention on dispersion of NF in matrix, because nanocomposites properties are strictly related with it. In positive case of exfoliated structure, highest quality composites are obtained. These could have much better mechanical behaviour or lower gas permeability and, in the same time, their weight and appearance (translucency or colour) stay unchanged. However, to ensure good dispersion is not easy step. It can be facilitated by organoclay as was written above. To keep dispersion on required level is another demanding part of nanocomposite preparation, which can be ensured by compatibilizer use. The compatibilizer is compound which is able to react with both polymer and NF and provides the bond between them [80]. For polystyrene matrix, styrene maleic anhydride can be used as compatibilizer which basically is the copolymer of styrene and maleic anhydride. This composition facilitates the link with PS due to their similar structure.

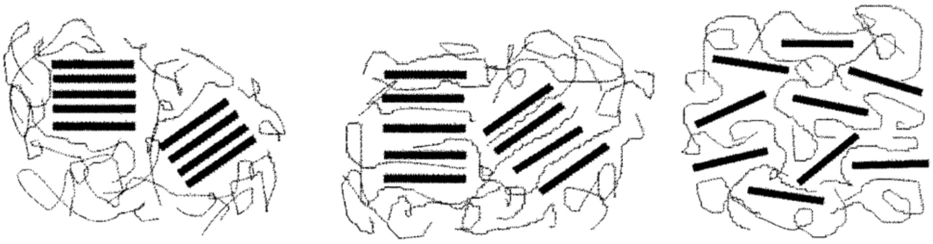

(a) Separated phases **(b) Intercalated structure** **(c) Exfoliated structure**

Figure 24 - Structure of nanocomposites [77]

Phyllosilicates are one example of additives, which are used as nanofillers. Others, for example, are carbon nanotubes, nano-$CaCO_3$ or titanium dioxide (TiO_2). All of them can be used in PS and the last one was the object of the 2006 study. It usually serves as pigment or antimicrobial agent, but Zan et al. confirmed that TiO_2 can be classified to another group of additives supporting the polymer decay under outdoor conditions. They prepared PS nanocomposite with grafted TiO_2 (PS-g-TiO_2) and exposed it to UV degradation with the result that this nanocomposite degrade in significantly higher degree than pure PS. For example, the mass loss after 396 hours of irradiation ($E = 2.5$ mW.cm^{-2}, $\lambda = 254$ nm) of PS-g-TiO2 was 18.9 %, while pure PS only 0.53 % [4]. This research showed that nanocomposites can contribute to faster photodegradation, therefore for Master's thesis experiment, five nanofillers and one classic filler were chosen to examine their influence on PS photodegradation and the differences, which will occur between them.

X-ray diffraction

For evaluation of degree of nanofiller intercalation and nanocomposite structure and therefore dispersion of NF, a method of X-ray diffraction (XRD) is commonly used. In general, it is the method for assessment of crystalline structure of compounds and therefore is also suitable for clay minerals, which evince layered regular structure. Theoretical background is based on Bragg's law expressed by equation (11) [81] which can be seen below.

$$n \cdot \lambda = 2 \cdot d \cdot sin\theta \tag{11}$$

where λ is wavelength of X-rays, d is crystal lattice spacing (distance of planes of similar atoms) and θ is incidence angle of X-ray.

Incident beams are of monochromatic character. They hit the sample and according to sample structure of crystal and their wavelength they are diffracted in different angles. The result of sample recording is spectrum, which is formed by dependence of diffracted beams intensity on diffraction angle, which is equal to 2θ. For structure of nanocomposites, some characteristic peaks can be observed in this spectrum. In general, peaks are formed when X-rays striking the sample meet Bragg's law. i. e. incident and diffracted beams are in phase [81]. For intercalated layered structure of clay minerals, these peaks move to lower values of angle °2θ, because the distance between particular layers (*d* in equation (11)) increases. In practice, when these peaks occur, it can be deduced that it probably is a nanocomposite with intercalated structure. On the other hand, no peak at lower angle region denotes the possibility of exfoliated structure and good dispersion of nanofiller [82]. These XRD measurements cannot be regarded as an unquestionable evidence of the nanocomposite structure because of NF dilution or orientation, as was proved by Morgan's research from 2003. Hence, XRD spectra must be always supplemented with transmission electron microscopic (TEM) photographs which provide information about morphology and spatial distribution of NF in localized area of nanocomposite [83].

4.2.2 Preparation of nanocomposites

Preparation ways, which lead to separation of the clay layers and introduction of the polymer chains between them, are of three different types and all of them should end with nanocomposite of required degree of intercalation or exfolation.

Intercalation of polymer from solution

At the beginning of this process the solvent for both polymer and silicate has to be chosen. It can be water, but more often organic liquid, such as chloroform or toluene. Then the silicate is swollen up to layers exfoliation. The polymer is solved too and both mixtures are put together, diffusion of polymer chains occurs and after solvent evaporation the nanocomposite is prepared. As stated above, the silicate has to be in the form of organoclay [73, 77, 78].

In situ intercalative polymerization

In this case, the silicate is solved in a liquid monomer. The monomer with small molecules is able to diffuse between layers and after that polymerisation takes place. So the polymer is created right between the silicate layers. The initiation of polymerisation is done by default ways [73, 77, 78].

Intercalation from polymer melt

Another method is based on polymer melting by temperature or shear stress. Silicate is mixed with the polymer melt, which gradually gets between the silicate layers. It is necessary to use modified silicate, but then exfoliated or intercalated nanocomposite can be prepared. On the other hand, the process is completely solvent-free, which is considered as a very positive aspect [73, 77, 78].

4.2.3 Types of nanofillers

All of the nanofillers introduced here are combination of silica and alumina. Their particular types differ in the ratio of these two components and other admixtures and trace elements. Some of them are also possible to use as both traditional filler and nanofiller. The choice of clays described here is intentional. They are not only the typical representatives, but all of them were used in the experimental research.

Montmorillonite

Montmorillonite (MMT) is clay mineral, which is formed from the volcanic dust. Its deposits are located around the world, but the well-known ones are in Montmorillon and Vienne in France and in several states of the USA. Chemical formula of MMT – $(Na, Ca)_{0.3}(Al, Mg)_2Si_4O_{10}(OH)_2.nH_2O$ – seems to be very complicated, but the main components are only silica (51 % SiO_2) and alumina (20 % Al_2O_3) [84].

MMT has typical layered silicate properties, which have already been outlined earlier in the text. It has a high ability of ion exchange in the layer gap and high swelling characteristics. Both of these features enable intercalation and nanocomposite preparation. For polymer industry they are distributed under the commercial name, e. g. Nanofil® or Cloisite® [67].

Halloysite

Halloysite (Hal) is another clay mineral, whose composition is mainly formed by silica and alumina. In this case, it is 46 % and 40 %, respectively. Chemical formula of Hal is $Al_2Si_2O_5(OH)_4$, but in contrary to MMT, particles of Hal have the shape of nanotubes. Thus it does not evince a typical layered structure. It can be found in Belgium, Germany or USA and in the nature, it arises from feldspar [85].

Silica

Its chemical formula is SiO_2. It is a simple compound with enormous possibilities of applications. It is the basic component of all silicates, which make up as much as one third of Earth’s minerals. It has four morphologies – quartz, cristobalite, tridymite and opal. Quartz is almost pure silica and has a lot of well-known coloured forms, such as violet amethyst, yellow citrine, gray chalcedony or common sand [67].

For purposes of polymer filling silica is modified and produced industrially in the form of fumed, fused and precipitated silicas. In *Figure 25*, the preparation steps of fumed silica can be seen. The process consists of evaporation of silicone tetrachloride, mixing with air and hydrogen, burning of this mixture, subsequent cooling, precipitation and HCl removal. During this process the temperature is held at 1 800 °C and after cooling spherical particles of silica join and create chain structures with a size of 7—30 nm. Unlike quartz it does not have crystalline structure, but amorphous. As nanofiller it is distributed under the commercial name Aerosil® [67].

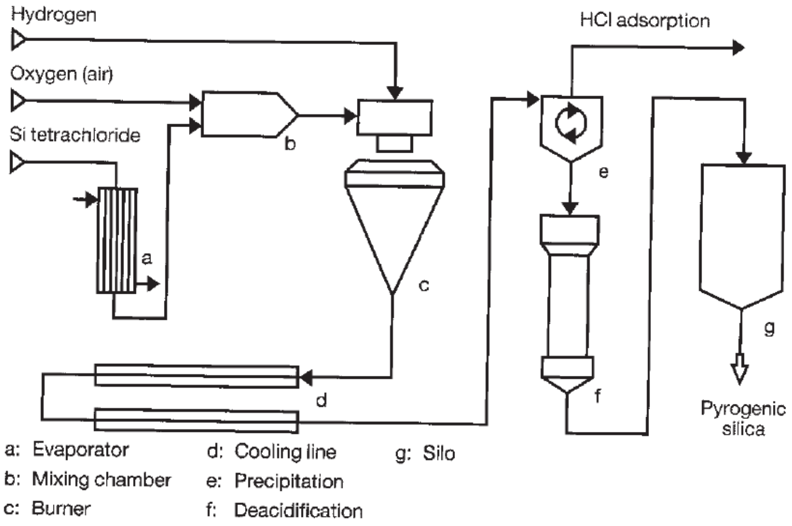


Figure 25 - Scheme of fumed (pyrogenic) silica preparation [67]

II. ANALYSIS

5 EXPERIMENT INTRODUCTION

The main goal of experiment was to examine the behaviour of several polystyrene and high impact polystyrene (nano)composites during artificial weathering and to compare their results with one microcomposite exposed to same conditions. Some of (nano)composites with HIPS matrix were prepared also with compatibilizer to assess its influence on photodegradation. Second part of experiment was focused on biodegradation of these nano and microcomposites to discover if nanofillers (NF) are able to make PS and HIPS more susceptible to biological decay.

5.1 Matrices, nanofillers and fillers

Two types of styrene polymers were chosen as matrices for the preparation of several types of composites. These were commercial polystyrene (PS) Krasten® 174 and high impact polystyrene (HIPS) Krasten® 552M delivered by SYNTHOS Kralupy a.s.

Layered nanofillers were represented by Cloisite® Na+ (Southern Clay Chemistry) – an unmodified montmorillonite and Nanofil® 5 (Südchemie, Germany) – an organically modified MMT. Other nanofillers were represented by Halloysite NT (Sigma-Aldrich) – silicate nanotubes and Aerosil® R 812 (Degussa) – nanosilica with particles of spherical shape. Moreover, one nanofiller with silver ions on zeolite carrier – IRGAGUARD® B 5 000 (BASF) – was added. A classic fillers were represented by micromilled calcite OMYA EXH 1sp (Calplex) with 1,5 μm size of spherical particles.

For better interaction of matrix and NF and attainment of good NF dispersion, several HIPS (nano)composites with Nanofil® 5 were prepared with compatibilizer of two different compositions. The compatibilizer was styrene-maleic anhydride (SMA) copolymer SMA® 1 000 P (ratio of styrene and maleic anhydride 1:1) and SMA® 3 000 P (ratio of styrene and maleic anhydride 3:1). SMA was purchased from Sartomer Company, Inc.

Sample preparation

For experimental research two sets of all composites were prepared. They differed in nanofillers loading which was 1 % and 3 %. (Nano)composites with SMA were prepared with 5 % of compatibilizer and they differed in Nanofil® 5 loading, which always was 1 %, 3 % and 5 %. All of these compounds were prepared in laboratory kneader Brabender Plasti-Corder with mixing bowls. The time of mixing was 10 min, the rotational speed was 30 min^{-1} and the temperature was kept at 180 °C. The specimens were prepared by compression moulding at the temperature 190 °C for 3 min. Cooling temperature was 20 °C (laboratory temperature). Specimen thickness was 1 mm and their final shape was trimmed to rectangle of 4 x 3 cm. All of them were marked with nanofiller or filler abbreviation and degree of filling as is listed in *Table 5*. These designations were also used in all figures.

Table 5 - List of used fillers and their abbreviations

<table>
<tr><th>Nanofiller</th><th colspan="6">Loading</th></tr>
<tr><td>Nanofil 5</td><td colspan="3">N5 1%</td><td colspan="3">N5 3%</td></tr>
<tr><td>Cloisite Na+</td><td colspan="3">Clo 1%</td><td colspan="3">Clo 3%</td></tr>
<tr><td>Aerosil</td><td colspan="3">Ars 1%</td><td colspan="3">Ars 3%</td></tr>
<tr><td>Halloysite</td><td colspan="3">Hal 1%</td><td colspan="3">Hal 3%</td></tr>
<tr><td>IRGAGUARD</td><td colspan="3">IRG 1%</td><td colspan="3">IRG 3%</td></tr>
<tr><th>Filler</th><th colspan="6">Loading</th></tr>
<tr><td>Calcite</td><td colspan="3">Cal 1%</td><td colspan="3">Cal 3%</td></tr>
<tr><th>Compatibilizer</th><th colspan="6">N5 loading</th></tr>
<tr><td>Styrene maleic anhydride 1:1</td><td colspan="2">SMA 1 N5 1%</td><td colspan="2">SMA 1 N5 3%</td><td colspan="2">SMA 1 N5 5%</td></tr>
<tr><td>Styrene maleic anhydride 3:1</td><td colspan="2">SMA 3 N5 1%</td><td colspan="2">SMA 3 N5 3%</td><td colspan="2">SMA 3 N5 5%</td></tr>
</table>

6 RESULTS AND DISCUSSION

6.1 Structure of (nano)composites

X-ray diffraction (XRD) measurements were performed with PANalytical X´Pert PRO diffractometer with a Cu tube source (λ = 0.1540 nm) operated at 1.2 kW. XRD spectra were taken for pure PS and HIPS, powders of layered nanofillers and specimens with these NF. Powders of pure nanofillers were measured by different measuring technique than other specimens because of their different consistence.

The purpose of these measurements was to clarify the structure of (nano)composites, which contain layered nanofillers. The goal was to determine preliminary if interacalated or exfoliated structure was reached. *Figure 26* shows XRD measurements of (nano)composites samples, which consist of Nanofil® 5 and Cloisite® Na+ (1% and 3% loadings) and HIPS matrix, and samples of pure HIPS, N5 and Clo. A pair of peaks, which identifies the structure of nanocomposites is located around 2 and 7 º2θ. As can be seen, they are visible on spectra of pure N5 and pure Clo, because they consist of layers, which reflects X-ray beams. On the other hand, on the scan of (nano)composites, these peaks, in case of both loadings of HIPS + Clo, disappeared. This fact suggests that structural character of layers disappeared and (nano)composites with Clo perhaps have exfoliated structure. However, this fact could also mean that Clo created large agglomerates in matrix, which XRD is not able to distinguish and therefore structure of nanocomposite cannot be considered. On contrary, HIPS + N5 (nano)composites probably has intercalated structure, because peaks, which indicates layered structure are still present and shifted to lower degrees. Similar results were also observed for layered (nano)composites with PS matrix.

In case of XRD measurements, TEM photographs have a decisive influence on correct evaluation of nanocomposites structure, as was stated in Chapter 4.2.1. This is the reason why it cannot be certainly decided if prepared samples are or are not nanocomposites and therefore their designation contains brackets – (nano)composites. Nevertheless, for this photodegradation experiment, the structure description by XRD spectra is sufficient and TEM photographs are being taken for future research.

Figure 27 and *Figure 28* depict XRD spectra of HIPS (nano)composites with N5 without and with compatibilizer – styrene-maleic anhydride. Influence of two compositions of SMA (styrene:maleic anhydride 1:1 and 3:1) on dispersion of N5 in HIPS matrix was investigated. As can be seen, in both figures, when 1% loading of N5 was used, peaks indicating layered structure disappeared. Unfortunately, it does not mean that the compatibilizer was efficient and better nanofiller dispersion was reached, but it probably reflects the fact that 1% loading of N5 is too low to be noticed by XRD measurement. However, when higher volume of N5 was used, the peak started to appear again and is visible at about 5 °2θ. Second peak from the pair is probably shifted to lower degrees of °2θ, which is under the measurable limit of the used device, and therefore is not visible on *Figure 27* and *Figure 28*.

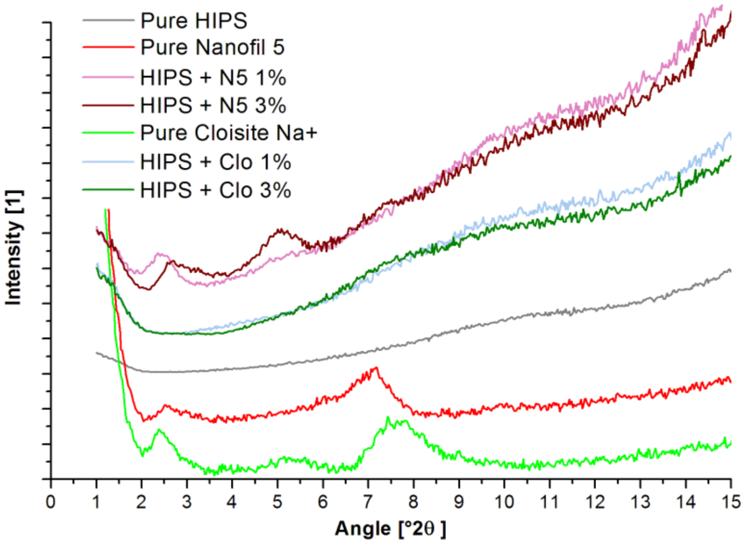


Figure 26 - XRD spectra of layered (nano)composites

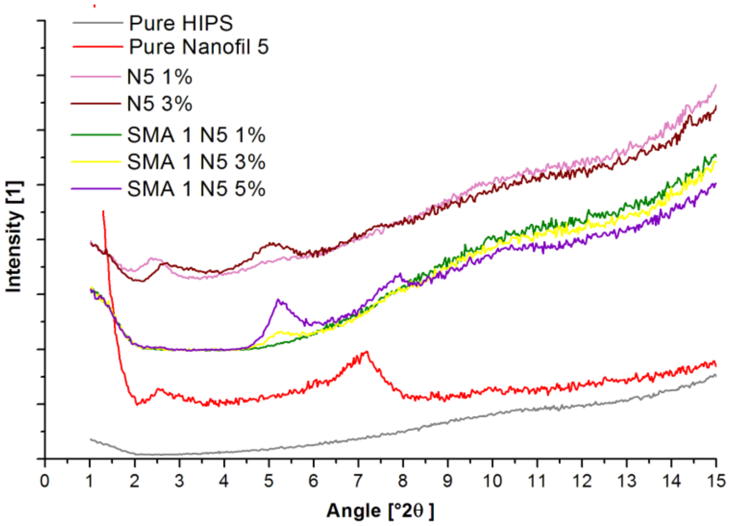


Figure 27 - Detail of XRD spectra of layered (nano)composites with compatibilizer SMA 1:1

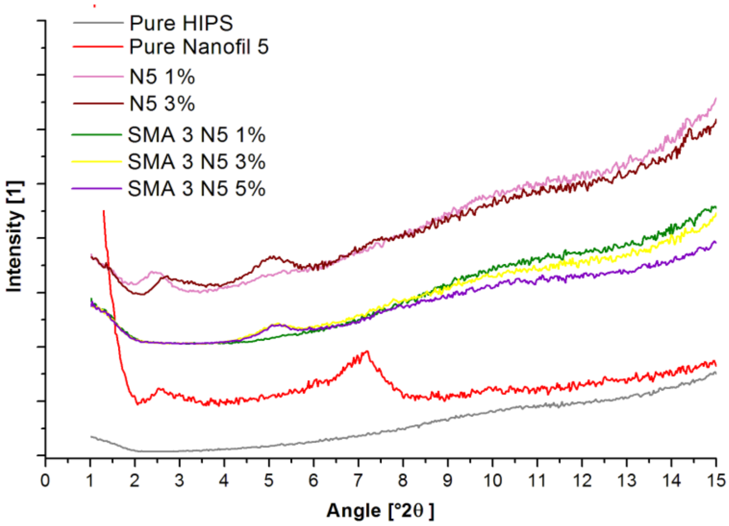


Figure 28 - Detail of XRD spectra of layered (nano)composites with compatibilizer SMA 3:1

This observation proposes that SMA probably is quite efficient, because every shift to lower degrees indicates the improvement of NF dispersion. There can also be seen little difference between SMA 1:1 and SMA 3:1. The first seems to be less active than the latter, because peaks of HIPS + N5 + SMA 1 are larger.

Other NF – Hal, Ars, IRG and Cal – have structure of particles with defined size and shape, which do not create layers. Therefore, it is not possible to evaluate their dispersion in matrix by XRD analysis and at the same time to obtain results, which would be comparable with XRD of layered clay NF. All of these samples are therefore regarded also as (nano)composites, whose NF dispersion is not further described.

IRGAGUARD nanofiller

IRGAGUARD nanofiller should contain silver ions on zeolite carrier, which is composition declared by its producer. However, previous research [86] showed that IRG contains vast amount of zinc oxide and very small amount of silver ions. IRG element analysis was done by X-ray fluorescence (XRF), whose result is in *Figure 29*. Moreover, zeolite should contain some SiO_2, but the XRF did not find any traces of Si atoms in IRG sample. Therefore, in photodegradation and biodegradation experiments, IRG was rather considered as ZnO than silver ions on zeolite carrier, but its mark IRG was left unchanged.

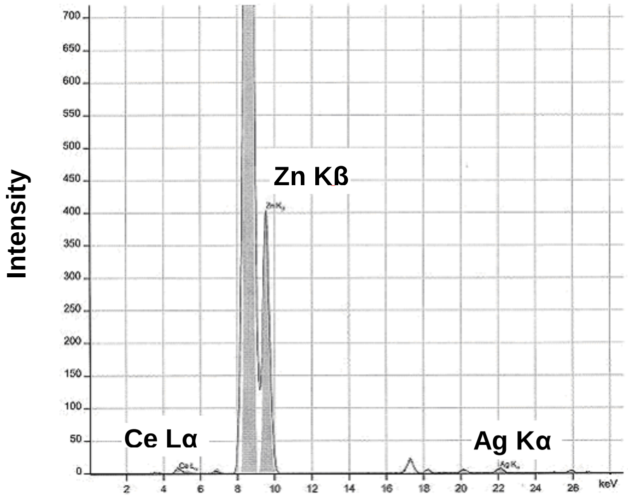


Figure 29 - XRF analysis of IRGAGUARD nanofiller [86]

6.2 Photodegradation – artificial weathering

Artificial weathering was assured by Xenotest® Alpha+ (Atlas) with xenon light as radiation source. The intensity of irradiation was kept at 125 $W.m^{-2}$, black standard temperature was set at 50 °C, chamber temperature at 35 °C and relative humidity at 0 %. There were some tolerances of these values, thus conditions in chamber were moving in the interval of ± 20 °C. Relative humidity was also little higher at about 10 %.

Total irradiation time was 560 hours, which is equivalent to almost 11 months of continuous sunshine. When average hours of daylight are taken into account, it roughly corresponds to double time (22 months) of exposure in real environment. An assumption that the intensity of xenon light was about 14 times higher than average intensity of sunlight was used for these conversions. Intervals of data collection were 70 hours.

6.2.1 FT-IR spectra and carbonyl index

Fourier transform infrared spectra were recorded with AVATAR 320 (Nicolet) spectrophotometer equipped with Omnic software. A method of ATR FT-IR was used and spectrum was recorded with 32 scans. A section with carbonyl group peak was identified in the plot of the absorbance vs the wavenumber. Carbonyl index *CI* was calculated according to equation (1) with maximum values of absorbance at this section.

Figure 30 shows the whole infrared spectrum of HIPS + IRG 3%. This specimen was chosen as a representative sample of the spectrum evolution during irradiation periods. According to theory of PS degradation (see Chapter 2.2.1), ATR FT-IR spectra were analysed in the region of 1 740—1 700 cm^{-1}, which corresponds to area of carbonyl groups. The peak that was used for calculation of carbonyl index was identified at about 1 725 cm^{-1} and was always accompanied by peak at 1 716 cm^{-1}. These values are characteristic for aldehyde and ketone group, respectively. As can also be seen in *Figure 30,* other changes in spectrum occurred. The second most noticeable peak growth is placed at about 1 030 cm^{-1} and is classified as hydroxyl group in aliphatic or cyclic alcohol. Next interesting fact, a merging of peaks, is observed in the region of methyl –CH3 and methylene –CH2– groups of aliphatic compounds (2 990—2 850 cm^{-1} and 1 450 cm^{-1}) and =CH– group in aromatic and unsaturated compounds at 3 100—3 000 cm^{-1}. Another decrease of absorbance is apparent at 1 490 cm^{-1}, which belongs to benzene ring. All of these findings indicate massive formation of carbonyl and hydroxyl groups along PS backbone. A reduction of the amount of methyl and methylene groups is associated with previous claim. Possible cleavage of benzene rings can be concluded from the absorbance decrease at 1 490 cm^{-1}.

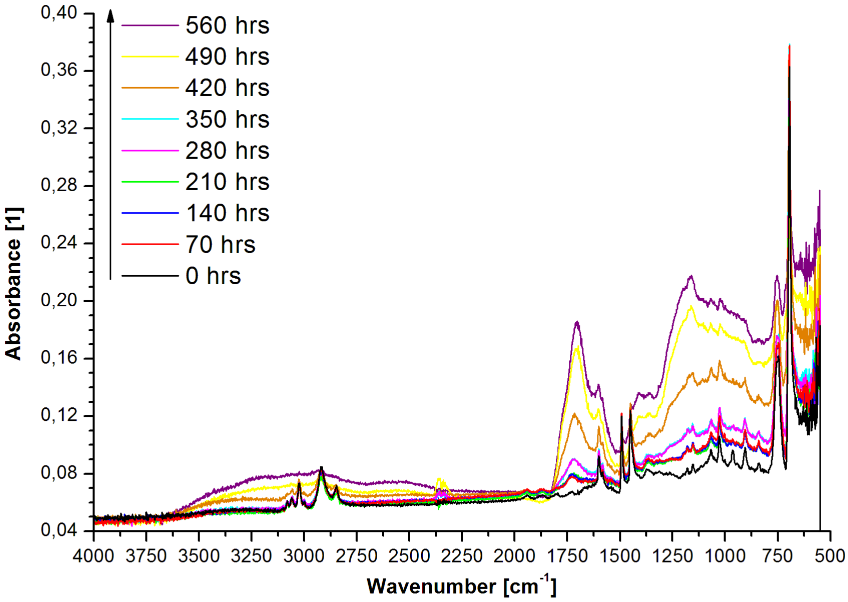


Figure 30 - Evolution of FT-IR spectrum during irradiation periods

PS matrix (nano)composites

Figure 31 (*A* and *B*) depicts carbonyl region of FT-IR spectra of (nano)composites with PS matrix after 560 hours of UV irradiation. There are clear differences between particular (nano)composites, their loading and pure PS sample. The curve of pure PS before photodegradation (0 hrs) is also displayed to show initial state. As can be seen, 1 % filling of all nanofillers (N5, Clo, Hal, Ars, IRG) and also microfiller (Cal) significantly increases the amount of formed carbonyl groups in PS matrix and therefore PS (nano)composites are more susceptible to photodegradation than pure polymer. There may be two possible explanations of this fact. Ions, which are present in nanofllers could act as catalysts for photooxidation reactions or 1% loading of fillers might be too low and layers and particles of nanofillers could work as some impurities in PS, which initiate degradation process. Similar trend can be observed for 3% loading with one important difference. Clo 3% in PS matrix strengthened (nano)composite resistance to UV light almost twice when compared with pure PS. This implies that unmodified nanofillers might be able to improve PS resistance to photodegradation, but they need to be used in proper loading. Other aspect, which should be taken into account, is (nano)composites structure. PS with Clo 3% probably has exfoliated structure. On the other hand, PS + N5 3% with possible intercalated structure evinces one of the worst results.

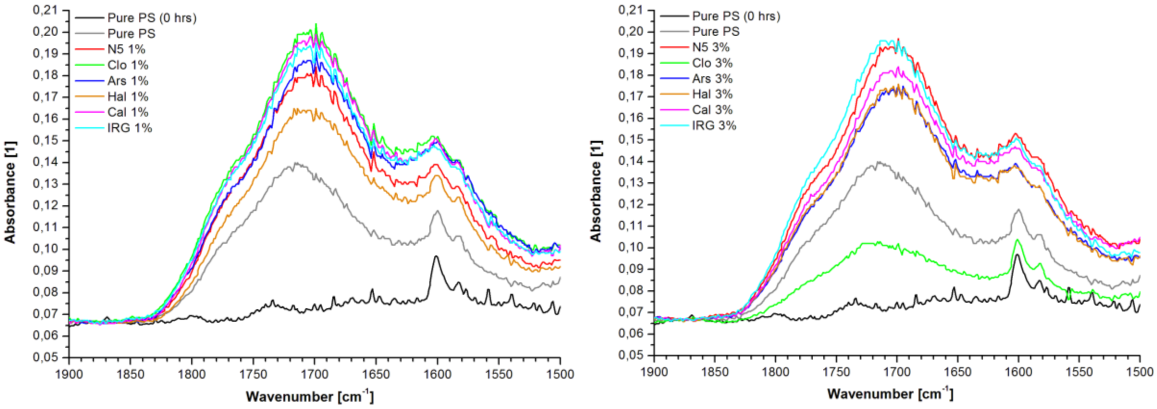


Figure 31 - Carbonyl group region of FT-IR spectrum after 560 hrs of photodegradation for PS (nano)composites with 1% (A) and 3% (B) loading

Values of *CI* confirm the previous findings, but other facts can be deduced from the whole course of carbonyl index in time. *Figure 32* and *Figure 33* show plot of *CI* vs photodegradation time and *Table 6* supports these figures with all values of carbonyl index obtained during periods of UV irradiation of all (nano)composites. As can be seen, first 140 hours of irradiation can be considered as induction period of photodegradation, because almost no changes occurred. After this time, changes in *CI* of both analysed loadings can be distinguished. There are alterations in degradation course for modified (N5) and unmodified (Clo) nanofiller, for NF with particle shape of nanotubes (Hal) and spheres (Ars) and also for microfiller (Cal). N5 and Clo reached completely contradictory results. In 1% loading, Clo evinces the worst and N5 average behaviour. Whereas, PS + Clo 3% improved its resistance by 20 % and N5 3% proved to be the worst. This fact denotes the possibility that better bond between the matrix and nanofiller (modified NF) might caused higher rate of photodegradation and this effect is more significant at higher loading. The importance of the percent of loading is also clear from samples with IRG. IRG influence is also more significant with 3% loading, which evinces longer induction period – it can be said that 210—350 hours, but then sharp increase is observed and for longer times IRG behaves similarly as other NF. Another goal of this experiment was to compare the behaviour of microfiller (Cal) with other NF. As can be observed, samples of both 1% and 3% loading of Cal rather belong among samples with worse results. However, there are slight differences. The induction period of degradation is longer for Cal 1%, but after 560 hours are *CI* values identical. These results suggest that microfiller is not certainly applicable for reduction of PS matrix photodegradation rate.

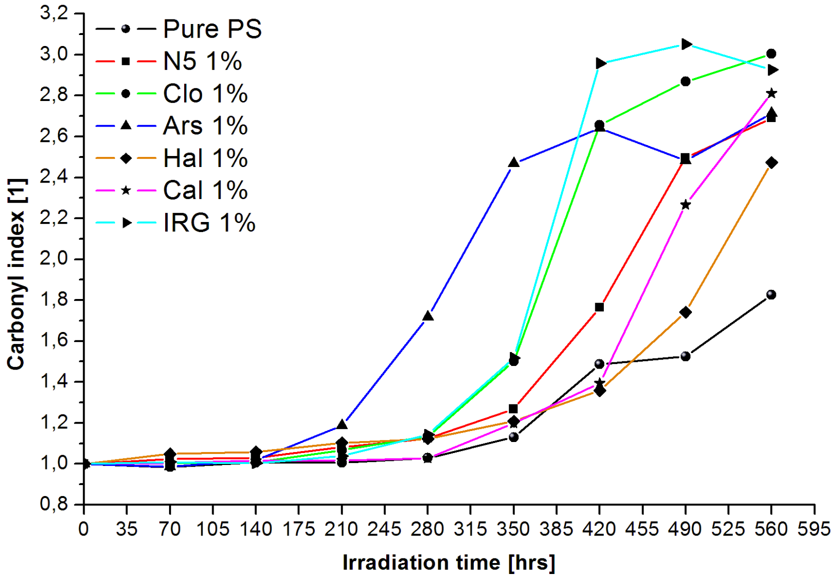


Figure 32 - CI during irradiation time for PS (nanocomposites with 1% loading

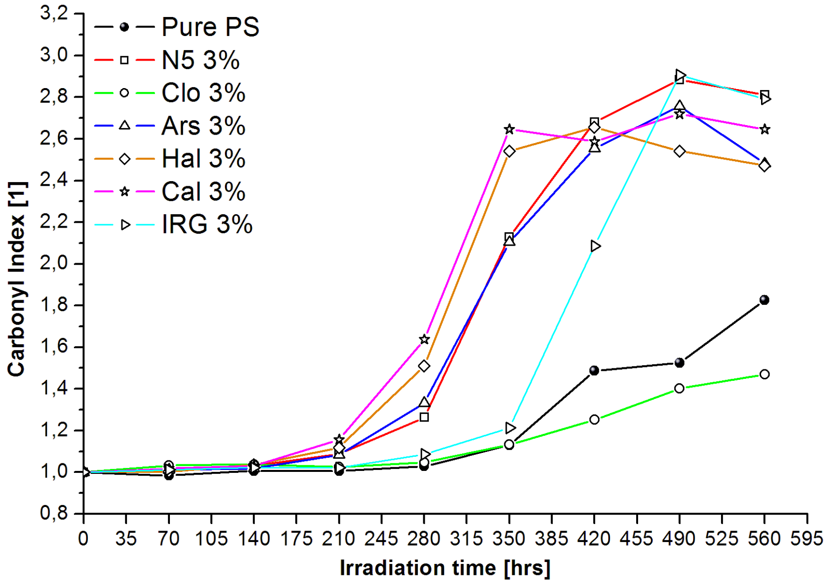


Figure 33 - CI during irradiation time for PS (nano)composites with 3% loading

Decrease of *CI* in figures (and from FT-IR spectra, also proportional decrease of the amount of hydroxyl groups) at longer times of some (nano)composites may be attributed to measurement error or some sample surface damage, because the individual differences in values are not very significant. On the other hand, no inappropriate steps were taken during measuring and additionally, this decrease is observed only for samples with high rate of photodegradation. It seems that these samples might reach maximum of their degradation potential. Thus, it would be beneficial to extend irradiation time for future researches to confirm or disprove this finding.

Table 6 - Values of carbonyl index of all PS (nano)composites during photodegradation

Irradiation time	Pure PS	N5	Clo	Ars	Hal	Cal	IRG
***CI* [1] – 1 % loading**							
0	1.00	1.00	1.00	1.00	1.00	1.00	1.00
70	0.98	1.02	1.00	0.99	1.05	1.00	1.01
140	1.01	1.03	1.01	1.02	1.06	1.01	1.00
210	1.01	1.08	1.07	1.19	1.10	1.02	1.04
280	1.03	1.12	1.14	1.72	1.12	1.03	1.14
350	1.13	1.27	1.50	2.47	1.21	1.20	1.52
420	1.49	1.76	2.66	2.64	1.36	1.39	2.96
490	1.53	2.50	2.87	2.48	1.74	2.27	3.05
560	1.83	2.69	3.00	2.71	2.47	2.81	2.93
***CI* [1] – 3 % loading**							
0	1.00	1.00	1.00	1.00	1.00	1.00	1.00
70	0.98	1.01	1.03	1.01	1.00	1.02	1.01
140	1.01	1.03	1.04	1.02	1.04	1.03	1.02
210	1.01	1.09	1.02	1.08	1.12	1.16	1.02
280	1.03	1.26	1.05	1.33	1.51	1.64	1.09
350	1.13	2.13	1.13	2.10	2.54	2.65	1.21
420	1.49	2.68	1.25	2.55	2.66	2.59	2.09
490	1.53	2.88	1.40	2.76	2.54	2.72	2.91
560	1.83	2.81	1.47	2.48	2.47	2.65	2.79

HIPS matrix (nano)composites

Samples with HIPS matrix exhibit absolutely opposite behaviour than PS (nano)composites. *Figure 34* and *Figure 35* depict the course of *CI* during irradiation periods for both 1% and 3% loading. As can be seen, pure HIPS is extremely labile under UV light. This tendency to photodegradation is presumably caused by presence of unsaturated rubber chains in the structure, because double bonds are predisposed to oxidation reactions. Therefore, all (nano)composites and also microcomposite managed to reduce HIPS photodegradation rate and all of them can be consider as suitable for the purposes of HIPS UV resistance enhancement. However, this improvement is not very significant for all samples with 1% filling, i. e. their abilities to reduce the amount of formed carbonyl groups are almost negligible. On the other hand, some HIPS (nano)composites with 3% loading, especially Clo 3% and IRG 3%, are able to prolong the onset of degradation at 210—350 hours of irradiation. Nevertheless, at longer times their effect is same as the effect of other NF. Both figures are also supplemented with *Table 7*, where all *CI* values are listed.

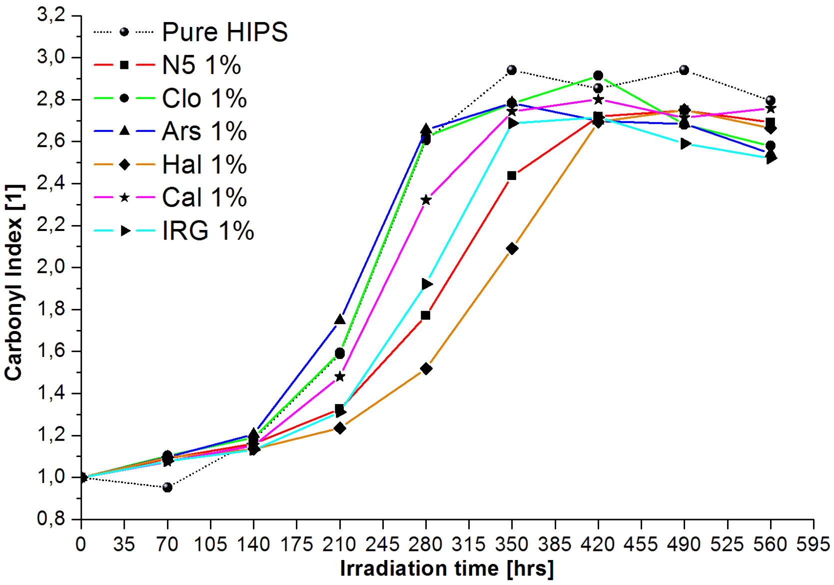


Figure 34 - CI during irradiation time for HIPS (nano)composites with 1% loading

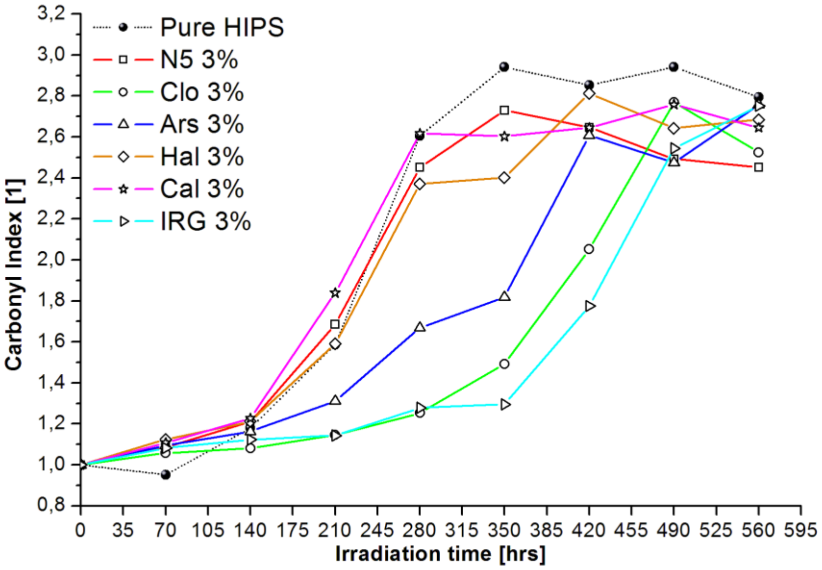


Figure 35 - CI during irradiation time for HIPS (nano)composites with 3% loading

Table 7 - Values of carbonyl index of all PS (nano)composites during photodegradation

Irradiation time	Pure HIPS	N5	Clo	Ars	Hal	Cal	IRG
***CI* [1] – 1 % loading**							
0	1.00	1.00	1.00	1.00	1.00	1.00	1.00
70	0.95	1.09	1.10	1.10	1.10	1.08	1.08
140	1.18	1.16	1.19	1.21	1.14	1.15	1.13
210	1.59	1.33	1.59	1.75	1.23	1.48	1.31
280	2.61	1.77	2.62	2.66	1.52	2.32	1.92
350	2.94	2.44	2.78	2.78	2.09	2.74	2.69
420	2.85	2.72	2.91	2.70	2.69	2.80	2.72
490	2.94	2.75	2.68	2.68	2.75	2.71	2.59
560	2.79	2.69	2.58	2.54	2.66	2.76	2.52
***CI* [1] – 3 % loading**							
0	1.00	1.00	1.00	1.00	1.00	1.00	1.00
70	0.95	1.08	1.06	1.10	1.12	1.11	1.08
140	1.18	1.21	1.08	1.16	1.21	1.23	1.12
210	1.59	1.69	1.15	1.31	1.59	1.84	1.14
280	2.61	2.45	1.25	1.67	2.37	2.62	1.28
350	2.94	2.73	1.49	1.82	2.40	2.60	1.29
420	2.85	2.65	2.05	2.61	2.81	2.64	1.78
490	2.94	2.49	2.77	2.47	2.64	2.76	2.54
560	2.79	2.45	2.53	2.76	2.68	2.64	2.75

HIPS (nano)composites with compatibilizer

SMA compatibilizer was used for attainment of better N5 dispersion in HIPS matrix. Thus, the behaviour of these (nano)composites with improved exfoliation level during photodegradation was also investigated. The goal was to assess, if better dispersion has any influence on photodegradation and to compare the influence of two SMA compositions on this. *Figure 36* and *Figure 37* provide time changes of *CI* of HIPS with three different N5 loadings and two compositions of SMA compatibilizer. The amount of SMA was in all cases 5 %. In figures, there are also curves of HIPS + N5 without compatibilizer for complex assessment. As can be found, the results are very similar and there is no significant difference between samples with better dispersion and samples without SMA and even between other HIPS results, which were already commented above. It appears that compatibilizer does not have any relevant influence on photodegradation rate of HIPS (nano)composites. When influence of two composition of SMA is compared, it might be said that SMA 3 reached slightly better results and corresponding to XRD conclusions, better N5 dispersion (with SMA 3) may provide higher resistance to UV light. However, this improvement (SMA 3 N5 1% and SMA 3 N5 3%) is almost unnoticeable and only in short-time degradation periods. On the other hand, SMA 3 N5 3% evinces rather worse behaviour and at longer times, the difference between all samples is inconsiderable. Therefore, no general claim of photodegradation rate dependence on N5 loading with SMA can be concluded.

CI values for HIPS (nano)composites with compatibilizer are summarized in *Table 8*.

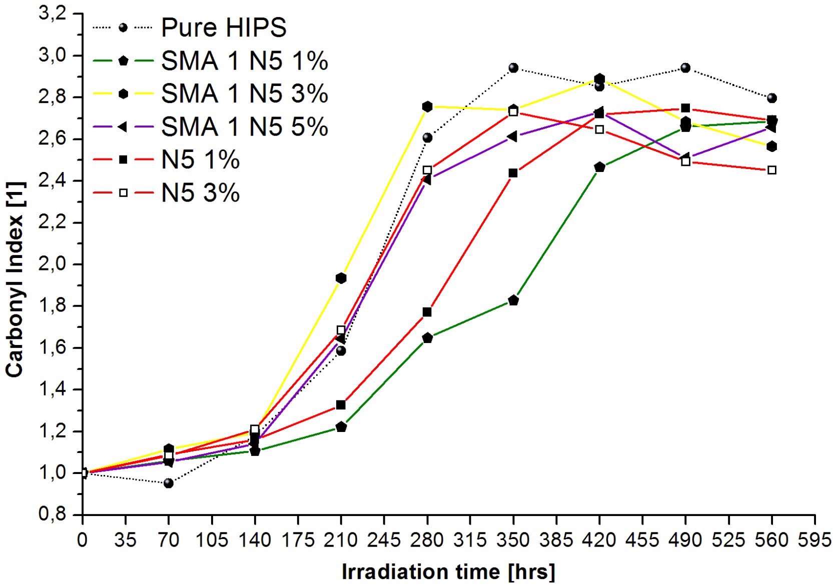


Figure 36 - CI of HIPS + N5 (1, 3 and 5% loading) with 5% of SMA 1:1

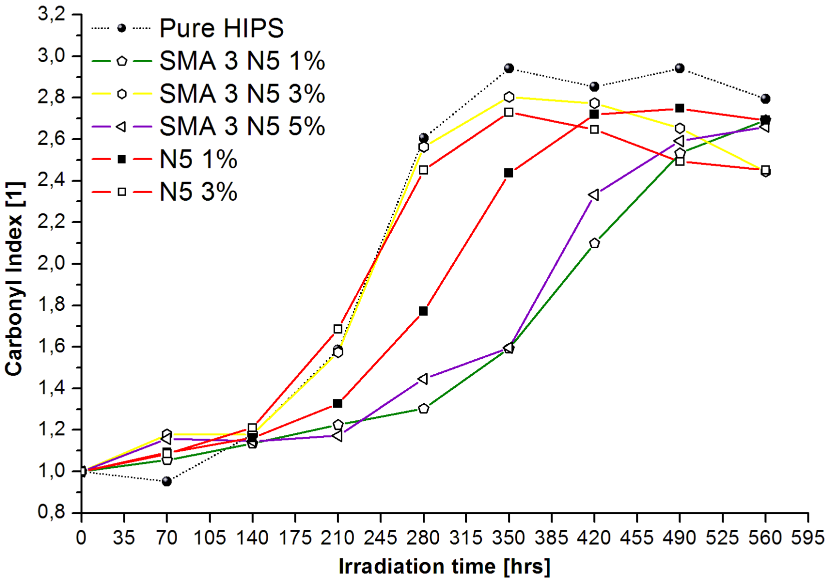


Figure 37 - CI of HIPS + N5 (1, 3 and 5% loading)with 5% of SMA 3:1

Table 8 - Values of carbonyl index of all HIPS + SMA (nano)composites

Irradiation time	Pure HIPS	HIPS + N5 1%	HIPS + N5 3%	HIPS + N5 5%
***CI* [1] – SMA 1:1**				
0	1.00	1.00	1.00	1.00
70	0.95	1.06	1.12	1.05
140	1.18	1.11	1.20	1.14
210	1.59	1.22	1.94	1.64
280	2.61	1.65	2.76	2.41
350	2.94	1.83	2.74	2.61
420	2.85	2.47	2.89	2.73
490	2.94	2.66	2.68	2.51
560	2.79	2.69	2.57	2.66
***CI* [1] – SMA 3:1**				
0	1.00	1.00	1.00	1.00
70	0.95	1.05	1.18	1.16
140	1.18	1.13	1.18	1.15
210	1.59	1.22	1.57	1.17
280	2.61	1.30	2.56	1.45
350	2.94	1.59	2.80	1.60
420	2.85	2.10	2.77	2.33
490	2.94	2.53	2.65	2.59
560	2.79	2.69	2.44	2.66

6.2.2 Yellowness index and colour

Spectrophotometer UltraScan PRO (HunterLab) with EasyMach QC software was used for measurement of yellowness index (*YI*). E313 ASTM method with D65 and 10° was set. Surface area of samples, on which measurements were taken, was of circle shape with 0.780 inches in diameter (approx. 12 cm^2). Better comparison of particular samples was achieved by calculation of percent change of *YI* according to equation (2). The evaluation by percent change was chosen because of original colour of samples, which was influenced by used nanofiller and microfiller even before the photodegradation test started. All measured values of *YI* for all types of (nano)composites. are listed in tables in Appendix P I.

Real appearance of samples for eye evaluation of their colour was documented by the form of photographs, which were taken with Panasonic DMC-TZ8 camera. These photographs can be found in Appendix P II.

PS matrix (nano)composites

Yellowness index was used for evaluation of samples colour change during photodegradation periods. PS is predisposed to yellow as double bonds are formed during degradation steps (see Chapter 2.2.1). *Figure 38* as well as *Figure 39* depict dependence of *YI* change (in percents) on irradiation time. The scale on axis y (*YI*) was intentionally arranged to 2 800 %, because curves of PS and following HIPS (nano)composites can be clearly compared. As can be seen, both nanofillers loading in PS matrix reached similar results. Only (nano)composites of Ars 1% and 3% evince higher degree of yellowness than pure PS. This fact indicates that along polymer chains of these samples, a higher amount of double bonds was probably formed. Cal 1% and Cal 3% achieved results as pure PS and the rest of (nano)composites finished photodegradation at maximum 300 % of initial *YI* value, i. e. they were three times yellower than at the beginning of experiment. To complete, PS finished five times yellower. Very good results can be observed for PS + IRG 3%, where no change occurred until 350 hours and then yellowness change reached only 100 % of initial value. Decrease of IRG *YI* is probably caused by slightly uneven colour appearance of samples.

Calculated values of *YI* change are listed in *Table 9*.

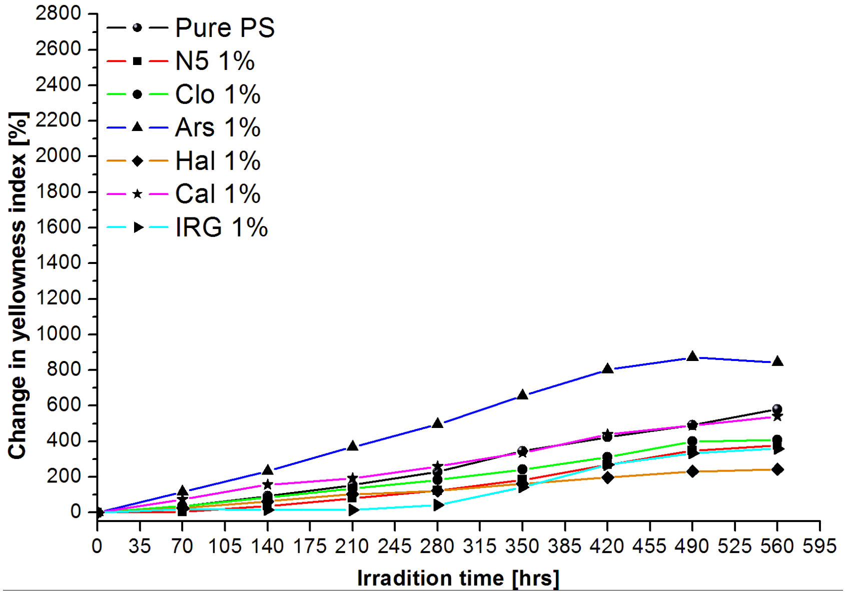


Figure 38 - Changes in YI for PS (nano)composites with 1% loading

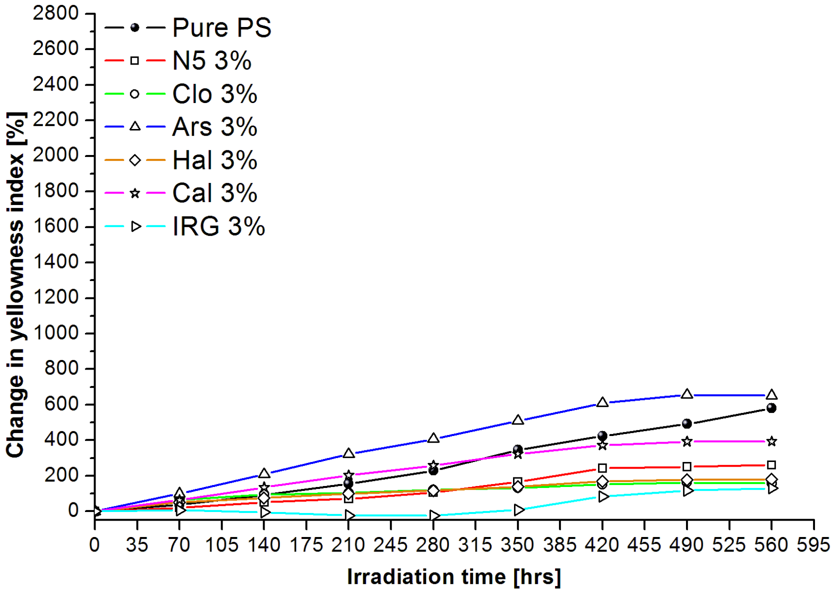


Figure 39 - Changes in YI for PS (nano)composites with 3% loading

HIPS matrix (nano)composites

A following pair of figures – Figure 40 and *Figure 41* – shows evolution of *YI* change in time for HIPS (nano)composites and pure polymer. As can be seen, all (nano)composites caused considerable decrease of the rate *of YI* change. Pure HIPS, i. e. polymer chains of PS and unsaturated rubber, is very susceptible to formation of double bonds as well as carbonyl groups. Compared with its (nano)composites, it can be said that yellowing of pure HIPS was certainly reduced to minimum and in some cases (e. g. Clo 1% and IRG 1%) was stopped until 350 hours of irradiation and then was also negligible. For both loadings, an order of nanofillers and microfiller (from the best to the worst influence on HIPS) can be arranged as follows: IRG, Clo, Hal, N5, Cal, Ars, This positive effect is more significant, when 3% loading is used. HIPS + Clo 3% reaches only 85 % of original *YI* value, while the same sample at 1% loading reaches 184% change of *YI* after 560 hours. Thus, the difference is 100 %. When it is analysed from the point of NF type, except IRG, unmodified layers of Clo and particles of Hal seem to be the best choice for reduction of colour change and for preparation of colour-stable material. Both of these NF are of natural origin. On the other hand, synthetic particles of Ars reduce the yellowness the least. Similar behaviour of Ars can be observed in *Figure 38* and *39*, which belong to PS.

All calculated values of *YI* change are listed in *Table 10*.

Table 9 - Values of change in YI of all PS (nano)composites during photodegradation

Irradiation time	Pure PS	N5	Clo	Ars	Hal	Cal	IRG
***ΔYI* [%] – 1 % loading**							
0	0	0	0	0	0	0	0
70	36	3	36	115	26	74	20
140	92	36	85	233	63	156	15
210	154	80	134	368	103	193	14
280	229	122	183	495	122	259	42
350	345	183	241	655	162	336	143
420	424	268	312	803	197	440	268
490	491	347	399	871	231	489	334
560	580	377	408	844	242	540	359
***ΔYI* [%] – 3 % loading**							
0	0	0	0	0	0	0	0
70	36	20	63	99	51	64	6
140	92	51	95	209	75	135	-5
210	154	70	103	321	99	203	-23
280	229	107	120	407	117	258	-25
350	345	166	133	509	139	323	8
420	424	242	151	608	169	372	83
490	491	250	162	655	177	393	117
560	580	260	158	651	179	394	130

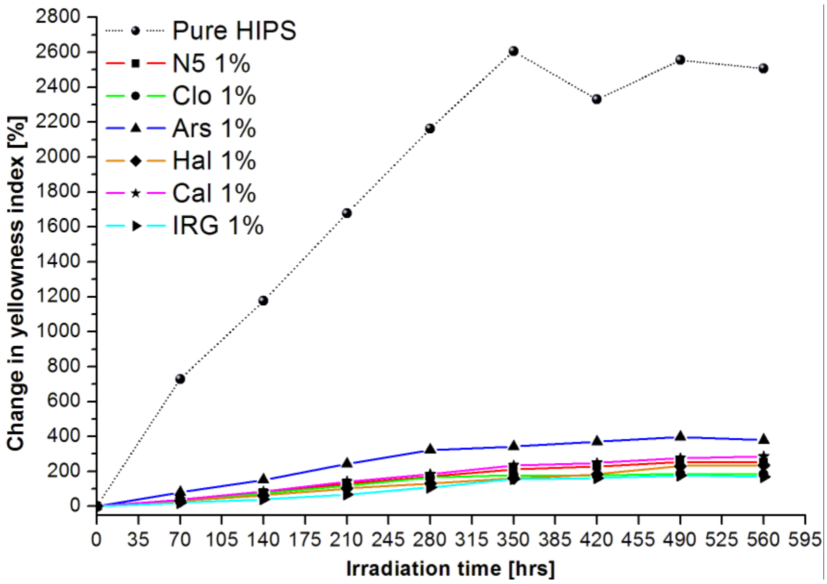


Figure 40 - Changes in YI for HIPS (nano)composites with 1% loading

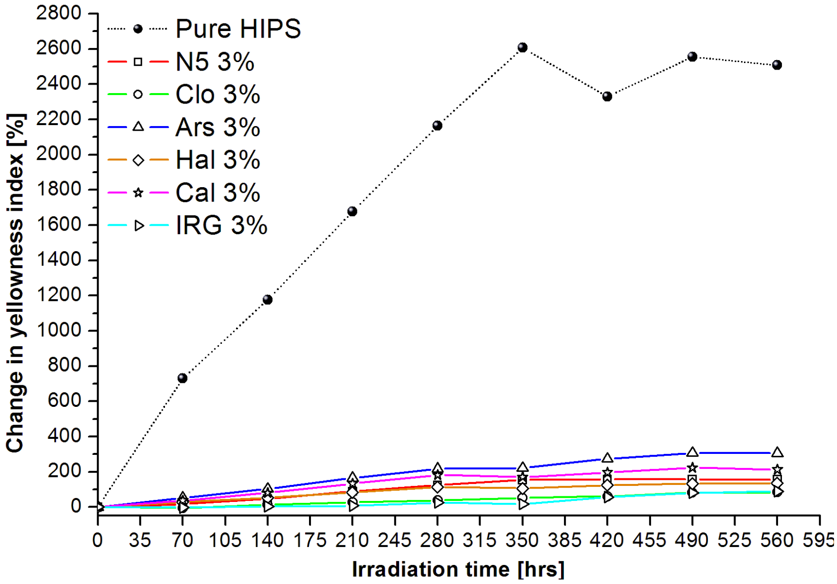


Figure 41 - Changes in YI for HIPS (nano)composites with 3% loading

HIPS (nano)composites with compatibilizer

Figure 42 and *Figure 43* show changes in *YI* plotted against irradiation time. As can be observed, the compataibilizer in HIPS (nano)composites further confirms positive influence of NF on reduction of yellowing, discussed in previous paragraph. In this case, modified nanofiller N5 is investigated and it can be clearly deduced that there is dependence between N5 loading and yellowness rate, as well as between type of SMA (1:1 or 3:1) and yellowness rate. First finding can be seen in both figures and even for both types of (nano)composites, i. e. with and without SMA. Higher loading of N5 reduces yellowing of samples and when compatibilizer was used, this reduction was more distinctive. All samples with SMA 1 can be consider as colour stable during the whole photodegradation cycle and especially first 350 hours. Samples with SMA 3 compatibilizer evince slightly worse results. It is expectable finding, because SMA 3 contains more styrene than maleic anhydride and styrene blocks behave similarly as PS.

Table 11, where calculated values of *YI* change are listed, complements figures and as can be seen, HIPS + SMA 1 N5 5% evinces after 560 hours the change only 43 % of the first value, which is indeed a small change.

Table 10 - Values of changes in YI of all HIPS (nano)composites during photodegradation

Irradiation time	Pure HIPS	N5	Clo	Ars	Hal	Cal	IRG
***ΔYI* [%] – 1 % loading**							
0	0	0	0	0	0	0	0
70	729	34	38	80	31	38	20
140	1176	76	73	151	63	85	40
210	1677	131	119	242	102	142	68
280	2163	170	164	322	130	184	108
350	2606	212	178	342	160	235	156
420	2329	228	176	370	183	249	162
490	2555	254	186	396	231	276	177
560	2507	250	184	379	236	286	169
***ΔYI* [%] – 3 % loading**							
0	0	0	0	0	0	0	0
70	729	17	-5	52	28	37	-3
140	1176	48	12	103	52	80	4
210	1677	89	28	165	83	133	8
280	2163	125	37	217	113	182	25
350	2606	154	51	221	106	170	17
420	2329	157	61	274	124	196	56
490	2555	158	81	307	132	223	80
560	2507	156	85	306	136	213	89

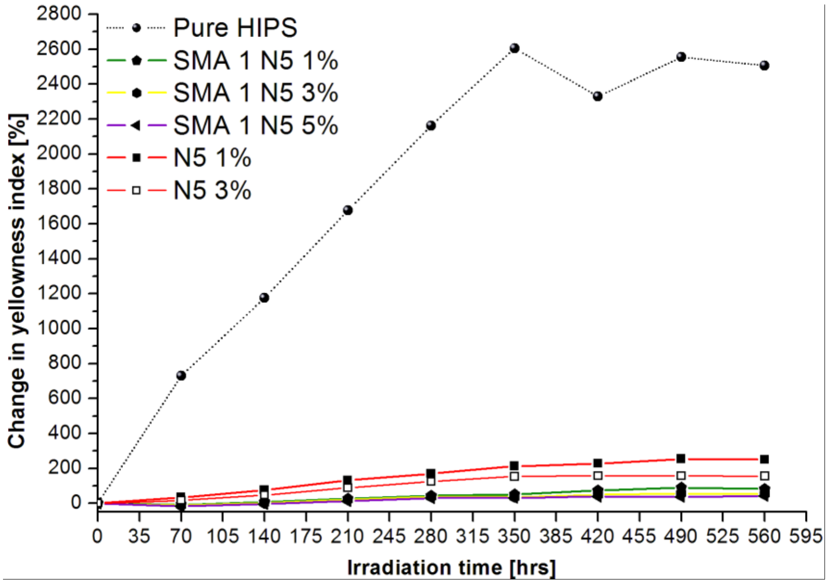


Figure 42 - YI of HIPS + N5 (1, 3 and 5% loading) with 5% of SMA 1:1

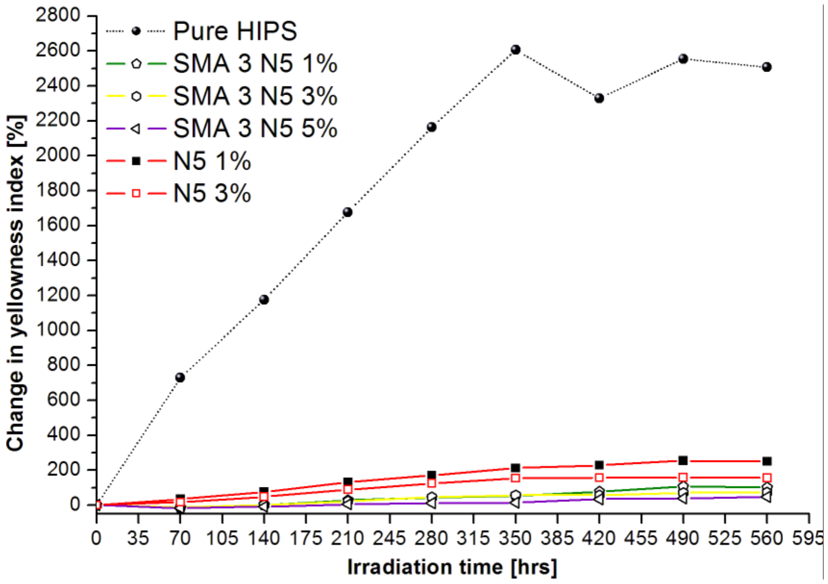


Figure 43 - YI of HIPS + N5 (1, 3 and 5% loading) with 5% of SMA 3:1

Table 11 - Values of change in YI of all HIPS + SMA (nano)composites

Irradiation time	Pure HIPS	HIPS + N5 1%	HIPS + N5 3%	HIPS + N5 5%
Δ*YI* [%] SMA 1:1				
0	0	0	0	0
70	729	-8	-13	-16
140	1176	7	1	-4
210	1677	27	20	12
280	2163	43	38	30
350	2606	51	36	31
420	2329	73	49	39
490	2555	89	57	37
560	2507	82	53	43
Δ*YI* [%] SMA 3:1				
0	0	0	0	0
70	729	-16	-13	-17
140	1176	0	1	-9
210	1677	28	22	5
280	2163	42	45	12
350	2606	52	57	15
420	2329	77	57	34
490	2555	107	71	39
560	2507	101	73	48

6.2.3 Other optical measurements

Colour appearance of samples was also investigated by measurement of precise colour CIELAB coordinates L*, a* and b*. All of them are displayed in Appendix P III. Evolution of colour change is shown in *Figure 44*, where three dimensional colour space with L*, a* and b* axes is shown. As can be seen, the lightness of all samples decreases and colour coordinates move to yellow and red area. Colour shift to yellow is much more obvious than to red. It is interesting that in this case of HIPS (nano)composites with 1% loading, the colour of all samples after 560 hours of irradiation evince very similar coordinates. This effect is visible also of HIPS (nano)composites with 3% loading, but at lesser extent.

For pure PS, decrease of lightness is almost negligible, while PS (nano)composites changed their colour in similar way as HIPS (nano)composites. The difference is only in the shift on a* axis, where PS gets to minus greener values. These indicates that NF can cause some colouration, which is better to take into account during products designing.

General result of this investigation can be summarized as follows. PS (nano)composites tend to get greener and yellow during UV irradiation and their evaluation by eyes results in yellow-grey and dark yellow colour. On the other hand, HIPS (nano)composites are much redder. This difference is also visible in Appendix P I, where all photographs can be observed. From the samples with HIPS with SMA, less change in colour evince the (nano)composite SMA 3 N5 1%. It suggest that maleic anhydride has rather negative influence on colour of the surface, because this best result is found for sample with lowest content of maleic anhydride expressed by ration of maleic anhydride and styrene.

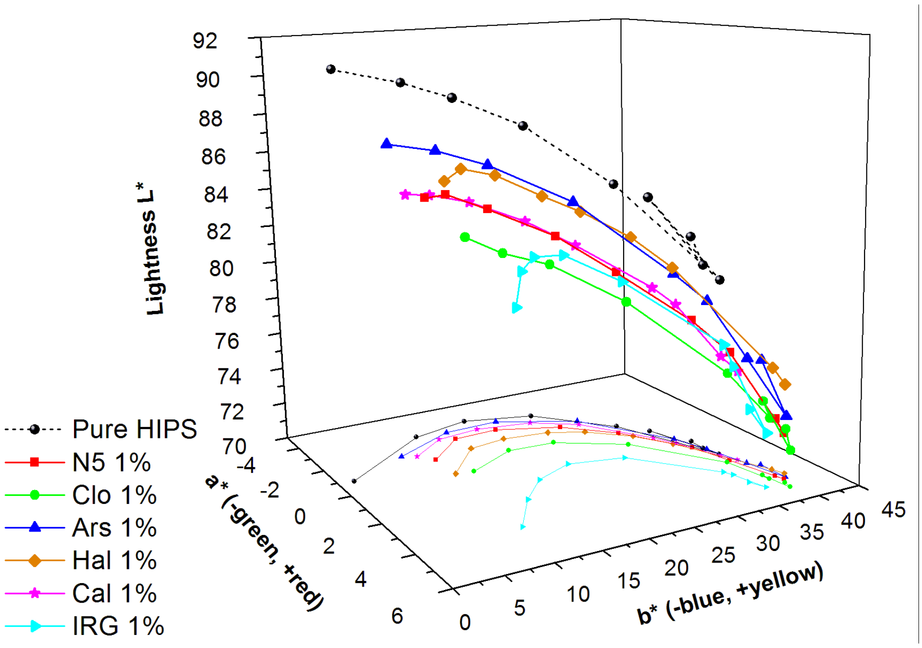


Figure 44 - Colour change during photodegradation of HIPS (nano)composites with 1% loading

Light transmission

Measurements of the ability of samples to transmit light were taken on the same device as yellowness index measurements. Their results were convert to percent change of light transmission (*LT*) also similarly as in case of *YI* according to following equation (12).

$$\Delta LT = \left(\frac{LT}{LT_0} \cdot 100 \right) - 100 \tag{12}$$

where LT is light transmission after and LT_0 before photodegradation.

Figure 45 shows change of *LT* of all PS samples during irradiation periods. As can be noticed, clear decrease of *LT* during photodegradation occurred. The vast majority of (nano)composites and also microcomposites could have undergone changes in structure, which influenced *LT* abilities of (nano)composites in extent, which does not exceed 15 % of original value. Between these samples, there are only slight changes for 1% and 3% loading. However, there are also three (nano)composites, which differ substantialy in their results. They are PS + Clo 3%, PS + IRG 1% and IRG 3%. As can be seen, the decrease of *LT* of these samples, and especially of IRG samples, reaches more then 40 % of original value. On the other hand, when the curve of pure PS is observed, it is obvious that nanofillers have negative influence on *LT*, because NF could be able to absorb the part transmitted light.

It is remarkable to compare the curves of *YI* and *LT* measurements. They correspond with each other as follows: the less significant increase of *YI* (less yellower samples), the more considerable decrease of *LT*. This probably suggest some changes in structure of samples and the fact if more UV resistant (nano)composite is required, some part of its transmission has to be sacrificed.

Figure 46 describes similar situation for HIPS (nano)composites. As can be seen, the situation is not as evident as in case of PS. It seems that all (nano)composites influence *LT* during photodegradation to a lesser extent in comparison with pure HIPS. This statement is completely valid for first 350 hours of irradiation. After this time, an increase in *LT* of pure HIPS occurred. However, this observation is very likely caused by some error during measurement and therefore it may be assumed that pure HIPS evinces the worst behaviour during all photodegradation. In this figure, there are also other confusing results. They can be seen for HIPS + Ars 3% and HIPS + IRG 3%. In these cases, clear increase of *LT* during irradiation can be noticed. This is little contradictory to the fact that during photodegradation, in general, colourfulness increases and lightness of samples decreases.

Figures 45 and *46* are supplemented with *Table 12* and *Table 13*, where all measured values of *LT* are listed.

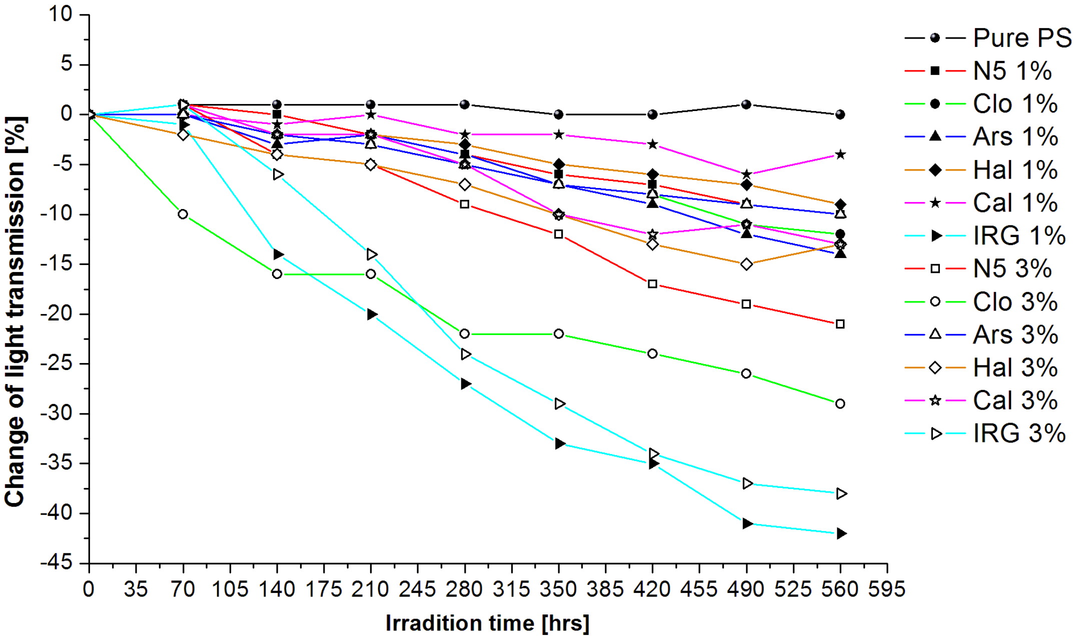


Figure 45 - Changes in LT for PS (nano)composites

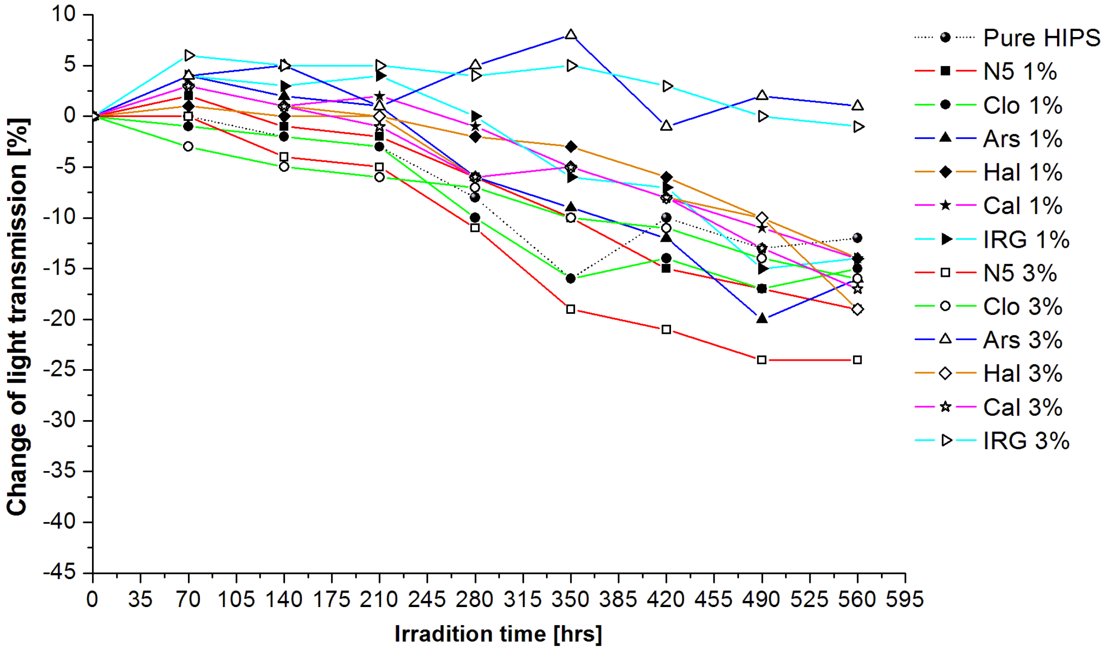


Figure 46 - Changes in LT for HIPS (nano)composites

Table 12 - Values of light transmission of all PS (nano)composites during photodegradation

Irradiation time	Pure PS	N5	Clo	Ars	Hal	Cal	IRG
***LT* [%] – 1 % loading**							
0	87.61	81.08	83.80	85.54	85.27	84.07	45.91
70	88.92	82.25	83.71	85.45	85.24	84.37	45.40
140	88.37	80.81	82.04	82.67	83.88	83.22	39.52
210	88.57	79.40	81.66	83.84	83.35	83.93	36.72
280	88.49	77.87	79.90	82.39	82.47	82.71	33.52
350	87.32	76.14	78.20	79.79	81.30	81.98	30.86
420	87.81	75.57	77.34	77.53	80.48	81.83	29.77
490	88.06	74.14	74.55	75.18	79.34	79.27	26.88
560	87.23	73.08	73.73	73.99	77.99	81.04	26.75
***LT* [%] – 3 % loading**							
0	87.61	74.36	66.85	79.37	79.62	76.53	35.43
70	88.92	75.44	60.28	79.43	77.92	77.10	35.75
140	88.37	71.27	55.86	77.49	76.20	75.33	33.45
210	88.57	70.61	56.04	77.36	75.73	75.32	30.53
280	88.49	67.75	52.30	75.24	73.65	72.98	26.84
350	87.32	65.13	51.93	73.77	71.37	69.05	25.15
420	87.81	61.45	50.55	72.71	69.64	67.64	23.49
490	88.06	60.08	49.64	72.07	67.85	68.00	22.20
560	87.23	59.10	47.57	71.57	68.97	66.83	21.97

Table 13 - Values of light transmission of all HIPS (nano)composites during photodegradation

Irradiation time	Pure HIPS	N5	Clo	Ars	Hal	Cal	IRG
***LT* [%] – 1 % loading**							
0	50.41	46.88	44.73	49.18	49.63	47.71	37.15
70	50.24	47.62	44.34	51.27	50.19	49.08	38.77
140	49.28	46.23	43.89	50.00	49.56	48.36	38.42
210	48.83	45.71	43.17	49.49	49.81	48.59	38.71
280	46.35	43.88	40.43	46.20	48.73	47.03	37.21
350	42.23	42.01	37.57	44.89	48.24	45.47	35.06
420	45.35	40.04	38.67	43.07	46.62	43.82	34.48
490	43.85	38.95	37.26	39.57	44.55	42.61	31.45
560	44.20	38.02	38.07	41.17	42.79	40.87	32.12
***LT* [%] – 3 % loading**							
0	50.41	42.71	40.47	44.53	79.62	46.85	23.07
70	50.24	42.86	39.45	46.50	77.92	48.13	24.45
140	49.28	41.10	38.25	46.73	76.20	47.11	24.23
210	48.83	40.40	38.00	45.00	75.73	46.41	24.27
280	46.35	38.12	37.55	46.72	73.65	43.95	24.03
350	42.23	34.76	36.35	48.20	71.37	44.63	24.33
420	45.35	33.68	35.99	44.21	69.64	42.97	23.78
490	43.85	32.33	34.77	45.49	67.85	40.88	23.12
560	44.20	32.36	34.15	44.89	68.97	39.05	22.90

Figure 47 depicts percent change of light transmission of HIPS (nano)composites with SMA compatibilizer, All curves for both types of SMA (1:1 and 3:1) together with pure HIPS and HIPS + N5 (1% and 3% loading) are displayed there. As can be seen, the results are very similar to HIPS (nano)composites without SMA. The biggest change of ability to transmit light is observed for

SMA 3 N5 3%, which evince only a small increase of *YI*. This finding was discussed above and the rest of (nano)composite with SMA behave in corresponding way with curves of *YI.*

Measured values, which were used for calculation of *LT* change are listed in *Table 14*.

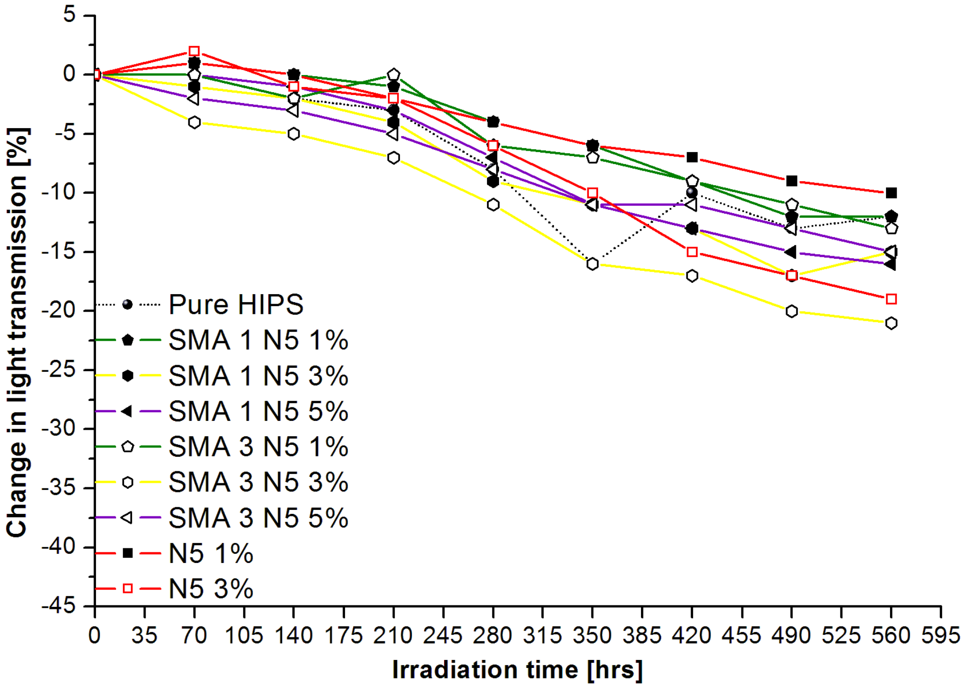


Figure 47 - LT of HIPS + N5 (1, 3 and 5% loading) with 5% SMA

Table 14 - Values of change in light transmission of all HIPS + SMA (nano)composites

Irradiation time	Pure HIPS	HIPS + N5 1%	HIPS + N5 3%	HIPS + N5 5%
***LT* [%] SMA 1:1**				
0	50.41	46.30	39.86	31.26
70	50.24	46.92	39.65	31.24
140	49.28	46.38	39.09	31.03
210	48.83	45.86	38.31	30.37
280	46.35	44.29	36.27	28.93
350	42.23	43.38	35.49	27.85
420	45.35	42.24	34.65	27.13
490	43.85	40.54	33.23	26.49
560	44.20	40.95	33.84	26.20
***LT* [%] SMA 3:1**				
0	50.41	48.07	36.92	37.95
70	50.24	48.28	35.59	37.21
140	49.28	46.91	35.01	36.72
210	48.83	47.87	34.40	36.14
280	46.35	45.14	32.89	34.94
350	42.23	44.59	31.04	33.94
420	45.35	43.97	30.5	33.65
490	43.85	42.96	29.46	33.08
560	44.20	42.00	29.22	32.20

6.3 Biodegradation – soil burial test

Biodegradation of (nano)composites was carried out by soil burial test. Homemade compost from garden waste was used as soil. The experiment was prepared in the form of lysimeter – a vessel with soil, which is aerated and irrigated. A scheme of lysimeter set is shown in *Figure 48*, where particular layers of soil and perlite can be seen. Perlite was added to soil to keep constant humidity and to ensure sufficient aeration. Perlite was prepared according to following *Table 15* one day before the whole lysimeter was assembled. This step was taken, because perlite had to be waterlogged to keep required humidity during experiment.

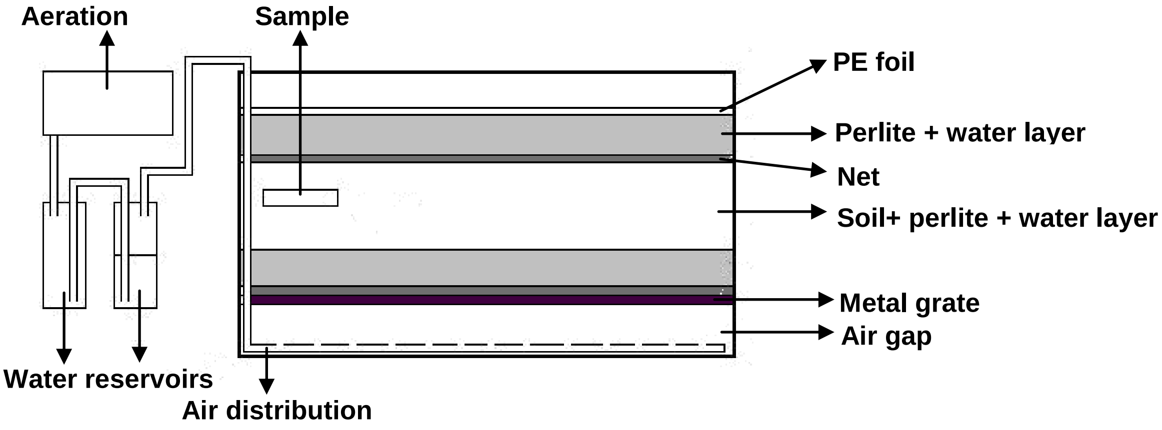


Figure 48 - Lysimeter scheme

The whole burial test took two months, which is not standard time. However, it was chosen as a time for initial test, whose purpose was to find, if PS and HIPS (nano)composites undergo any changes. The soil temperature was 24 °C and its irrigation was done once a week. Before and after experiment, solids and *pH* of the compost were assessed and weight of all samples was measured. Samples were also objected to investigation of surface colour by yellowness index measurement. In addition, their appearance was eye evaluated and monitored by photographs, which are displayed in Appendix P IV. FT-IR was also considered as a perspective method for evaluation of changes in sample structure after biodegradation, but due to the fact that changes of PS and HIPS after biodegradation was negligible, IR spectra was not recorded.

Table 15 - Perlite initial wetting

Perlite amount [g]	Water amount [ml]	Ratio perlite : water
650	1300	1:2
650	1300	1:2
650	650	1:1

pH assessment

A solution of potassium chloride (KCl) in the amount of 50 ml was prepared in the concentration of 0.2 mol.l^{-1}. The compost of 20 g was put into this solution and left for 24 hours. After this time, a mixture was filtered and *pH* was measured with WTW Series inoLab pH/ION 735 device. Used amounts of KCl and compost with all results are listed in *Table 16*. As can be seen, *pH* stayed almost unchanged at the value of 6.9 during the whole experiment, which denotes that soil environment was of neutral character and polymer probably did not influenced it.

Solids assessment

Three samples of compost (approx. 2.5 g) were put into laboratory drying oven and left 4 hours at 103 °C. After this period, samples were weighted again and the amount of solids was calculated. Results and all data are shown in *Table 16*. Average value of solids content before biodegradation was 38.6 % and after biodegradation was 39.3 %. From these values, it can be considered that humidity of compost was kept at constant value of about 60 %, which is very suitable for this type of biodegradation experiment.

Table 16 - Data and results of pH and solids assessment of compost used for burial test

pH		m_{KCl} [g]	m_C [g]	c [mol.l^{-1}]	pH
Before biodegradation		0.771	20.357	0.206	6.976
After biodegradation		0.757	20.227	0.203	6.911
Solids		m_{BD} [g]	m_{AD} [g]	Δm [g]	S [%]
Before biodegradation	1	2.7237	1.0715	1.6522	39.3
	2	2.6466	1.0092	1.6374	38.1
	3	2.8705	1.1014	1.7691	38.4
After biodegradation	1	2.3782	0.9220	1.4562	38.8
	2	2.6784	1.0537	1.6247	39.3
	3	2.7202	1.0807	1.6395	39.7

Where m_{KCl} [g] is weight of KCl used for preparation of solution, m_C [g] is weight of compost, c [mol.l^{-1}] is real concentration of solution, m_{BD} [g] *and* m_{AD} [g] is weight of compost for solids assessment before and after drying, Δm [g] is difference of compost weights before and after drying.

Mass loss

The weight of all samples was measured before and after biodegradation test and both values were compared. Each weighing was done three times for every sample, i. e. three specimens of each sample were prepared and tested. All average values of these weights are listed in *Table 17*. There can also be seen the average change of weight after biodegradation. Results show that probably no changes occurred in PS and HIPS (nano)composites, as well as in pure matrices, during two month soil burial test. Changes of values that can be observed in *Table 17* are minimal and are detected only at thousandths and ten thousandths of original weight. These values move in the interval about zero (plus, minus) and are certainly influenced by conditions during weighing, e. g. moves of persons around. From these results cannot be claimed that tested samples underwent some biodegradation. It is very probable that no interaction between compost and polymers occurred. Additionally, when PS and HIPS properties are considered, there is no reason to believe that longer time of experiment could change the course of their biodegradation.

Table 17 - Averages of measured values of weight of PS and HIPS (nano)composites

PS	m_{BB} [g]	m_{AB} [g]	Δm [g]	**HIPS**	m_{BB} [g]	m_{AB} [g]	Δm [g]
Pure PS	0.47604	0.47594	0.00010	Pure HIPS	0.45346	0.45341	0.00005
N5 1%	0.44851	0.44814	0.00037	N5 1%	0.37256	0.37234	0.00022
Clo 1%	0.46487	0.46494	-0.00007	Clo 1%	0.46241	0.46250	-0.00009
Ars 1%	0.91218	0.91218	0.00000	Ars 1%	0.40668	0.40677	-0.00009
Hal 1%	0.83462	0.83458	0.00004	Hal 1%	0.42286	0.42292	-0.00007
Cal 1%	0.88865	0.88852	0.00013	Cal 1%	0.43881	0.43885	-0.00005
IRG 1%	0.43235	0.43221	0.00014	IRG 1%	0.41712	0.41713	-0.00001
N5 3%	0.48153	0.48150	0.00003	N5 3%	0.42748	0.42748	0.00000
Clo 3%	0.40880	0.40914	-0.00034	Clo 3%	0.45764	0.45775	-0.00011
Ars 3%	0.81530	0.81532	-0.00002	Ars 3%	0.42493	0.42499	-0.00006
Hal 3%	0.83410	0.83405	0.00005	Hal 3%	0.40304	0.40315	-0.00011
Cal 3%	0.91923	0.91925	-0.00002	Cal 3%	0.45638	0.45636	0.00002
IRG 3%	0.47261	0.47254	0.00007	IRG 3%	0.40303	0.40305	-0.00002

Where m_{BB} [g] is average value of the weight of three specimens before biodegradation, m_{AB} [g] is average value of the weight of three specimens after biodegradation, Δm [g] is difference of m_{BB} and m_{AB}.

Yellowness index and colour

Colour of samples surface stayed almost unchanged. Yellowness indices of all samples are summarized in *Table 18*, where initial values, terminal values and change of these values are listed. Results of mass loss and *YI* measurements were reason, according to which the decision about no recording of FT-IR spectra was taken.

Table 18 - Averages of measured values of YI of PS and HIPS (nano)composites

PS	YI_{BB} [1]	YI_{AB} [1]	ΔYI [1]	**HIPS**	YI_{BB} [1]	YI_{AB} [1]	ΔYI [1]
Pure PS	3.9	3.8	-0.1	Pure HIPS	2.6	4.4	1.8
N5 1%	10.5	9.1	-1.3	N5 1%	22.0	17.5	-4.6
Clo 1%	12.7	11.3	-1.4	Clo 1%	27.2	19.7	-7.6
Ars 1%	10.6	7.9	-2.7	Ars 1%	15.8	14.8	-1.0
Hal 1%	23.9	20.4	-3.6	Hal 1%	23.1	17.6	-5.5
Cal 1%	10.8	9.8	-1.0	Cal 1%	19.1	14.6	-4.6
IRG 1%	12.3	15.5	3.2	IRG 1%	26.8	22.0	-4.8
N5 3%	19.9	19.2	-0.7	N5 3%	31.3	24.6	-6.7
Clo 3%	31.1	30.2	-1.0	Clo 3%	44.0	25.8	-18.2
Ars 3%	11.7	11.9	0.2	Ars 3%	17.3	9.8	-7.5
Hal 3%	50.3	43.1	-7.2	Hal 3%	35.0	32.2	-2.8
Cal 3%	20.8	19.1	-1.7	Cal 3%	23.8	18.6	-5.2
IRG 3%	17.2	20.0	2.8	IRG 3%	29.5	21.7	-7.8

Where YI_{BB} [1] is average value of the yellowness index of three specimens before biodegradation, YI_{AB} [1] is average value of YI of three specimens after biodegradation, ΔYI [1] is difference of YI_{BB} and YI_{AB}.

CONCLUSION

An influence of various types of nanofillers (modified, unmodified, plaletes, spheres, nanotubes) on photodegradation of PS and HIPS matrices was observed during 560 hours of accelerated weathering. Several HIPS (nano)composites of Nanofil® 5 were also prepared with compatibilizer styrene-maleic anhydride and compared with other samples. The overall results indicates that use of nanofillers for the purpose of reduction of the photodegradation rate is possible only for (nano)composites with HIPS matrix. On the other hand, all PS (nano)composites, with one exception, evinced the worsening of the samples resistance against UV light. This resistance was expressed by carbonyl index, which was calculated from FT-IR measurements and which can be compared to the amount of carbonyl groups created during photodegradation. Therefore, the presence of nanofillers in PS matrix is not generally convenient for this purposes. However, all types of nanofillers in HIPS matrix managed to slow photodegradation rate, even thought in some cases in a small extent. Despite this positive behaviour of HIPS (nano)composites, it is not possible to claim that these samples achieved some remarkable results, because their efficiency to limit photodegradation is significant only in shorter periods of UV irradiation, and after 560 hours, their results are very similar to pure HIPS. However, there is one exception among all PS and HIPS samples. It is the sample of PS with 3% loading of Cloisite® Na+, whose degradation rate was after 560 hours the lowest of all samples. This result indicates that unmodified layered clays with probably exfoliated structure (according to XRD measurement) have some potential to prolong the resistance of PS against UV light. Nevertheless, the vast majority of results shows that use of nanofillers is not sufficient, even in common products, for prevention of UV degradation instead stabilizers, even thought it would be very beneficial, because some nanofillers are of natural origin.

Another property, which was investigated, was appearance of samples. This evaluation was done with yellowness index, light transmission and determination of precise coordinates of the surface colour. Overall, the yellowness was substantially positively influenced by nanofillers presence. In all cases, samples after the whole photodegradation period evinced lower change in yellowness index, which means that they kept their initial colour. This influence of nanofillers is particularly noticeable in HIPS (nano)composites, where the change of yellowness index was reduced by more than 2 000 %. HIPS (nano)composites with SMA compatibilizer achieved even better results. Therefore, it is certain that nanofillers, and mainly IRG (ZnO), are able to save colour of samples from yellow changes. However, investigation of surface colour coordinates showed that changes in colour are not only of yellow character, because samples of HIPS (nano)composites evinced relatively significant shift to red. All of these colour alterations are caused by changes in polymers structure, e. g. creation of double bonds, and presented results therefore indicate that nanofillers in polymer matrix limit these changes. However, this Master's thesis does not imply precise evaluation of structure of studied (nano)composites, which could clarify the relations between changes of polymer chains and their following influence on colour. Last optical measurement was dedicated to light transmission of samples. This investigation provided finding that rate of light transmission is inversely connected with yellowness index.

Photodegradation was ended after 560 hours, which roughly corresponds to two years of the exposure in natural conditions. Therefore, obtained results can be consider as valuable and at least indicate the main direction of behaviour of polystyrene (nano)composites.

One third of experiment was also focused on biodegradation of the same samples. On contrary to photodegradation, the results are clear and common to all samples, because the soil burial test confirmed that PS and HIPS are strictly non-biodegradable and even natural nanofillers, such as clays, did not influenced it.

From the both experiments generally results that the resistance of PS (nano)composites to photodegradation is weaker than the resistance of pure PS. These results together with fact that biodegradation cannot be considered in both cases of PS and HIPS (nano)composites exclude the possible use of (nano)composites for the purposes of PS and HIPS waste volume reduction. On the other hand, HIPS (nano)composites showed some improvement of their behaviour under UV light in comparison with pure HIPS, but this improvement is not sufficient enough, especially in longer time periods, to consider the use of nanofillers instead stabilizers.

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LIST OF ABBREVIATIONS

ABS	Acrylonitrile-butadiene-styrene copolymer
Ars	Aerosil®
ASA	Acrilonitrile-styrene acrylate
BR	Butadiene rubber
Cal	Calcite
CI	Carbonyl index
Clo	Cloisite®
EPS	Expandable polystyrene
FT-IR	Fourier transition infrared spectroscopy
GPPS	General purpose polystyrene
Hal	Halloysite
HALS	Hindered amine light stabilizer
HIPS	High impact polystyrene
iPS	Isotactic polystyrene
IRG	IRGAGUARD
LT	Light transmission
MFI	Melt flow index
MMT	Montmorillonite
N5	Nanofil® 5
NF	Nanofiller
PA	Polyamide
PE-HD	High density polyethylene
PE-LD	Low density polyethylene
PE-LLD	Linear low density polyethylene
PET	Polyethylene terephtalate
PMMA	Polymethyl methacrylate
PP	Polypropylene
PS	Polystyrene
PS-MAH	Copolymer of polystyrene and maleic anhydride
PUR	Polyurethane
PVC	Polyvinylchloride
SAN	Styrene-acrylonitrile copolymer
SB	Styrene-butadiene copolymer

SBR	Styrene-butadiene rubber
SBS	Styrene-butadiene-styrene copolymer
SMA	Styrene-maleic anhydride copolymer
sPS	Syndiotactic polystyrene
TEM	Transmission electron microscopy
Tf	Flow temperature
Tg	Glass transition temperature
Tm	Melting temperature
UV	Ultraviolet
XRD	X-ray diffraction
YI	Yellowness index

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APPENDICES

APPENDIX P I: MEASURED VALUES OF YELLOWNES INDEX

Measured values of yellowness index of all PS (nano)composites

Irradiation time	Pure PS	N5	Clo	Ars	Hal	Cal	IRG
***YI* [1] – 1 % loading**							
0	3.94	10.5	12.7	6.6	16.0	7.3	12.3
70	5.36	10.8	17.3	14.2	20.1	12.7	14.7
140	7.57	14.2	23.6	22.0	26.1	18.7	14.1
210	10.01	18.8	29.8	30.9	32.5	21.4	14.0
280	12.98	23.2	36.0	39.6	35.5	26.2	17.4
350	17.53	29.7	43.5	49.9	42.0	31.9	29.8
420	20.63	38.5	52.5	59.7	47.6	39.5	45.1
490	23.3	46.7	63.5	64.2	53.1	43.0	53.2
560	26.78	49.9	64.7	62.4	54.9	46.8	56.2
***YI* [1] – 3 % loading**							
0	3.94	19.9	31.1	8.5	29.1	14.4	17.22
70	5.36	23.9	50.7	17.0	44.0	23.5	18.28
140	7.57	30.1	60.6	26.3	50.8	33.7	16.4
210	10.01	33.8	63.2	35.9	57.7	43.5	13.26
280	12.98	41.2	68.4	43.2	63.2	51.4	12.99
350	17.53	52.8	72.4	51.9	69.5	60.7	18.68
420	20.63	68.1	78.1	60.3	78.2	67.8	31.49
490	23.3	69.5	81.5	64.4	80.6	70.8	37.45
560	26.78	71.6	80.2	64.0	81.0	70.9	39.53

Measured values of yellowness index of all HIPS (nano)composites

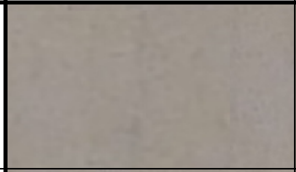
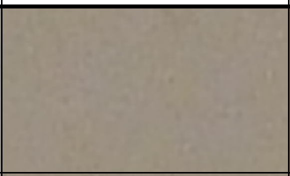
Irradiation time	Pure HIPS	N5	Clo	Ars	Hal	Cal	IRG
***YI* [1] – 1 % loading**							
0	2.6	22.0	27.2	15.8	23.1	19.1	26.8
70	21.4	29.5	37.6	28.4	30.3	26.5	32.0
140	32.9	38.7	47.2	39.5	37.7	35.4	37.4
210	45.8	50.8	59.6	53.8	46.6	46.3	45.0
280	58.4	59.5	72.0	66.5	53.1	54.4	55.7
350	69.8	68.6	75.8	69.7	60.1	64.2	68.7
420	62.7	72.2	75.0	74.1	65.3	66.8	70.2
490	68.5	78.0	77.8	78.1	76.3	72.0	74.1
560	67.3	77.1	77.4	75.5	77.7	73.9	72.1
***YI* [1] – 3 % loading**							
0	2.6	31.3	44.0	17.3	35.0	23.8	29.48
70	21.4	36.6	41.7	26.3	44.6	32.5	28.65
140	32.9	46.5	49.4	35.3	53.2	42.9	30.79
210	45.8	59.2	56.1	45.9	64.1	55.5	31.9
280	58.4	70.6	60.3	55.0	74.4	67.0	36.81
350	69.8	79.6	66.4	55.6	72.0	64.1	34.58
420	62.7	80.6	70.8	64.9	78.5	70.5	46.08
490	68.5	80.9	79.5	70.5	81.1	76.9	52.96
560	67.3	80.3	81.2	70.4	82.5	74.4	55.81

Measured values of yellowness index of all HIPS (nano)composites with SMA

Irradiation time	Pure HIPS	HIPS + N5 1%	HIPS + N5 3%	HIPS + N5 5%
***YI* [1] SMA 1:1**				
0	2.6	42.4	55.4	60.9
70	21.4	39.2	48.4	51.5
140	32.9	45.6	55.9	58.6
210	45.8	54.0	66.5	68.1
280	58.4	60.8	76.8	79.1
350	69.8	64.3	75.6	79.9
420	62.7	73.3	82.7	84.8
490	68.5	80.0	86.9	83.7
560	67.3	77.2	84.7	87.2
***YI* [1] SMA 3:1**				
0	2.6	36.2	46.9	54.9
70	21.4	30.4	40.9	45.5
140	32.9	36.4	47.2	49.9
210	45.8	46.3	57.2	57.6
280	58.4	51.6	68.0	61.8
350	69.8	54.9	73.5	63.0
420	62.7	64.3	73.4	73.4
490	68.5	75.0	80.0	76.3
560	67.3	72.8	80.9	81.4

APPENDIX P II: PHOTOGRAPHS – PHOTODEGRADATION

Photographs of surface of pure PS and Nanofil® 5 (nano)composites

PS	Pure PS	N5 1%	N5 3%
0 hrs			
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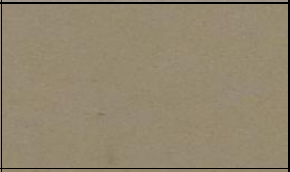
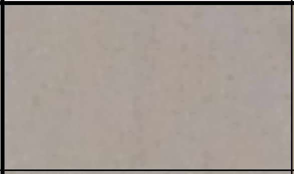
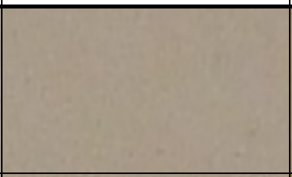
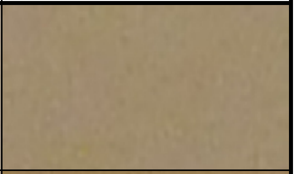
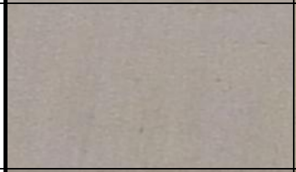
210 hrs			
280 hrs			
350 hrs			
420 hrs			
490 hrs			
560 hrs			

Photographs of surface of pure PS and Cloisite® Na+ (nano)composites

PS	**Pure PS**	**Clo 1%**	**Clo 3%**
0 hrs			
70 hrs			
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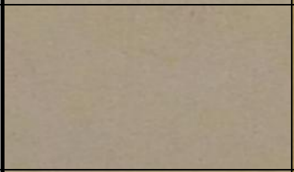
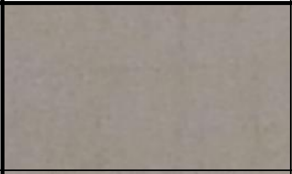
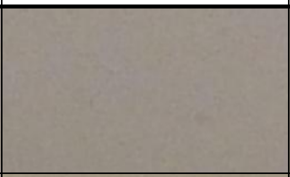
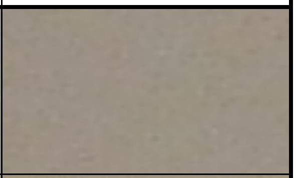
420 hrs			
490 hrs			
560 hrs			

Photographs of surface of pure PS and Aerosil® (nano)composites

PS	Pure PS	Ars 1%	Ars 3%
0 hrs			
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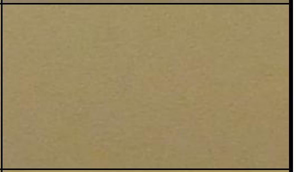
210 hrs			
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350 hrs			
420 hrs			
490 hrs			
560 hrs			

Photographs of surface of pure PS and Halloysite (nano)composites

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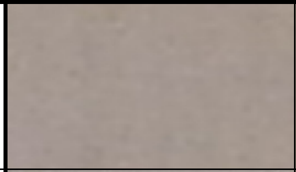
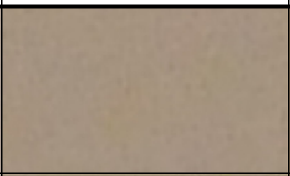
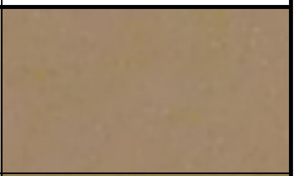
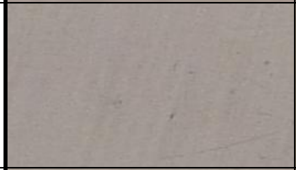
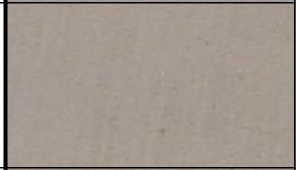
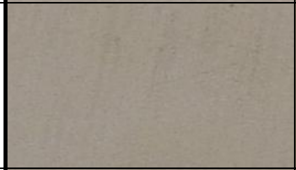
0 hrs			
70 hrs			
140 hrs			
210 hrs			
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350 hrs			
420 hrs			
490 hrs			
560 hrs			

Photographs of surface of pure PS and calcite microcomposites

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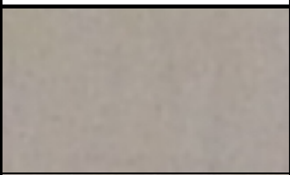
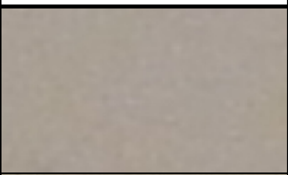
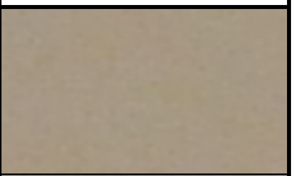
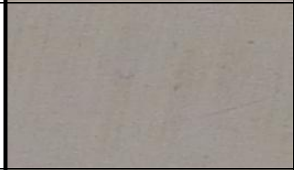
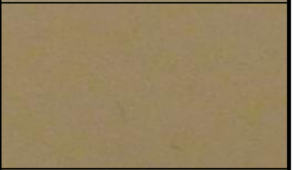
0 hrs			
70 hrs			
140 hrs			
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280 hrs			
350 hrs			
420 hrs			
490 hrs			
560 hrs			

Photographs of surface of pure PS and IRGAGUARD (nano)composites

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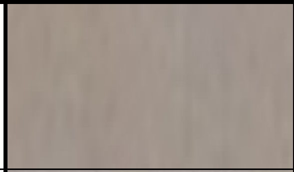
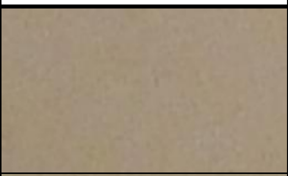
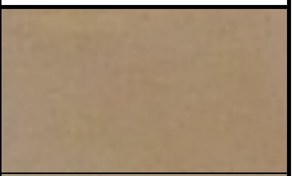
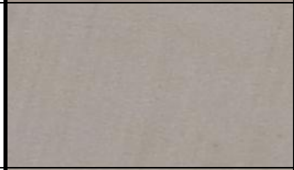
0 hrs			
70 hrs			
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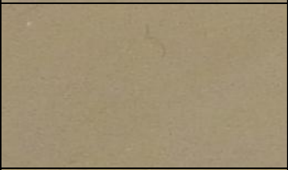
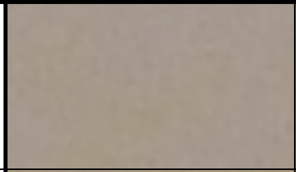
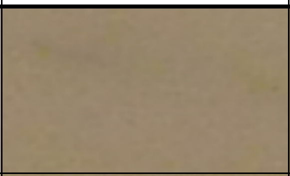
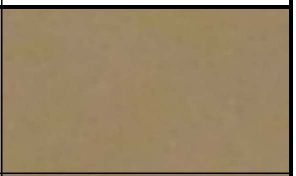
210 hrs			
280 hrs			
350 hrs			
420 hrs			
490 hrs			
560 hrs			

Photographs of surface of pure HIPS and Nanofil® 5 (nano)composites

HIPS	**Pure HIPS**	**N5 1%**	**N5 3%**
0 hrs			
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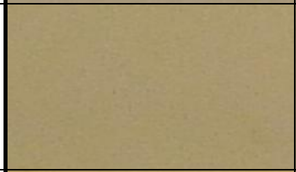
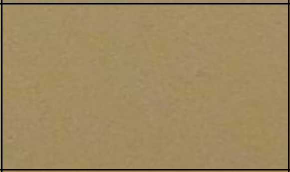
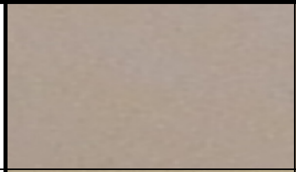
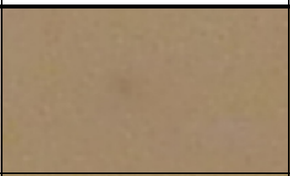
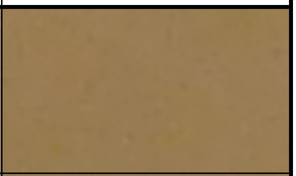
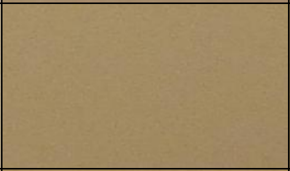
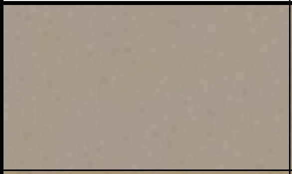
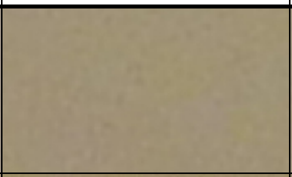
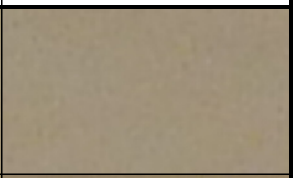
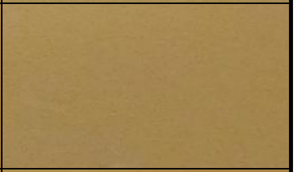
140 hrs			
210 hrs			
280 hrs			
350 hrs			
420 hrs			
490 hrs			
560 hrs			

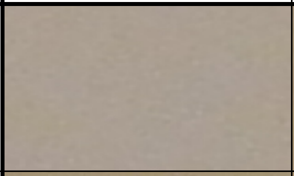
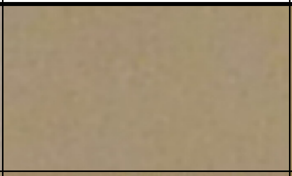
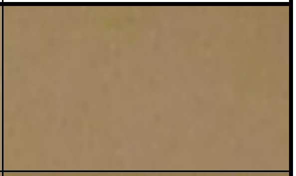
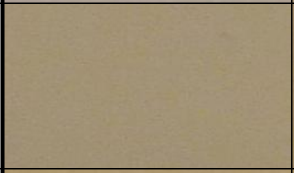
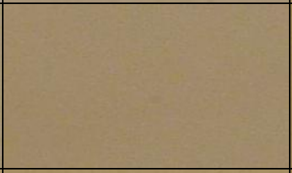
Photographs of surface of pure HIPS and Cloisite® Na+ (nano)composites

HIPS	Pure HIPS	Clo 1%	Clo 3%
0 hrs			
70 hrs			
140 hrs			
210 hrs			
280 hrs			
350 hrs			
420 hrs			
490 hrs			
560 hrs			

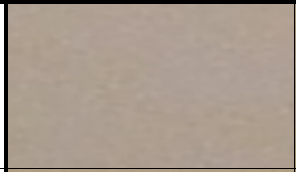
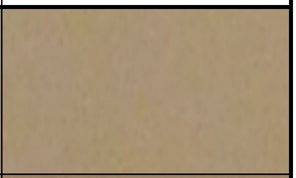
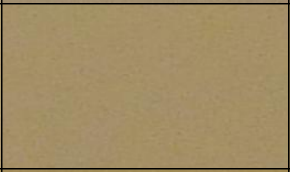
Photographs of surface of pure HIPS and Aerosil® (nano)composites

HIPS	Pure HIPS	Ars 1%	Ars 3%
0 hrs			
70 hrs			
140 hrs			
210 hrs			
280 hrs			
350 hrs			
420 hrs			
490 hrs			
560 hrs			

Photographs of surface of pure HIPS and Halloysite (nano)composites

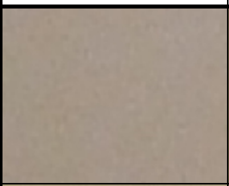
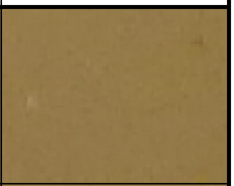
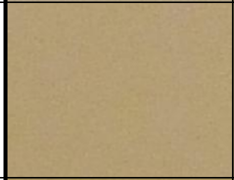
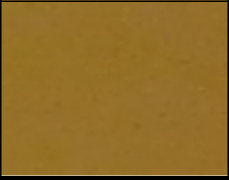
HIPS	**Pure HIPS**	**Hal 1%**	**Hal 3%**
0 hrs			
70 hrs			
140 hrs			
210 hrs			
280 hrs			
350 hrs			
420 hrs			
490 hrs			
560 hrs			

Photographs of surface of pure HIPS and calcite microcomposites

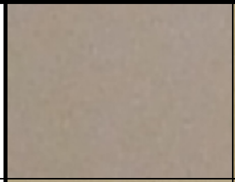
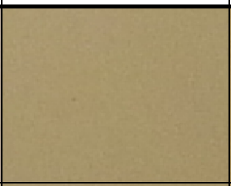
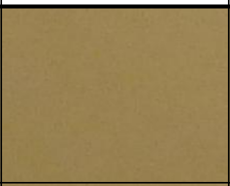
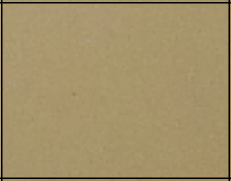
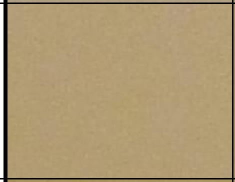
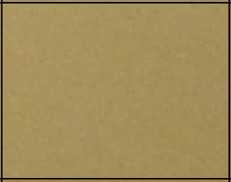
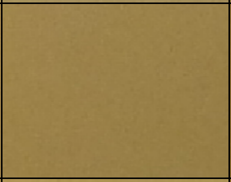
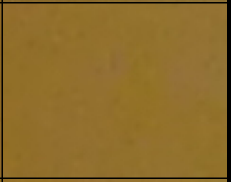
HIPS	**Pure HIPS**	**Cal 1%**	**Cal 3%**
0 hrs			
70 hrs			
140 hrs			
210 hrs			
280 hrs			
350 hrs			
420 hrs			
490 hrs			
560 hrs			

Photographs of surface of pure HIPS and IRGAGUARD (nano)composites

Photographs of surface of pure HIPS and Nanofil® 5 (nano)composites with SMA 1:1

HIPS	**Pure HIPS**	**SMA 1 N5 1%**	**SMA 1 N5 3%**	**SMA 1 N5 5%**
0 hrs				
70 hrs				
140 hrs				
210 hrs				
280 hrs				
350 hrs				
420 hrs				
490 hrs				
560 hrs				

Photographs of surface of pure HIPS and Nanofil® 5 (nano)composites with SMA 3:1

HIPS	Pure HIPS	SMA 3 N5 1%	SMA 3 N5 3%	SMA 3 N5 5%
0 hrs				
70 hrs				
140 hrs				
210 hrs				
280 hrs				
350 hrs				
420 hrs				
490 hrs				
560 hrs				

APPENDIX P III: COORDINATES OF SURFACE COLOUR

Coordinates of surface colour of all PS (nano)composites

1% loading												
Irradiation time	Pure PS			N5			Clo			Ars		
	L*	a*	b*	L*	a*	b*	L*	a*	b*	L*	a*	b*
0	87.5	-0.9	2.3	84.2	-1.1	5.5	84.5	-1.3	6.8	86.3	-0.7	3.5
70	87.5	-1.2	3.1	84.7	-1.4	5.8	84.0	-1.6	9.2	86.2	-2.0	7.9
140	87.1	-1.5	4.3	84.0	-1.9	7.7	83.1	-2.0	12.6	85.4	-2.8	12.4
210	87.2	-1.9	5.8	83.4	-2.6	10.4	82.3	-2.3	16.0	84.7	-3.5	17.6
280	87.0	-2.3	7.5	82.8	-2.9	12.8	81.3	-2.5	19.5	83.8	-3.7	22.6
350	86.5	-2.8	10.1	82.2	-3.3	16.4	80.6	-2.5	23.8	82.3	-3.0	28.6
420	86.4	-3.2	11.9	81.2	-3.3	21.4	79.3	-2.1	29.0	79.6	-1.5	33.6
490	86.6	-3.5	13.6	79.8	-2.7	25.8	76.8	-0.6	34.7	78.2	-0.7	35.8
560	86.2	-3.8	15.6	79.1	-2.3	27.3	76.2	-0.3	35.1	78.6	-1.0	34.8
Irradiation time	Pure PS			Hal			Cal			IRG		
	L*	a*	b*	L*	a*	b*	L*	a*	b*	L*	a*	b*
0	87.5	-0.9	2.3	84.8	-1.1	8.4	84.7	-1.0	3.9	84.1	-0.4	6.1
70	87.5	-1.2	3.1	84.9	-1.6	10.7	84.5	-1.8	6.9	84.7	-1.4	7.8
140	87.1	-1.5	4.3	84.1	-2.1	14.1	84.0	-2.4	10.3	85.0	-1.3	7.5
210	87.2	-1.9	5.8	83.4	-2.4	17.8	83.9	-2.7	11.9	85.4	-1.5	7.5
280	87.0	-2.3	7.5	82.8	-2.5	19.5	83.5	-3.1	14.6	85.6	-2.0	9.6
350	86.5	-2.8	10.1	82.3	-2.7	23.4	83.2	-3.3	17.8	84.8	-2.7	16.6
420	86.4	-3.2	11.9	81.6	-2.7	26.8	82.3	-3.4	22.2	82.6	-1.8	25.0
490	86.6	-3.5	13.6	80.7	-2.3	29.9	81.9	-3.4	24.3	81.0	-0.6	29.0
560	86.2	-3.8	15.6	80.3	-2.0	30.8	81.3	-3.1	26.4	80.0	0.2	30.3
3% loading												
Irradiation time	Pure PS			N5			Clo			Ars		
	L*	a*	b*	L*	a*	b*	L*	a*	b*	L*	a*	b*
0	87.5	-0.9	2.3	82.0	-1.8	10.4	77.8	-0.6	15.2	84.7	-0.7	4.4
70	87.5	-1.2	3.1	81.6	-2.1	12.7	71.9	2.4	23.2	84.6	-2.3	9.4
140	87.1	-1.5	4.3	80.5	-2.3	15.9	68.0	4.4	26.5	83.9	-3.3	14.8
210	87.2	-1.9	5.8	80.4	-2.3	18.0	66.7	5.0	27.2	83.0	-3.8	20.4
280	87.0	-2.3	7.5	79.4	-2.1	21.9	64.6	6.0	28.8	82.0	-3.7	24.6
350	86.5	-2.8	10.1	77.6	-1.3	28.2	63.8	6.5	30.6	81.1	-3.0	29.6
420	86.4	-3.2	11.9	73.7	1.4	35.4	62.1	7.1	32.9	79.4	-1.7	34.0
490	86.6	-3.5	13.6	73.0	1.9	35.8	61.4	7.5	34.5	78.5	-0.8	36.1
560	86.2	-3.8	15.6	72.1	2.4	36.5	59.6	8.3	32.1	78.7	-0.9	35.9
Irradiation time	Pure PS			Hal			Cal			IRG		
	L*	a*	b*	L*	a*	b*	L*	a*	b*	L*	a*	b*
0	87.5	-0.9	2.3	81.5	-0.3	14.6	83.8	-1.0	7.4	85.4	1.0	8.1
70	87.5	-1.2	3.1	79.9	-0.5	22.9	83.1	-2.1	12.6	84.9	0.8	8.7
140	87.1	-1.5	4.3	79.1	-0.5	26.9	82.3	-2.6	18.4	84.7	0.9	7.7
210	87.2	-1.9	5.8	78.3	-0.4	31.1	81.1	-2.6	24.0	86.0	0.2	6.5
280	87.0	-2.3	7.5	77.4	0.0	34.3	79.8	-2.1	28.4	86.3	-0.1	6.5
350	86.5	-2.8	10.1	76.7	0.8	38.0	78.3	-0.7	33.3	86.5	-0.9	9.8
420	86.4	-3.2	11.9	73.8	2.6	42.1	76.4	0.9	36.6	85.6	-1.6	17.2
490	86.6	-3.5	13.6	73.1	3.3	43.1	75.6	1.7	37.9	85.2	-1.6	20.6
560	86.2	-3.8	15.6	73.0	3.4	43.3	75.7	1.7	38.0	84.8	-1.4	21.7

Coordinates of surface colour of all HIPS (nano)composites

1% loading												
Irradiation time	Pure HIPS			N5			Clo			Ars		
	L*	a*	b*	L*	a*	b*	L*	a*	b*	L*	a*	b*
0	90.8	-0.9	1.7	84.0	-1.2	11.5	82.3	0.1	13.5	86.7	-1.9	8.7
70	89.5	-3.1	12.6	83.6	-2.4	16.1	80.8	-0.8	19.5	85.8	-3.0	16.1
140	88.4	-3.6	19.5	82.5	-2.5	21.3	79.9	-0.7	24.9	84.7	-3.1	22.6
210	86.7	-3.0	27.0	80.9	-1.7	28.0	77.9	0.5	31.6	82.6	-1.9	30.7
280	83.7	-0.9	33.6	79.1	-0.4	32.6	74.8	3.0	37.6	79.2	0.8	36.8
350	79.4	2.4	38.3	77.0	1.6	37.0	73.2	4.5	38.5	78.1	1.9	38.1
420	83.1	-0.1	36.0	75.8	2.9	38.2	73.9	4.2	38.5	75.6	3.3	39.2
490	80.0	1.8	37.9	72.4	4.7	39.7	71.9	5.2	38.9	73.2	4.6	40.2
560	81.3	1.2	38.0	73.0	4.4	39.5	72.8	4.9	39.2	75.6	3.6	40.1
Irradiation time	Pure HIPS			Hal			Cal			IRG		
	L*	a*	b*	L*	a*	b*	L*	a*	b*	L*	a*	b*
0	90.8	-0.9	1.7	85.2	0.0	11.6	84.1	-1.7	10.2	80.5	3.9	11.2
70	89.5	-3.1	12.6	85.2	-1.5	16.3	83.6	-2.6	14.5	81.4	2.5	14.8
140	88.4	-3.6	19.5	84.6	-1.7	20.7	82.9	-2.8	19.6	81.5	1.5	18.3
210	86.7	-3.0	27.0	83.3	-1.5	25.9	81.6	-2.5	25.8	81.1	0.9	23.0
280	83.7	-0.9	33.6	82.4	-1.0	29.6	80.3	-1.6	30.2	79.5	1.3	29.1
350	79.4	2.4	38.3	81.1	0.0	33.5	78.4	0.4	35.1	76.7	3.5	35.6
420	83.1	-0.1	36.0	79.7	1.1	35.9	77.7	1.1	36.3	75.7	3.8	36.0
490	80.0	1.8	37.9	75.4	4.0	40.3	75.4	2.5	38.2	72.8	4.9	36.8
560	81.3	1.2	38.0	74.7	4.4	40.7	74.8	3.0	38.9	73.8	4.4	36.2
3% loading												
Irradiation time	Pure HIPS			N5			Clo			Ars		
	L*	a*	b*	L*	a*	b*	L*	a*	b*	L*	a*	b*
0	90.8	-0.9	1.7	81.7	-0.7	16.0	76.7	1.3	21.2	86.2	-1.4	9.3
70	89.5	-3.1	12.6	80.9	-1.6	19.3	76.1	0.6	20.1	86.4	-2.8	14.9
140	88.4	-3.6	19.5	79.6	-1.3	24.8	74.3	1.3	23.7	85.5	-3.0	20.1
210	86.7	-3.0	27.0	77.4	0.1	31.5	72.9	1.8	27.0	84.5	-2.7	26.4
280	83.7	-0.9	33.6	74.8	2.3	37.0	72.5	2.2	29.2	82.9	-1.6	31.4
350	79.4	2.4	38.3	70.8	5.1	39.7	71.6	3.0	32.3	83.1	-1.6	31.9
420	83.1	-0.1	36.0	69.8	5.6	39.6	70.6	3.7	34.4	80.8	0.5	36.4
490	80.0	1.8	37.9	69.3	5.9	39.4	68.0	5.5	38.0	78.4	2.2	38.5
560	81.3	1.2	38.0	70.0	5.8	39.3	67.3	5.9	38.5	79.0	2.1	38.8
Irradiation time	Pure HIPS			Hal			Cal			IRG		
	L*	a*	b*	L*	a*	b*	L*	a*	b*	L*	a*	b*
0	90.8	-0.9	1.7	82.3	2.0	16.9	83.7	-1.2	12.4	78.1	5.4	11.5
70	89.5	-3.1	12.6	81.0	1.1	22.7	83.4	-2.1	17.7	79.3	4.6	11.7
140	88.4	-3.6	19.5	80.0	1.3	27.6	82.4	-2.1	23.6	79.6	3.9	13.2
210	86.7	-3.0	27.0	78.3	2.2	33.8	80.6	-1.1	30.7	79.1	3.5	13.9
280	83.7	-0.9	33.6	75.7	4.2	38.8	77.7	1.4	36.2	78.7	3.0	16.7
350	79.4	2.4	38.3	77.4	3.8	38.1	79.3	0.6	35.3	79.0	2.5	15.8
420	83.1	-0.1	36.0	74.5	5.6	40.3	76.9	2.4	37.7	78.4	2.8	22.0
490	80.0	1.8	37.9	73.0	6.4	41.1	73.4	4.4	39.5	76.8	3.4	25.3
560	81.3	1.2	38.0	72.4	6.8	41.4	75.6	3.4	39.3	76.0	3.8	26.6

Coordinates of surface colour of HIPS (nano)composites with SMA compatibilizer

SMA 1:1												
Irradiation time	Pure HIPS			HIPS + N5 1%			HIPS + N5 3%			HIPS + N5 5%		
	L*	a*	b*	L*	a*	b*	L*	a*	b*	L*	a*	b*
0	90.8	-0.9	1.7	80.5	-1.1	22.4	74.6	2.8	26.6	68.5	5.1	26.4
70	89.5	-3.1	12.6	80.2	-2.1	21.0	73.9	0.3	23.5	68.4	2.1	22.8
140	88.4	-3.6	19.5	79.3	-1.9	24.5	73.2	0.6	27.7	68.0	2.1	26.7
210	86.7	-3.0	27.0	78.0	-1.3	29.1	71.4	1.9	33.0	66.3	3.1	31.2
280	83.7	-0.9	33.6	76.6	-0.4	32.6	69.0	3.9	37.6	64.3	4.9	36.3
350	79.4	2.4	38.3	75.6	0.6	34.0	68.6	4.4	36.3	63.3	5.5	35.9
420	83.1	-0.1	36.0	73.8	2.5	38.4	66.4	6.0	39.1	61.7	6.8	37.4
490	80.0	1.8	37.9	70.9	4.4	40.7	63.8	7.1	39.9	61.4	7.0	36.2
560	81.3	1.2	38.0	72.1	3.6	39.6	65.0	6.7	39.2	59.8	7.7	37.3

SMA 3:1												
Irradiation time	Pure HIPS			HIPS + N5 1%			HIPS + N5 3%			HIPS + N5 5%		
	L*	a*	b*	L*	a*	b*	L*	a*	b*	L*	a*	b*
0	90.8	-0.9	1.7	83.5	-3.2	20.4	76.6	0.0	23.5	75.9	1.1	27.6
70	89.5	-3.1	12.6	81.5	-2.5	16.3	74.6	-0.9	20.1	74.3	0.2	22.0
140	88.4	-3.6	19.5	80.8	-2.4	19.5	74.0	-0.9	23.6	73.2	0.1	24.3
210	86.7	-3.0	27.0	79.6	-2.3	25.2	72.0	-0.1	28.5	71.9	0.6	28.3
280	83.7	-0.9	33.6	78.5	-1.8	28.0	69.8	1.6	33.6	71.5	1.3	30.4
350	79.4	2.4	38.3	77.9	-1.2	29.6	67.2	3.0	35.2	69.5	1.3	30.4
420	83.1	-0.1	36.0	75.8	0.0	34.4	68.6	3.2	35.6	68.8	3.1	35.8
490	80.0	1.8	37.9	73.0	2.5	39.3	64.9	5.3	37.0	68.1	3.7	37.1
560	81.3	1.2	38.0	73.9	2.2	38.2	64.2	5.6	36.9	66.3	5.3	38.6

APPENDIX P IV: MEASURED VALUES OF LIGHT TRANSMISSION

Measured values of light transmission of all PS (nano)composites

Irradiation time	Pure PS	N5	Clo	Ars	Hal	Cal	IRG
***YI* [%] – 1 % loading**							
0	87.61	81.08	83.80	85.54	85.27	84.07	45.91
70	88.92	82.25	83.71	85.45	85.24	84.37	45.40
140	88.37	80.81	82.04	82.67	83.88	83.22	39.52
210	88.57	79.40	81.66	83.84	83.35	83.93	36.72
280	88.49	77.87	79.90	82.39	82.47	82.71	33.52
350	87.32	76.14	78.20	79.79	81.30	81.98	30.86
420	87.81	75.57	77.34	77.53	80.48	81.83	29.77
490	88.06	74.14	74.55	75.18	79.34	79.27	26.88
560	87.23	73.08	73.73	73.99	77.99	81.04	26.75
***YI* [%] – 3 % loading**							
0	87.61	74.36	66.85	79.37	79.62	76.53	35.43
70	88.92	75.44	60.28	79.43	77.92	77.10	35.75
140	88.37	71.27	55.86	77.49	76.20	75.33	33.45
210	88.57	70.61	56.04	77.36	75.73	75.32	30.53
280	88.49	67.75	52.30	75.24	73.65	72.98	26.84
350	87.32	65.13	51.93	73.77	71.37	69.05	25.15
420	87.81	61.45	50.55	72.71	69.64	67.64	23.49
490	88.06	60.08	49.64	72.07	67.85	68.00	22.20
560	87.23	59.10	47.57	71.57	68.97	66.83	21.97

Measured values of light transmission of all HIPS (nano)composites

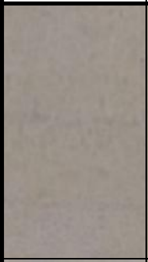
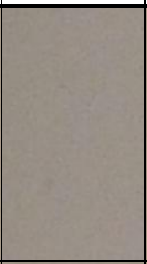
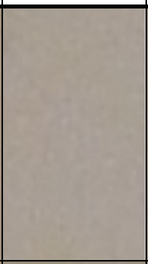
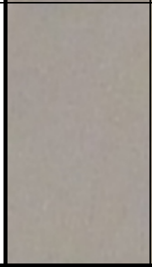
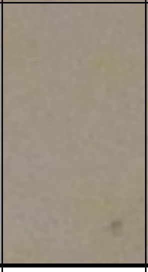
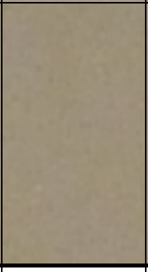
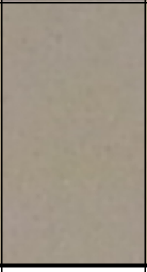
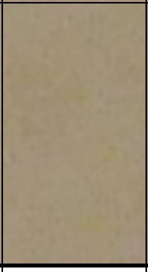
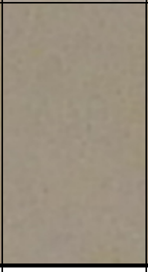
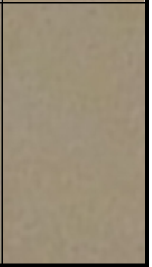
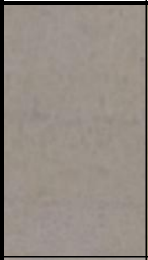
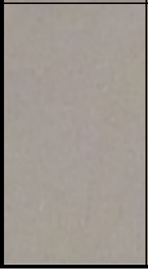
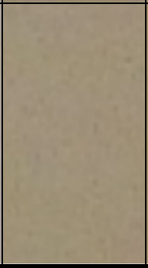
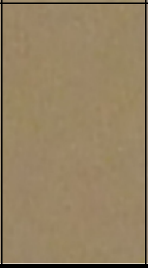
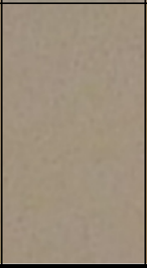
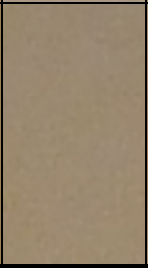
Irradiation time	Pure HIPS	N5	Clo	Ars	Hal	Cal	IRG
***YI* [%] – 1 % loading**							
0	50.41	46.88	44.73	49.18	49.63	47.71	37.15
70	50.24	47.62	44.34	51.27	50.19	49.08	38.77
140	49.28	46.23	43.89	50.00	49.56	48.36	38.42
210	48.83	45.71	43.17	49.49	49.81	48.59	38.71
280	46.35	43.88	40.43	46.20	48.73	47.03	37.21
350	42.23	42.01	37.57	44.89	48.24	45.47	35.06
420	45.35	40.04	38.67	43.07	46.62	43.82	34.48
490	43.85	38.95	37.26	39.57	44.55	42.61	31.45
560	44.20	38.02	38.07	41.17	42.79	40.87	32.12
***YI* [%] – 3 % loading**							
0	50.41	42.71	40.47	44.53	79.62	46.85	23.07
70	50.24	42.86	39.45	46.50	77.92	48.13	24.45
140	49.28	41.10	38.25	46.73	76.20	47.11	24.23
210	48.83	40.40	38.00	45.00	75.73	46.41	24.27
280	46.35	38.12	37.55	46.72	73.65	43.95	24.03
350	42.23	34.76	36.35	48.20	71.37	44.63	24.33
420	45.35	33.68	35.99	44.21	69.64	42.97	23.78
490	43.85	32.33	34.77	45.49	67.85	40.88	23.12
560	44.20	32.36	34.15	44.89	68.97	39.05	22.90

Measured values of light transmission of all HIPS (nano)composites with SMA

Irradiation time	Pure HIPS	HIPS + N5 1%	HIPS + N5 3%	HIPS + N5 5%
***YI* [%] SMA 1:1**				
0	50.41	46.30	39.86	31.26
70	50.24	46.92	39.65	31.24
140	49.28	46.38	39.09	31.03
210	48.83	45.86	38.31	30.37
280	46.35	44.29	36.27	28.93
350	42.23	43.38	35.49	27.85
420	45.35	42.24	34.65	27.13
490	43.85	40.54	33.23	26.49
560	44.20	40.95	33.84	26.20
***YI* [%] SMA 3:1**				
0	50.41	48.07	36.92	37.95
70	50.24	48.28	35.59	37.21
140	49.28	46.91	35.01	36.72
210	48.83	47.87	34.40	36.14
280	46.35	45.14	32.89	34.94
350	42.23	44.59	31.04	33.94
420	45.35	43.97	30.5	33.65
490	43.85	42.96	29.46	33.08
560	44.20	42.00	29.22	32.20

APPENDIX P V: PHOTOGRAPHS – BIODEGRADATION

Photographs of PS (nano)composites surface before and after biodegradation

PS	Pure PS	N5 1%	Clo 1%	Ars 1%	Hal 1%	Cal 1%	IRG 1%
Before							
After							
PS	**Pure PS**	**N5 3%**	**Clo 3%**	**Ars 3%**	**Hal 3%**	**Cal 3%**	**IRG 3%**
Before							
After							

Photographs of HIPS (nano)composites surface before and after biodegradation