Structure and properties of wood/polypropylene composites

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The aim of the thesis is to prepare the composites based on wood flour and polypropylene and evaluate their final properties. Composites will be prepared via twin screw extrusion. Several ratios of wood/polypropylene and processing conditions will be applied. Both neat and thermally modified wood flour will be employed as a filler. Special attention will be paid to mechanical properties of processed composites.

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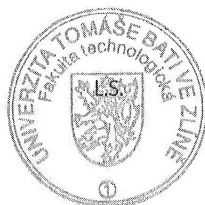
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ABSTRACT

The aim of this thesis is to study the properties of polypropylene/wood flour composites. Five types of wood flour were used as filler for polypropylene; untreated wood flour and four thermally treated (retified) wood flours. The properties of samples were investigated by rheology measurements, differential scanning calorimetry, wide-angle X-ray diffraction, tensile testing, thermogravimetric analysis, scanning electron microscopy and dynamic mechanical analysis. It was found that the thermal treatment of poplar wood flour under given conditions can lead to the improvement of the polypropylene/wood interaction which was demonstrated by the changes in crystallization and mechanical properties of the materials.

Keywords: polypropylene, wood flour, retification, wood plastic composites, wood polypropylene composites

ABSTRAKT

Cílem této diplomové práce je studium vlastností kompozitů polypropylenu s dřevní moučkou. Bylo použito pět typů dřevní moučky; přírodní neupravená dřevní moučka a čtyři teplotně upravované (retifikované) dřevní moučky. Vlastnosti vzorků byly zkoumány reologickými měřeními, diferenciální skenovací kalorimetrií, rentgenovou difrakcí, tahovými zkouškami, termogravimetrickou analýzou, skenovací elektronovou mikroskopií a dynamicko-mechanickou analýzou. Bylo zjištěno, že tepelná úprava topolového dřeva za určitých podmínek, může vést ke zlepšení interakce mezi polypropylenem a dřevem, což bylo demonstrováno změnami v krystalizaci a v mechanických vlastnostech materiálů.

Klíčová slova: polypropylen, dřevní moučka, retifikace, kompozity polypropylenu s dřevní moučkou

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INTRODUCTION

Production of wood flour (WF) thermoplastics composites can bring several environmental and economical advantages. Although the use of the wood-based fillers is not as popular as the use of mineral and inorganic fillers, wood-derived fillers have several advantages over the traditional fillers and reinforcing materials: low density, flexibility during the processing with no harm to the equipment, acceptable specific strength properties and low cost per volume basis.

Wood plastics composites (WPC) are relatively new and high-value products comprising wood flours as fillers and reinforcements and thermoplastics polymers as matrices. Pine, maple, and oak are commonly used wood species, whereas polyethylene, polypropylene, and polyvinyl chloride are usually used as the thermoplastics. [1]

Recently the production and the application of thermoplastics reinforced with the wood flour and the natural fibers increased considerably. The main drawbacks of such composites are their water sensitivity and the relatively poor dimensional stability, changing the wood fiber characteristics with origin and the time of the harvest, and the poor adhesion to basically all matrix polymers. The main application area of wood flour filled composites is building and automotive industry, but they are also applied for packaging, for the preparation of various household articles, furniture, office appliances and the other items. [2, 3]

The aim of the thesis is to prepare the composites based on wood flour and polypropylene and evaluate their processing and final properties. Composites will be prepared via twin screw extrusion. One ratio of wood/polypropylene and processing conditions will be applied. Both neat and thermally modified wood flour will be employed as filler. Special attention will be paid to the mechanical properties of processed composites.

I. THEORETICAL PART

1 COMPOSITES

1.1 Fillers in general

Important changes in the properties of plastics resulting from the incorporation of special additives permit their use in applications where the polymer alone would have had small chance to meet certain performance specifications. Fillers and reinforcements are solid additives that differ from the plastics matrices with respect to their composition and structure. The basic role of a filler is to 'fill', i.e., increase the bulk at low cost, thereby improvingeconomics while, by definition, the main function of a reinforcing filler is to improve the physical and mechanical properties of the basic polymer. Out of these properties, stiffness and strength are the most important among 'short-term' properties in engineering applications. Resistance to creep and fatigue failure is principal long-term properties. The effect of heat on both these groups of properties is shown by the heat deflection temperature (HDT) and dimensional stability. All these properties can be upgraded by reinforcing fillers. Non-mechanical properties of the basic polymer, e.g., electrical properties, abrasion resistance, flammability, may also be strongly modified by the presence of reinforcing fillers. With fibrous fillers, the influence of the fibre aspect ratio and the anisotropic effect of fibre orientation can further magnify the improvements. [4]

That is why the most effective reinforcing fillers are fibres of high modulus and strength. Modern fillers can take on many of the functions of reinforcements. Usually, fibres and lamina structure are counted as reinforcements, while the ball type additives are counted as fillers. Inert fillers or extender fillers increase the bulk, solve some processing problems and lower the price; no improvement is seen in the mechanical or physical properties compared with the unfilled polymer, although by a higher thermal conductivity, they improve the production rates. [4]

Active fillers, enhancers, and reinforcements produce specific improvements of certain mechanical or physical properties, including modulus, tensile and impact strength, dimensional stability, heat resistance, and electrical properties. Most particulate fillers have a higher specific gravity than polymers, but some, such as hollow ceramic or glass spheres, expandable beads, have been developed to reduce the weight of the compound. [4]

Liquid extenders are used in elastomers. Particulate mineral additives are classified as two- or three-dimensional. The two-dimensional silicates in layers (such as talc and mica) essentially induce rigidity and thermal stability, but do not attain the stiffening effect of fibre-type reinforcements. Average particle diameter, specific surface and surface energy are decisive in the reinforcing effect of fillers in elastomers. [4]

For their use in plastics the most important characteristics of fillers are: chemical composition, particle shape, average diameter, grain distribution, specific surface and value of surface energy, thermo-oxidative and UV-stability for outdoor applications and moisture and water-soluble compounds content. [4]

1.2 Wood fillers

Wood-based copmposites have been and are in use for a long time in various applications. Wood can be used in many different forms as reinforcement, e.g. in the form of wood flours or fibre.

1.2.1 Structure of wood

In the surface of the tree there is a thin layer called the cambium that creates a new wood layer inside it each year. On the outside the cambium creates a bast layer that, in turn, creates the bark. An annual ring consists of the light earlywood (grown in the spring) and the dark latewood (grown in the summer). The difference between earlywood and latewood is, for example, the chemical structure and the density. The latewood has higher cellulose content than the earlywood. Fibres in wood are long cells. They vary in size and function. Each cell forms a fibre. A fibre consists mainly of cellulose, hemicellulose and lignin. The cellulose forms the frame of the cell wall; on the other hand, hemicellulose and lignin form the surrounding intercellular substance. [5]

Cellulose and hemicellulose are hydrophilic chain polymers that have hydroxyl groups (-OH). The wall of the wood fibre is built up of an outer layer (primary wall) and a three-layered inner layer (secondary wall). The fibres are surrounded by lignin. The outer layer consists mainly of lignin and has only a little cellulose. The inner layer consists mostly of cellulose and hemicellulose and has only some lignin. [5]

As mentioned earlier, cellulose is the main component of wood fibre. It therefore determines the properties of the fibres and makes it possible to use them, for example, in the paper-making industry. Having a hydrophilic nature, their ability to absorb water is strong and therefore water will affect the properties of the fibres. The humidity can change the dimensions but also affect the mechanical properties. [5]

Hemicellulose molecules are smaller than those of cellulose. They can be divided into three groups: hexocane, pentosane and polyurenoids. Hemicellulose affects the ability of fibres to form bonding between each other. Lignin is a polymer that bonds fibres and gives wood its stiffness. The lignin content depends on the type of tree. In coniferous trees there is about 28% (dry weight) of lignin and in deciduous trees about 20% (dry weight) of lignin. [5]

1.2.2   Wood flour

Wood flour is finely pulverized wood that has a consistency fairly equal to sand, but can vary considerably, with particles ranging in size from a fine powder to roughly the size of a grain of rice. Most wood flour manufacturers are able to create batches of wood flour that have the same consistency throughout. All high quality wood flour is made from hardwoods because of its durability and strength. Very low grade wood flour is occasionally made from sapless softwoods such as pine or fir. Wood flour is commonly used as filler in thermosetting resins such as polyoxybenzylmethylenglycolanhydride, also known as Bakelite; and in Linoleum floor coverings. Wood flour is also the main ingredient in wood/plastics composite building products such as decks and roofs. [6]

1.2.3   Wood fiber

Wood fibres are cellulose fibres that are extracted from trees, straw, bamboo, cotton seed, hemp, sugarcane and other sources. The main source is paper. [6]

Paper fibre in this context means the raw material used in paper processing industry and is in the shape of a fibre. It is mechanically ground or chemically made organic material from trees. Both mechanically made and chemically made cellulose fibres are called wood fibres. Mechanically made wood fibres contain lignin but the lignin has been removed from the cellulose fibres. Both fibre types are often mixed in the processing of paper in order to combine their properties. [5]

1.2.3.1   Wood fibre plastics composites

In fibre reinforced composites the composite strength is determined by the strength of the fibre and by the ability of the matrix to transmit stress to the fibre. Transmission of stress to the fibre is affected by fibre orientation (as opposed to stress direction), geometry (e.g. diameter) and interfacial bond between fibre and matrix. The critical fibre length is the minimum length necessary for effective transmission of stress from matrix to fibre. It is possible to decrease this critical length by improving the interfacial bonds. [5, 6, 7]

The composite with natural wood fibres contains a wide distribution of fibres, both longer and shorter than the critical length, making a theoretical calculation of the composite properties difficult. Furthermore, for example, the fibre orientation in the injection-moulded test specimen is not random, making comparison with theoretical results still more vague. [5, 6, 7]

2 WOOD PLASTICS COMPOSITES

There are two types of composites made of polymer and wood, which have to be distinguished – *wood polymer composites* and *wood plastics composites*. The difference is in the preparation of these composites.

2.1 Wood polymer composites

Wood polymer composites are materials in which wood is impregnated with monomers that are then polymerized in the wood. If wood is vacuum impregnated with certain liquid vinyl monomers that do not swell wood and are later polymerized *in situ* by gamma irradiation or chemical catalyst-heat systems, the resulting polymer resides almost exclusively in the lumens. Methyl methacrylate is a common monomer used for wood polymer composites. It is converted to polymethyl methacrylate.

The resulting properties of these materials, from lightness and enhanced mechanical properties to greater sustainability, has meant a growing number of applications in such areas as building, construction and automotive engineering. [8, 9]

2.2 Wood plastics composites

Wood plastics composites (WPC) are materials prepared by blending wood flour or wood fibers (WFs) with the polymer melt. Virgin or recycled polymer can be used. Wood flour is made commercially by grinding postindustrial material, such as planer shavings, chips, and sawdust, into a fine, flour-like consistency. Wood fibers, although they are more difficult to process than wood flour, can lead to superior composite properties and act more as reinforcement than as filler. Wood fibers are available from both virgin and recycled sources. Recycled sources include pallets, demolition lumber and old newsprint. Wood from small-diameter trees and under-utilized species can also be used. [10, 11]

The properties of the composites are affected by many factors: materials, content of WFs and processing parameters. In composites some problems are inevitable and depend on the matrix material. The WFs are polar materials and so there is poor adhesion between them and non-polar polymers such as polyolefins. This presents a problem in composites containing WFs and non-polar polymers that cannot wet the polar WFs without coupling agents. On the other hand, the lignin improves adhesion between WFs and polyolefin. If

adhesion is poor, WFs work mainly as filler in the matrix and therefore the tensile strength can even decrease. When the adhesion is adequate, the WFs will work as reinforcement in the matrix. Water absorption is also quite an important problem with all wood materials. In composites the water absorption of the matrix material increases due to the hydrophilic WFs. [10, 11]

The primary criteria in selecting thermoplastics for WPC are those with a processing temperature less than approx. 250 °C. Above this threshold, unmodified lignocellulosic materials undergo rapid thermal degradation. This thermal criterior has limited WPC to polyolefins. Commonly used thermoplastics include polypropy1ene (PP), high and low density polyethylene (HDPE, LDPE), polyviny1chloride (PVC) and polystyrene (PS). In addition, impact modified versions of PP and PS have been explored. Both recycled and virgin sources of these commodity thermoplastics are commonly employed in powder or pellet forms. [10, 11]

Figure 1 *WPC – top left: polyethylene granules, top right: wood flour, bottom: wood-plastic composite pellets* [11]

2.2.1 Wood and thermoplastics compatibility and dispersion

Most of the physical and mechanical properties WPC depend mainly on the interaction developed between wood and the thermoplastics material. One way to improve this interaction is incorporating a coupling agent as additive. In general, the additives help the compatibility between hydrophilic wood and hydrophobic plastics allowing the formation

of single-phase composite. Wood-plastics composites also have problems when they are exposed to UV rays, their natural wood or pigmented color may tend to fade away. Therefore, depending on the final application, UV filters have to be added to stabilize their colors for a longer time. When designing a commercial composite, the effect of particle size is one of the most important parameters affecting overall products properties. The use of optimum size of particle might improve the mechanical properties of a composite, but the incorporation of a preservative should also be considered if it will be used for an application where biological resistance of this product is important. [12, 13]

The most varied of components added to WPC formulations are materials aimed at improving the compatibility of the wood and thermoplastics. These components include surfactants, copolymers, and reactive compounds. The energetic differences that exist between the wood and thermoplastics impede both adhesion and dispersion of the two phases. The chemical treatments may be applied prior to composite processing. Preliminary applications typically include coating or copolymerization in solvents. However, commercial operations most commonly use methods of direct mixing in dry blending, melt compounding, or extrusion steps. In many of these compounds both the chemical structure and the modification procedure have great influence on the effectiveness of a coupling agent. [13]

The most popular coupling agents include maleic anhydride (MA), maleic anhydride modified polypropylene (MAPP), isocyanates, and silanes. MA, MAPP, and PMPPIC (polymethy1ene polyphenylisocyanate) are very effective for improving the mechanical properties of composites presumably by improving the wood-thermoplastics interface. Silanes exhibit some coupling effects but seem more dependent on the types of plastics. Some physical methods like corona and plasma discharges can have a positive influence on mechanical properties of WPC. Most coupling agents are proposed to facilitate chemical linkages and/or hydrogen bonds between the wood and thermoplastics. Although the interaction between unmodified wood and thermoplastics is limited at best, commercial materials are often produced with no chemical treatment. [14]

Small particle sizes increase dispersion and mechanical properties when coupling agents are not employed. This fact bolsters the use of wood flour in commercial applications that do not employ chemical treatments. [14]

2.2.2   Physical and Mechanical Properties

The combination of wood and thermoplastics results in materials with unique physical properties. In general, the wood component tends to increase the stiffness, thermal stability, UV resistance, and workability of the composite. Thermoplastics improve moisture resistance, resistance to decay, and impart thermoforming characteristics. Mechanical properties are often the most studied of the physical properties. In all cases, the material performance is significantly influenced by the processing methods used. [13, 14, 15]

Mechanical properties of WPC are influenced by composition in different ways. Elastic modulus increases with increasing wood fractions. Although the trend is consistent across the type of thermoplastics and wood particle, the magnitude of the increase appears to be influenced by several factors. Composite strength is highly dependent on several factors, including the wood form, plastics type, processing method, and wood-thermoplastics interaction. In unmodified composite systems, small particle sizes are more effective at increasing the elastic modulus, favoring the use of wood flour. However, it appears more difficult to improve strength properties with wood flour. Decreased strength properties are generally cited with increasing wood content with a few exceptions. Impact strength decreases with fiber loading in all cases, although elastomeric coupling agents lessen the effect. Moisture absorption and swelling performance of WPC improve with increasing thermoplastics fraction. [15, 16]

2.3   Wood polypropylene composites

Polypropylene is very suitable for filling, reinforcing and blending. Compounding PP with fibrous natural polymers of biomass origin is one of the most promising routes to create natural-synthetic polymer composites. The key question is whether they are cheap filled compounds or high value, reinforced composites. It depends on the adhesion, cooperation between the synthetic PP matrix and the natural fiber. There has been much research done in the last two decades to bring together wood fiber, which is an irregular, hygroscopic, thermally sensitive, polar polymer, with polypropylene, which is an nonpolar, hydrophobic, highly crystalline synthetic polymer, requiring relatively high temperature to melt together with a compounding partner. To compatibilize such incompatible materials, several physical, chemical and technological solutions have been proposed, such as: intensive, intimate melt mixing without additives; mixing with special compatibilizers and processing

aids; mixing in presence of reactive additives; reactive processing (reactive extrusion, injection molding) applying special simultaneous treatments (electron-beam, ultraviolet, etc.). [17]

2.3.1   Coupling agents

A chemical substance capable of reacting with both the reinforcement and the resin matrix of a composite material. It may also bond inorganic fillers or fibers to organic resins to form or promote a stronger bond at the interface. It may be applied from a solution or the gas phase to the reinforcement, added to the resin, or both. Agent acts as interface between resin and glass fiber (and mineral filler) to form a chemical bridge between the two. Organotrialkoxysilanes, titanates, zirconates and organic acid-chromium chloride coordination complexes are the most commonly used. [18]

Maleated coupling agents (MaPOs) are widely used to strengthen composites containing fillers and fibre reinforcements. The established role of MaPOs results from two main factors, economical manufacturing and the efficient interaction of maleic anhydride with the functional surface of fibre reinforcements. [14]

2.3.1.1   Coupling agents for wood polypropylene composites

The use of maleic anhydride polyolefine (MaPO) coupling agents for glass-reinforced composites is well known and widely practiced. In natural filler composites, weak adhesion may result from poor dispersion and incompatibility between the hydrophilic natural fillers and the hydrophobic polymer. Poor composite strength results from the lack of stress transfer from the polymer matrix to the load bearing natural fillers. A direct measure of adhesion between natural fillers and thermoplastics is bonding strength. Interactions between the anhydride groups of maleated coupling agents and the hydroxyl groups of natural fillers can overcome the incompatibility problem to increase tensile and flexural strengths of natural filler thermoplastics composites. [14, 19]

The success of MaPO coupling agents may be attributed to two main reasons. First, MaPOs can be readily and economically produced. By the judicious choice of peroxide and reaction temperature, the grafting of maleic anhydride onto PP or PP copolymers can be controlled to give a polyolefin with the desired level of grafted maleic anhydride. The

peroxide grafting of the maleic anhydride occurs at the tertiary carbons of the polymer chain or at the terminal unsaturation of the chain. [14, 19]

The grafting utilizes the carbon–carbon unsaturation of the maleic anhydride group to form the bond to the polymer chain thus leaving the anhydride group free to react as an anhydride in the newly formed polymer. It is the presence of the relatively polar anhydride group on the olefin which imparts the unique set of properties to the graft polymer that make these polymers good couplers for natural fillers in polyolefins.

The second reason for the success of MaPO couplers pertains to their excellent balance of properties to bridge the interface between polar and nonpolar species. A coupler holds dissimilar materials together. In the case of a MaPO, the coupler may co-crystallize with the continuous polyolefin while the maleic anhydride portion of the molecule can interact with the more polar wood surface. [14, 19]

2.3.2 Chemical treatment of wood

In order to achieve the required combination of properties, interfacial interactions are often modified in the WPC. Interfacial adhesion can be changed by the chemical or physical modification of the wood or by surface coating of wood. [20]

Cellulose and wood flour are often modified chemically in order to increase the strength of the particles, to decrease water absorption or to improve composite properties generally. Esterification (cellulose reacts with fatty acid chlorides of various chain lengths) or etherification of their hydroxyl groups is the most often applied approach for modification, but attempts are made also for the impregnation of the wood flour with various monomers and their subsequent polymerization. Benzylation and also plastification of wood are used for the preparation of all wood (or wood/wood) composites. All these reactions lead to the substitution of the hydroxyl groups of the cellulose by less polar groups, which decrease water absorption and the tendency for aggregation. They might have disadvantageous effect on other properties. [20]

The interaction of wood particles as well as their water sensitivity may be decreased also by covering the particles with a surfactant. This technology is extensively used for the surface modification of particulate fillers. At very high wood content the particles may aggregate or touch each other purely from geometrical reasons. Surfactants can improve the

processability and aesthetics of the product by decreasing interaction and friction among them, and they may decrease water absorption as well. [20]

3 HEAT TREATMENT OF WOOD - RETIFICATION

In order to reduce environmental risks during the service life of the treated wood and to find new alternative developments on the durability of wood, some research and technology development have been made on thermal treatment. Retification is one of these processes. Retification induces chemical modification of the lignin and cellulosic components and modifies the intrinsic properties of wood: efficient increases of the durability against fungi and insects increase of the dimensional stability decrease of the mechanical properties. The interest of this process is to reduce the environmental impact during the service life. [21]

Retification allows materials to acquire new qualitative characteristics. This process involves reduced pyrolysis of wood that makes the wood more stable and more mycosis-resistant, but slightly impairs its mechanical properties.

The name of retification is derived from the combination of reticulation, which is a disposal changes in some molecular chains due to heat and torrefaction, which is a mild pyrolysis process. The process was developed by research activities, which started in the late 1970´s at the École Nationale Supérieure des Mines de Saint-Étienne (EMSE) in France, during the search of an alternative wood fuel product to reduce the dependency of petrol products, through the torrefaction process. In the middle of 80´s more reseraches were done in the physical and higher durability of the product obtain by this mild pyrolysis at a temperature below 280 °C and carry out in a neutral (low oxygen content) atmosphere. In 1995 the society NOW (New Option Wood) was created to develop the retification technology. [21]

3.1 Retification process

Retification is a heat treatment at the temperature of 200º - 280º C and short time deficiency of air. The term "retified wood" implies the material obtained by retification of natural wood, i.e. as a result of a chemical transformation (creation of new bonds) on molecular level wood components crystallize. This thermal process occurs under specific conditions of pressure, temperature, and at an accurately set level of temperature. [22]

During the high-temperature treatment, a portion of water contained in wood is extracted. Under these conditions and in an inert atmosphere carbon monoxides and dioxides are

released, thus, resulting in the alteration of wood constituents. This is a complicated and multilateral process of heat wood treatment that leads to numerous reactions that occur at various stages of the treatment. However, real-time control of temperature, duration, gas pressure and cooling atmosphere facilitates the thermal condensation reaction of certain constituents of internal wood structure without any losses of main ingredients (cellulose and lignin). [22, 23]

Wood becomes much more moisture-proof during the first minutes of retification; the material releases 4% of moisture into the external atmosphere. The weight decline is accounted for by the fact that water filling up the cracks of pentosan derivatives (semichemical pulp) provides the stability of the dimensions. [22, 23]

The stability of the dimensions appears due to furfural polymers derived from the destruction of sugars that are less hydroscopic than hemicellulose.

Thus the main features of the products obtain for recapitulation are:

     a. lower hydrophilic ability, reducing the values of equilibrium moisture content;

     b. better dimensional stability reducing the swelling of the treated materials;

     c. higher durability against biological and fungal degradation, with exception of termites;

     d. reduction in the flexing strenght and elasticity;

     e. increasing the surface hadrness.

[21, 22, 23]

3.2 Principles of retification process

3.2.1 Materials

Both softwoods and hardwoods are modified using retification process; actually this is done in a comercial scale for the following species: Scots pine (Pinus sylvestris), maritime pine (P. pinaster), Norway spruce (Picea abies), silver fir (Abies alba), poplar (Populus sp), beech (Fagus sylvatica), ash (Fraxinus sp.) and birch (Betula sp.). The moisture content of

the input materilas for the process ranges from 10 to 18 percent, being the minimum value for hardwoods and the maximum for softwoods. [21]

3.2.2 Equipment

The heat used for the process is coming from electric resistances and the atmosphere inside the reactor must have a low content of O_2, for that reason N_2 gas is usually injected N_2 gas. The main users of these reactors are small transformation wood industries, so their sizes are ranging from 4 to 8 m^3, having a potential annual production of thermal modified wood products from 1 700 to 3 500 m^3. There is a medium size reactor, which is fed with gas, having a bigger load size of 12 m^3 and a potential year production of 7 000 m^3. [21, 23]

3.2.3 Process

The retification process has four phases, which are carried out in a N_2 atmosphere:

      i.   Drying.

     ii.   Glass transition.

    iii.   Heat treatment or curing.

    iv.   Cooling.

During the first drying phase, the temperature inside the reactor is raised up to 80-100 °C, with a rate of 4-5 °C/min. This temperature is held until that the core of the wood has also reached that temperature. The lenght of this phase is up to the species and dimensions, but for a thickness of 27-28 mm, can last a period of two hours. [21, 22, 23]

At that point the glass transition phase starts, increasing the temperature with a ratio of 4-5 °C/min to a value known as glass transition temperature. This value ranges from 170 °C to 180 °C, depending on the species and is defined as the average temperature, where the wood components moves from the elastic to the plastics mechanical behaviour area. This means that in temperatures over this point, the wood pieces will not recover their initial dimensions after the application of a strain, while under the glass transition temperature the pieces will recover their dimensions, once the force is not applying any longer. The temperature inside the reactor is kept to this value until the instant, when all the section from the core to the surface has achieved that temperature, which usually happens after 3 hours. [21, 23, 24]

Curing phase starts once the whole piece of wood has achieved the glass transition temperature. The oven temperature is again raised to the thermal treatment temperature, which depends on the specie, dimensions an end use of the pieces, with a rate of 4-5 °C to 200-260 °C. For monitoring the changes during this curing phase, emissions from acetic acid, carbon dioxide or monoxide can be registered, using them as a hemicelluloses degradation indicator. The duration of this phase varies from 20 minutes to 3 hours, depending on species and end uses of the pieces. [21, 22, 23, 24]

After the heat treatment the temperature in the oven is reduce for a period of 4-6 hours, where the moisture content of the wood pieces is also increased to 3-6. The quality of the final products is partly affected by the initial quality of the treated timber with aspects like defects, humidity, sawing pattern and geometry of the wood, but also by process parameter like achieved temperature at each phase, increasing temperature rate, kind of gas atmosphere and quality in the reactor ventilation. [21, 22, 23, 24]

3.2.4 Features of the product

3.2.4.1 Density

As a result of the hemicellulose degradation and the water reduction, densities values are lower for retified pieces than for untreated ones. These changes were bigger for hardwoods than for softwoods; this reduction (dry oven) was 9.4 percent for beech, 7.9 for poplar, 5.4 for fir and 3.3 for pine. This reduction happens mainly during the drying phase (water until 80 °C and at the beginning of the heat treatment at temperatures (hemicelluloses degradation) between 180-200 °C, after this the weight is reduced following a linear pattern up to 260 °C. Losses are minimal during the glass transition phase. [21, 24, 25]

3.2.4.2 Equilibrium moisture content

For the range of studied species, the reduction in equilibrium moisture content (EMC), was higher for beech and poplar (52-62 percent) than for pine and fir (43-46 percent). The changes seems to be more affective by relative humidity for beech, while minor changes were observed in different relative humidity conditions for the other three wood species. [21, 24, 25]

3.2.4.3 Dimensional stability

The retification process improves the dimensional stability of wood products. According with the manufactures information, ASE values ranged from 53.4 percent for poplar to 25.2 percent for maritime pine, having Scots pine and Norway Spruce values around 45.5 percent and silver fir 28.7 percent. This represents a volumetric shrinkage of 7 percent for poplar; spruce and Scots pine retified pieces, while for fir and maritime pine, those losses were close to 9 percent. The untreated volumetric values ranged from 11.4 percent for silver fir to 13 percent for Norway spruce. The increment of the treating time has a positive effect in the increment of the dimensional stability of the products, reducing the volumetric shrinkage of treated pieces. [21, 24, 25]

3.2.4.4 Reduction of properties

One of the main disadvantages of retified wood is the reduction on some mechanical properties like modulus of rupture (MOR); during this process the elastic behaviour of wood pieces is also modified. The highest reduction in MOR values were for Scots pine with 27 percent and Norway spruce with 15.5 percent, while minor reduction ranging from 9.5 percent to 6.7 percent, affected silver fir, maritime pine and poplar. [21, 24, 25]

3.2.4.5 Wettability

The wettability of spruce, poplar, and beech and Scots pine, retified at 240 °C for 5 hours was studied using the contact angle. This value increased for the study species, being more notorious for poplar, Scots pine, and spruce and smaller for beech. According with this data, wettability is reduced by the retification process for these species. [21, 24, 25]

3.2.4.6 Fungi degradation

Heat treated products durability against fungi degradation is clearly improved and retified products are not an exception. Experiments done with maritime pine, spruce, beech and poplar heat treated for 1 to 24 hours and temperatures ranging from 200 to 260 °C show that the weight reduction for the attack of brown and white fungus was lower for treated specimens. [21, 26]

3.2.4.7 Weathering experiments

During artificial weathering experiments carried out for ash, beech, maritime pine, and poplar heartwood retified pieces treated at 240 °C for 2 hours: the changes in colour were measured. These changes were lower than for untreated specimens, this could be caused by the mild degradation of lignin during the heat treatment. While for untreated wood pieces, there was a drastic change in colour at the beginning of the weathering process, which was not the case for treated pieces. Ash seems to be less sensitive to UV degradation, while poplar showed higher colour instability against UV, having beech and maritime pine intermediate behaviours. Even with a higher stability to UV, retified wood as other heat treated products turns brownish. [21, 24, 25]

3.2.5 Products and processing capacity

The potential production of retified wood was 20 000 m^3 with six active reactors during year 2004, but according to data from NOW society, the production was not higher than 15 000 m^3. There is a broad range of products already available in the market like:

1. outdoor claddings and noise reduction walls

2. flooring and outdoor decking products done

3. garden furniture

4. windows, shuttes and other window protection elements

5. fencing, playground products and other outdoor wooden products, without a structural use

6. indoors wood panels, decoration products and furniture

The commercial species are Norway spruce, poplar, Scots pine, maritime pine, European beech and silver fir. [21, 27]

II. EXPERIMENTAL PART

4 MATERIALS

4.1 Polypropylene

The basic material used as a polymer matrix was polypropylene, with trade name HE125MO, manufactured by Borealis AG, Vienna, Austria. It is a homopolymer intended for injection moulding. This grade is characterized by good flow properties and high stiffness and is especially suitable for high-speed injection moulding of articles demanding easy flow. Its' very good organoleptic properties allows this grade to be used with any masterbatch without discoloring problems.

Property	Value	Unit	Test Method
Density	908	kg/m^3	ISO 1183
Melt flow rate (230 °C/2,16 kg)	12	g/10 min	ISO 1133
Tensile modulus (1mm/min)	1.550	MPa	ISO 527-2
Tensile strain at yield (50mm/min)	9	%	ISO 527-2
Tensile stress at yield (50 mm/min)	34.5	MPa	ISO 527-2
Heat deflection temperature (0.45 N/mm²)	88	°C	ISO 75-2
Charpy impact strength, notched (23 °C)	3.5	kJ/m^2	ISO 179/1eA
Hardness, Rockwell (R-scale)	100	-	ISO 2039-2
Melting point/range	130 - 170	°C	-

Table 1 *Characteristics of PP HE125MO*

4.2 Wood flour

The wood flour (WF) was made from natural poplar wood. Within the study five types of this poplar wood flour was used. The first was natural untreated WF; the others were treated by the retification process. All of the types were predried for 24 hours at the 100 °C. The types of WF are described in the following table.

	Wood flour	Retification process (min/°C)	Drying (hours/°C)	Particle size (μm)
1	Untreated poplar	0/0	24/100	<250
2	Retified poplar	5/220	24/100	<250
3	Retified poplar	60/220	24/100	<250
4	Retified poplar	5/240	24/100	<250
5	Retified poplar	5/260	24/100	<250

Table 2 *Types of used wood flour*

The particle proportions of WF were investigated by grain size analysis. Five different sieves were used.

Figure 2 *Apparatus for grain size analysis*

The particle size distribution of each type of WF is shown in the following table.

poplar wood flour					
	untreated	retified			
		5min220℃	60min220℃	5min240℃	5min260℃
Particle proportions (μm)	percentage (%)	percentage (%)	percentage (%)	percentage (%)	percentage (%)
250<x≤200	86.96	89.96	74.04	70.51	56.03
200<x≤100	9.2	6.35	18.51	21.51	26.28
100<x≤ 90	2.69	2.03	3.60	5.32	10.41
90<x≤50	0.51	1.27	3.34	1.99	6.12
50<x≤40	0.13	0.25	0.26	0.44	0.66
40<x<0	0.51	0.14	0.25	0.23	0.50

Table 3 *Particle size distribution of used WF*

The following figures show column graphs that represent the particle size distributions.
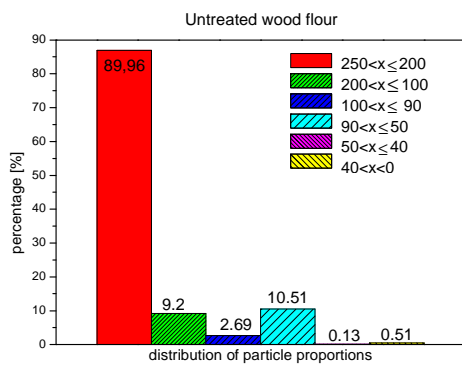
Figure 3 *Particle size distribution, untreated WF*
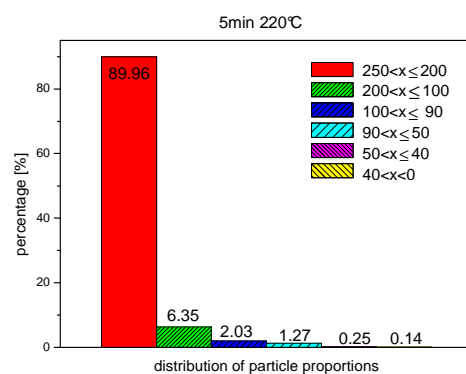
Figure 4 *Particle size distribution, WF retified for 5 min at 220 °C*
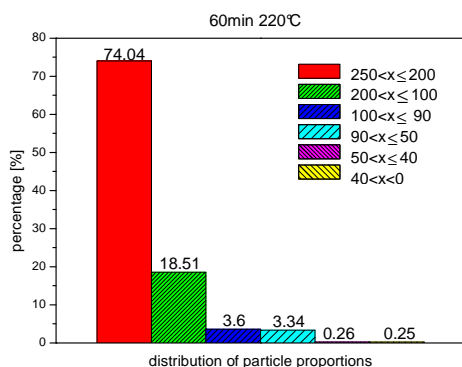
Figure 5 *Particle size distribution, WF retified for 60 min at 220 °C*
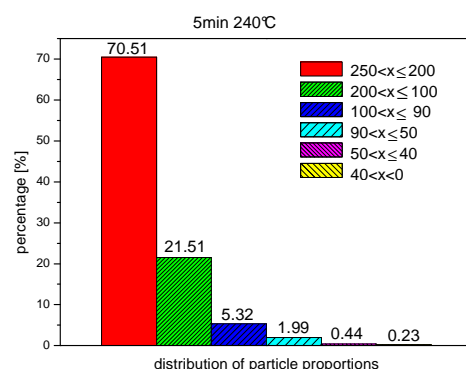
Figure 6 *Particle size distribution, WF retified for 5 min at 240 °C*
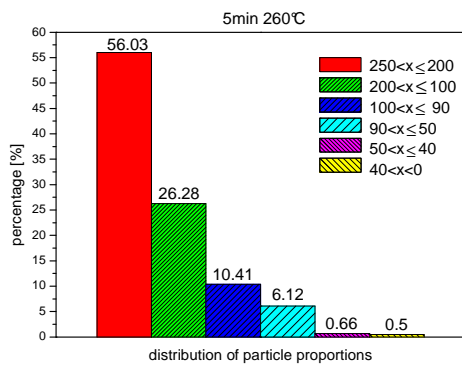
Figure 7 *Particle size distribution, WF retified for 5 min at 240 °C*

In the figures above it can be seen that in all types of WF the highest ratio is presented by the particles with the size from 200 μm to 250 μm. The particles with proportions between 90 and 50 μm are most substituted in the case of untreated WF.

In the following figures, there are five micrographs of used WF. It can be seen, that particle size is widely diverse.

Figure 8 *SEM micrograph of noretified WF*

Figure 9 *SEM micrograph of WF retified for 5 min at 220 °C*

Figure 10 *SEM micrograph of WF retified for 60 min at 220 °C*

Figure 11 *SEM micrograph of WF retified for 5 min at 240 °C*

Figure 12 *SEM micrograph of WF retified for 5 min at 260 °C*

5 PREPARATION OF BLENDS

For the preparation of blends PP/WF HAAKE Minilab Rheomex microcompounder intermeshing co-rotating twin screw extruder was employed.

Figure 13 *Haake Minilab Rheomex microcompounder intermeshing co-rotating twin screw extruder*

The specific temperature was 180 °C, rotational speed was 60 rpm, and blends were mixed for 8 minutes and then extruded. Five polypropylene/wood flour (PP/WF) blends were prepared. The concentration of WF was 30 wt.%. The weight of the blend was 7 g.

The following table specifies the nomenclature of composites, which are used in this work.

	Type of blend	Wood treatment min/°C	Notation
1	PP/WF	no	0m0C
2	PP/WF	60/220	60m220C
3	PP/WF	5/220	5m220C
4	PP/WF	5/240	5m240C
5	PP/WF	5/260	5m260C

Table 4 *Nomenclature of composite materials*

In the following figures, there are photos of used wood flour (left) and extruded strings of PP/WF blend (right).

Figure 14 *Untreated WF*

Figure 15 *0m0C blend*

Figure 16 *WF treated for*

5 min at 220 °C

Figure 17 *5m220C blend*

Figure 18 *WF treated for*

60 min at 220 °C

Figure 19 *60m220C blend*

Figure 20 *WF treated for*

5 min at 240 °C

Figure 21 *5m240C blend*

Figure 22 *WF treated for*   Figure 23 *5m260C blend*

5 min at 260 °C

From the figures above it can be seen that the color of WF becomes darker with increasing temperature of retification.

6   SAMPLES PREPARATION

The samples for DSC and thermogravimetric analysis were cut directly from the extrudates. The sample weight was approx. 10 mg in both cases.

The samples for X-ray diffraction, tensile testing and dynamic mechanical analysis were compression-moulded using a manual press and mould with inside dimensions 125x30x0.5 mm at the following conditions:

- temperature: 200 °C;

- pressing time: 7 min;

- cooling time: 5 min.

From this plates the small dumbbell specimens with following dimensions were cut:
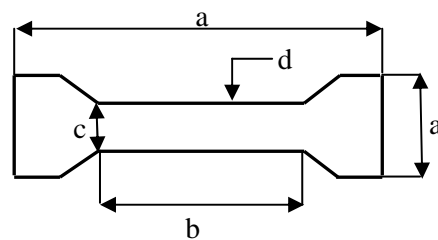
Figure 24 *Sample dimensions*

- a (overall dimension) = 30x10 mm

- b (working part size) = 10 mm

- c (working part width) = 5.2 mm

- d (working part average thickness) = 0.48 mm

- average cross-section size = 2.48 mm^2

The dumbbell specimens were used for a tensile testing.

For a dynamic mechanical analysis, the small strips were cut from moulded plates. They had the following dimensions:

- size: 9 mm;

- width: 2.77 mm;

- thickness: 0.42 mm.

For a scanning electron microscopy the broken specimens from a tensile test were used. On the microscope, the fracture area of the broken samples was investigated.

7   METHODS AND DEVICES

7.1   Rheology measurements

For rheology measurements the HAAKE Minilab Rheomex microcompounder intermeshing co-rotating twin screw extruder was employed. The microcompounder was filled with PP pellets and 30 wt.% of WF. After the blend mixing, the rheology measurement started. The conditions for measuring were:

- PP granules weight: 4.9 g;

- WF weight: 2.1 g;

- temperature: 180 °C;

- microcompounder filling time: 4 min;

- blend mixing time: 5 min;

- rotational speed within filling: 20 rpm;

- rotational speed within mixing: 60 rpm;

- rotational speed within rheology measuring: 1 – 120 rpm;

- rheology measuring time: 8 min.

After the measurement, blends were extruded into extrudate with round cross-section.

7.2   Differential scanning calorimetry

Differential scanning calorimetry (DSC) measurements have been carried out in a differential scanning calorimeter Perkin-Elmer Pyris 1. Nitrogen as a purge gas was used. For temperature calibration the indium was performed as a standard. To obtain the results of the melting and crystallization, the following conditions were set:

1. the samples were heated up from 70 to 200 °C at a heating rate 10 °C/min and maintained at this temperature for 5 min in order to eliminate the thermal history of the material;

2. the samples were cooled down to 70 °C at a cooling rate 10 °C/min;

3. the temperature 70 °C was hold for 5 min;

4. the samples were heated up to 200 °C again at the same heating rate.

Figure 25 *Differential scanning calorimeter*

7.3   Wide-angle X-ray diffraction

The structure of PP in composite materials was analyzed by means of wide angle X-ray diffraction (WAXD). This measurement was performed with PANalytical X' pert PRO device. The diffractometer was equipped with anode Cu with a radiation Kα with an average wave lenght 0.1542 nm. The X-ray diffraction pattern was recorded in angle range of 2θ = 7-30 ° by steps of 0.03 °. Counting time was 32.64 s.

Figure 26 *PANalytical X' pert PRO*

7.4 Tensile testing

Tensile testing was performed on the Tensometer 2000, Alpha technologies. Five specimens from each moulded plate (each blend) were prepared. The samples were strained without extensometer because of their small dimensions. The strain rate was 10 mm/min.

7.5 Thermogravimetric analysis

For thermogravimetric analysis (TGA) Setaran Setsys 1200 Evolution was employed. The samples of approx. 10 mg were heated up from 25 to 700 °C at the heating rate 20 °C/min.

7.6 Scanning electron microscopy

Scanning electron microscopy (SEM) was performed on the microscope VEGA LMU, Tescan.

Figure 27 *Scanning electron microscope VEGA LMU, Tescan*

The broken samples from tensile test were used. The tensile fracture surfaces were investigated.

7.7 Dynamic mechanical analysis

For dynamic mechanical analysis (DMA) the DMA/SDTA861^e, Mettler toledo was employed.

Figure 28 *DMA/SDTA861^e, Mettler toledo*

Nitrogen as a purge gas was used. At first, the test for investigation of linear viscoelasticity (linearity tension) was done. The temperature was fixed at -55 °C and the sample was extended from 0.05 to 1 μm. The test finished, when the module of the sample decreased with increasing deformation.

According to the test of linear viscoelasticity the following dynamic mechanical test was set up:

- temperature: samples heated from -50 to 110 °C;

- heating rate: 3 °C/min;

- tension force: 1 N;

- extension: from 1 to 10 μm (10 μm were used at the higher temperature).

In the following figure, there is a section through DMA measuring cell.
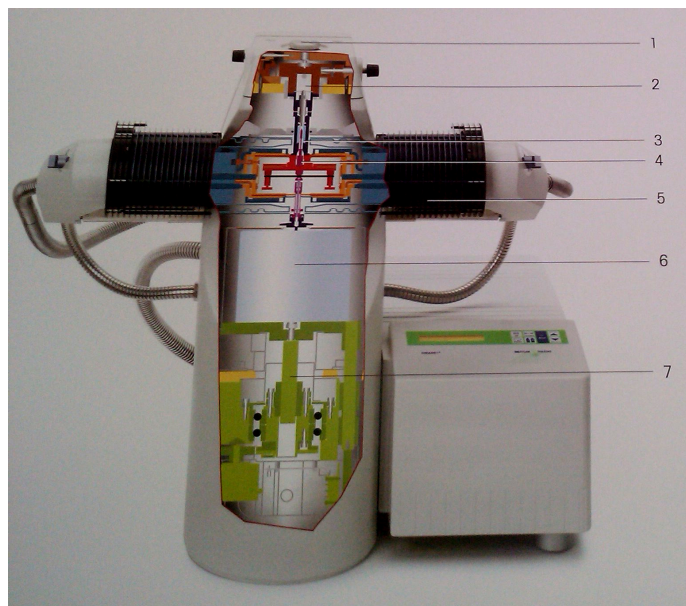
Figure 29 *Section through DMA measuring cell; 1. 4-axis alignment, 2. force sensor (piezoelectric), 3. displacement sensor, 4. clamping assembly and sample holder, 5. furnace, 6. drive motor, 7. Z-axis table*
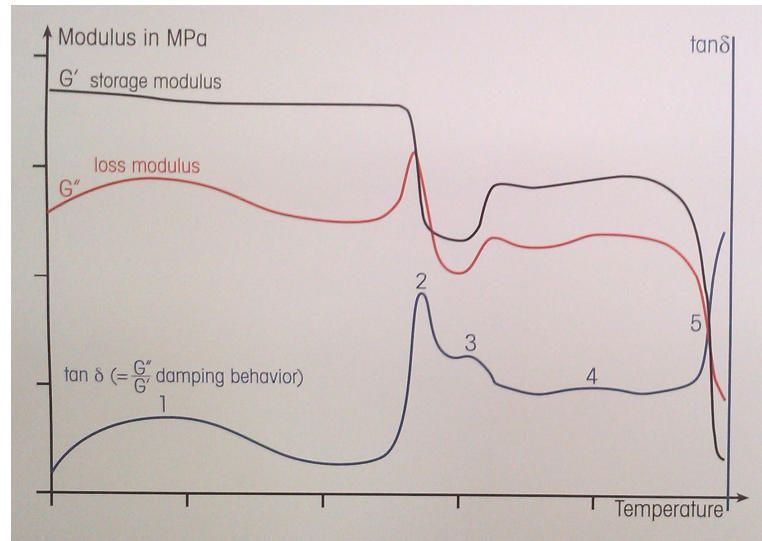
Figure 30 *Graphic representation of G' (storage modulus), G'' (loss modulus), tan δ; 1. secondary relaxation, 2. glass transition, 3. cold crystallization, 4. recrystallization, 5. melting*

In the figure above, there are the graphic representation of two components of dynamic modulus G; storage modulus (G') and loss modulus (G''). The difference between these moduli is presented by tan δ. Number one, situated on the tan δ curve, presents the peak of secondary relaxation of investigated material, number two the peak of glass transition, number three cold crystallization, number four recrystallization and number five melting.

III. RESULTS AND DISCUSSION

8 RHEOLOGY MEASUREMENTS

Rheology measurements were used to describe the melt behavior of the samples. Viscosity, shear stress and shear rate were measured. In the following graphs the logarithmic plot of viscosity and shear rate of all samples are presented.
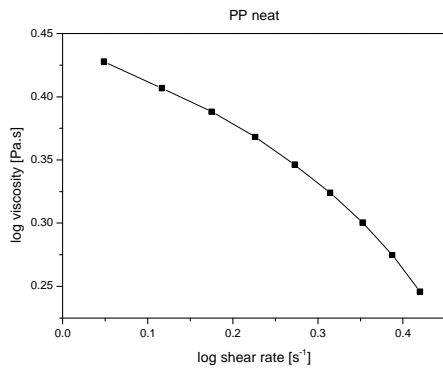
Figure 31 *Flow curve of neat PP*
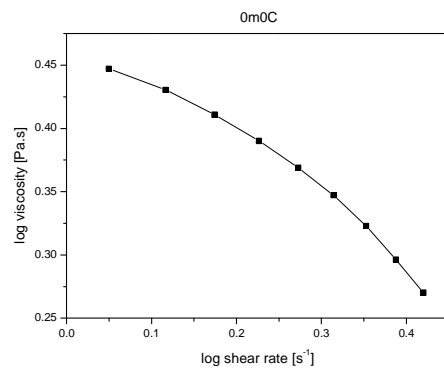
Figure 32 *Flow curve of 0m0C*
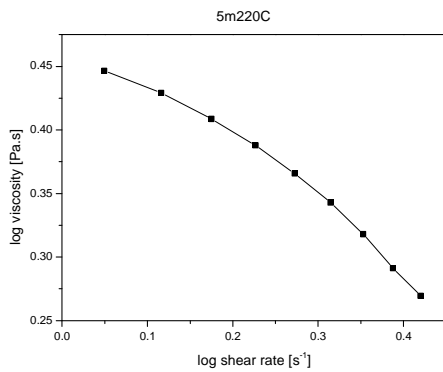
Figure 33 *Flow curve of 5m220C*
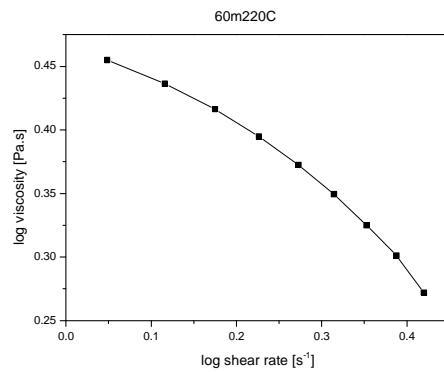
Figure 34 *Flow curve of 60m220C*
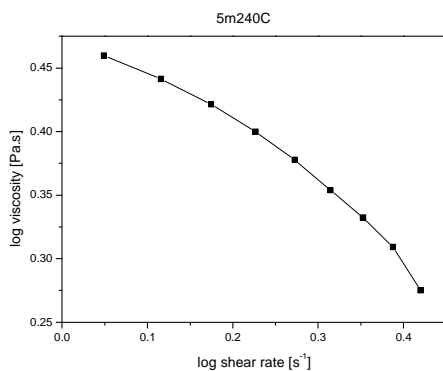
Figure 35 *Flow curve of 5m240C*
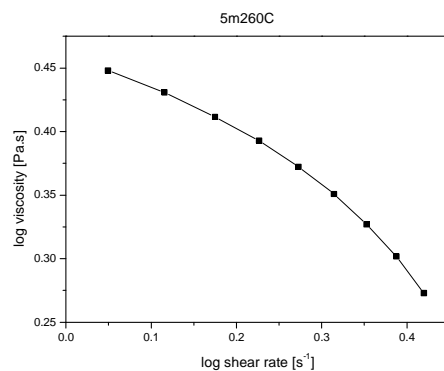
Figure 36 *Flow curve of 5m260C*
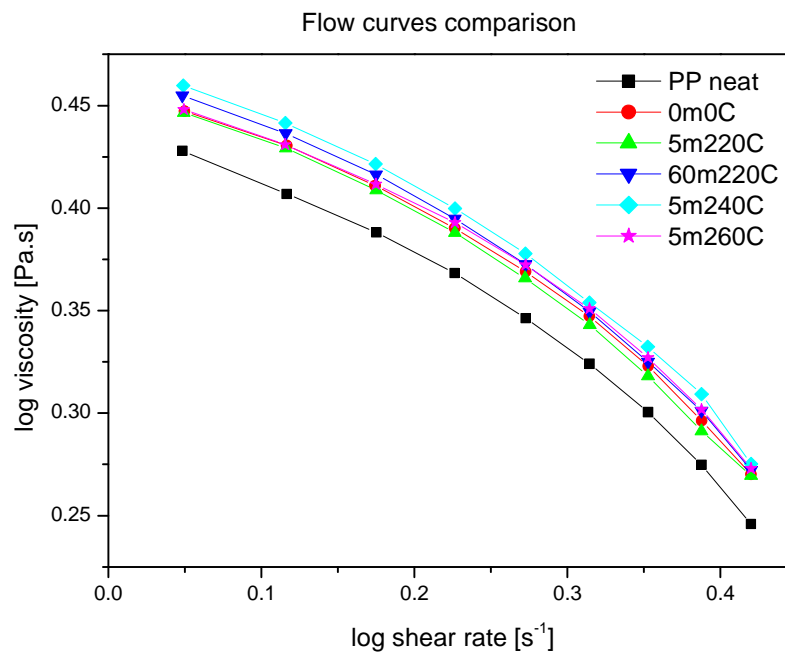
Figure 37 *Flow curves comparison*

From the figure above is seen that the highest viscosity was measured in the case of the blend 5m240C.

9 DIFFERENTIAL SCANNING CALORIMETRY

Differential scanning calorimetry was used to describe melting, crystallization and re-melting processes. The melting (T_m) and the crystallisation temperatures (T_c) of composites were obtained from the maximum of the endothermic and exothermic peaks, respectively. All results are ordered in the following table.

| | sample | Heating scan | | Cooling scan |
		Melting temperature (℃)	Enthalpy (J/g)	Crystallization temperature (℃)
1	PP neat	161.3	102.1	116.9
2	0m0C	162.3	61.3	117.9
3	5m220C	**163.6**	71.2	119.8
4	60m220C	162.1	69.5	120.5
5	5m240C	162.5	71.0	**121.8**
6	5m260C	162.0	69.2	119.8

Table 5 *DSC results*
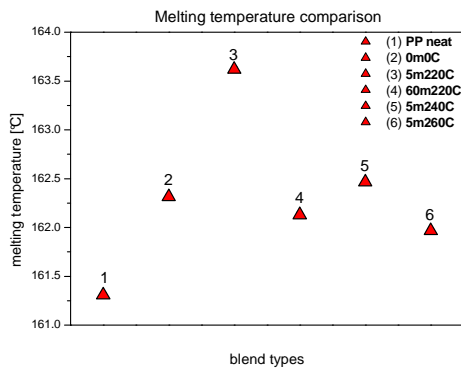
Figure 38 *Melting temperature comparison*
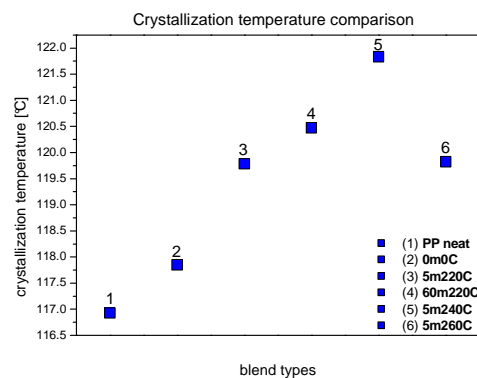
Figure 39 *Crystallization temperature comparison*

The figure 38 represents the melting temperatures of the investigated blends. The melting temperatures are taken from the second heating scan and they range between 161–164 °C. The highest temperature was measured in the case of 5m220C blend.

The figure 39 represents the crystallization temperatures of the investigated blends. The temperatures range between 117–122 °C. It is generally known that the crystallization temperature increases with the presence of heterogeneous nucleationg agent in the system.

In the figure 39, the crystallization temperatures are higher in the cases of the blends than in the case of the neat polypropylene. This can be explained by the fact that the particles of wood flour may influence a creation of the crystallites in all blends, thus the wood flour acts as a heterogeneous nucleation agent. In addition, higher crystallization temperatures were measured in the cases of the blends with retified wood flour. This can be caused by better compatibility between retified (hydrophobic) WF and PP. The highest crystallization temperature was measured in the case of 5m240C blend.

By the DSC measurement it was also confirmed that small particles of WF can act as nucleation agents more effectively than the big ones. From the blends containing the retified WF, the lowest crystallization temperature was measured in the case of 5min220C blend. From the grain size analysis (chap. 4.2) it can be seen, that the WF included in this blend contains the highest percentage of particles with dimensions above 200 μm. On the other hand, the 5min240C blend with the highest crystallization temperature contains WF with the large amount of particles smaller than 200 μm.
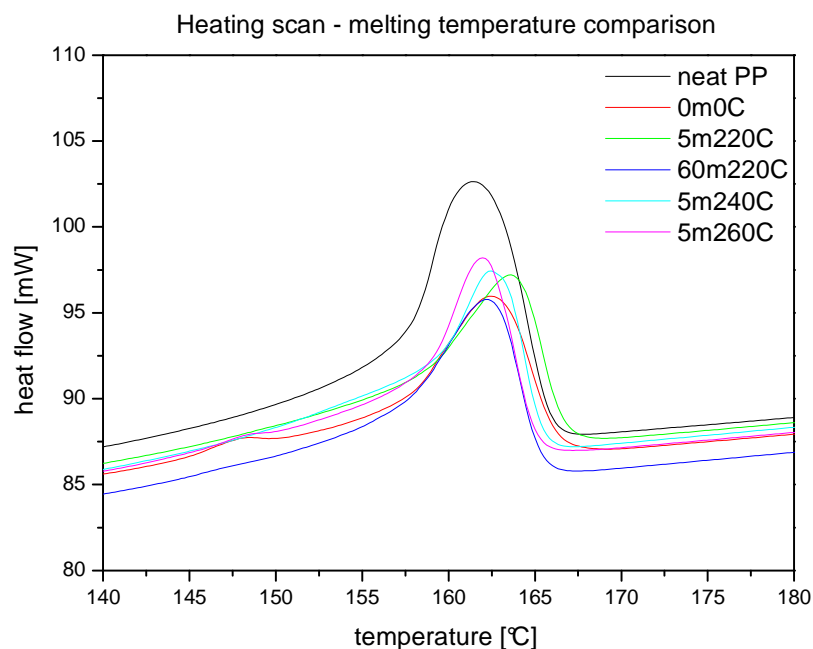
Figure 40 *Heating scan – melting temperature comparison*
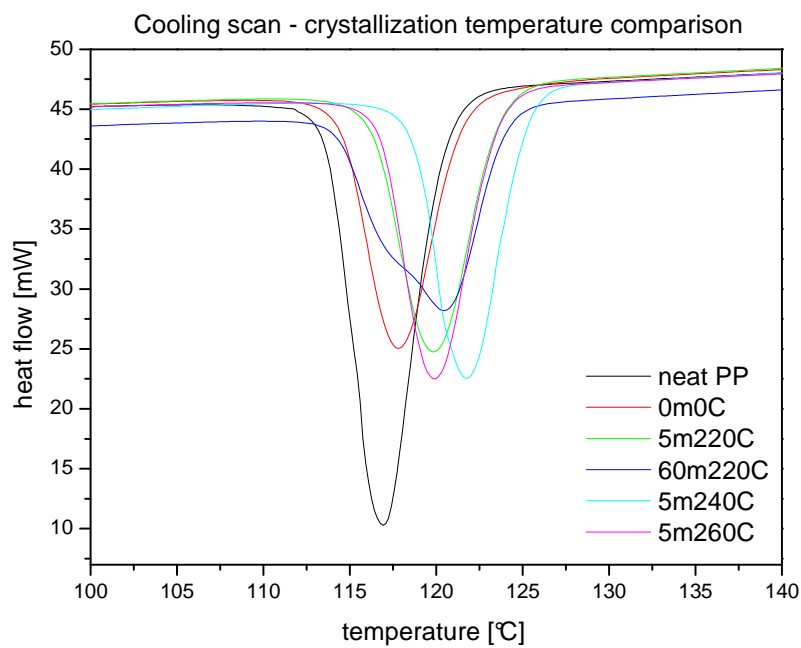
Figure 41 *Cooling scan – crystallization temperature comparison*

In sum, the addition of the wood flour to PP causes increasing of melting and crystallization temperatures, which is more pronounced with the retified wood flour. There is a significant difference among crystallization temperature of the neat PP and PP with retified wood flour content.

10 WIDE-ANGLE X-RAY DIFFRACTION

Polypropylene can exist in three morphological forms, depending on the tacticity of the chain and the crystallization conditions, such as pressure, temperature, and cooling rate: α–form, β–form and γ–form. The forms can coexist, and one polymorphic form can change into another as conditions change.

The typical reflections for α – form of PP are: 2θ = 14.2°, 17.0°, 18.8°; for β – form of PP: 2θ = 16.2°. γ-form of polypropylene does not usually form under typical processing conditions. It can occur in low molecular weight materials during crystallization at elevated pressures, or in chains with regular defects, produced using metallocene catalysts. [28]

Wide-angle X-ray diffraction was employed to observe the morphology of the neat PP and PP/WF samples. In the following figures there are the diffractograms, which show the typical reflections for a polypropylene at angles mentioned above. The diffractograms of samples differ in a proportion of individual peaks and also in the occurence of the β – form.
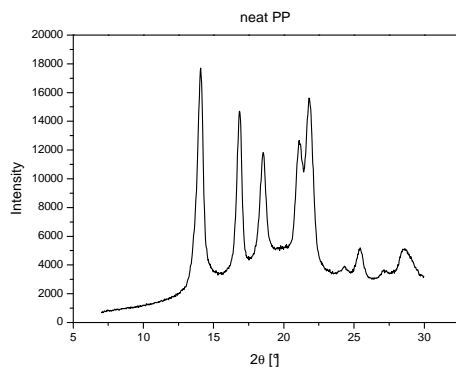
Figure 42 *Diffractogram of PP neat*
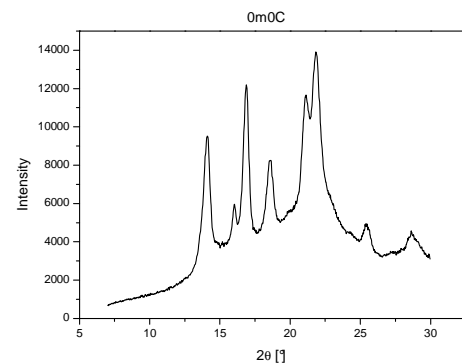
Figure 43 *Diffractograms of 0m0C*
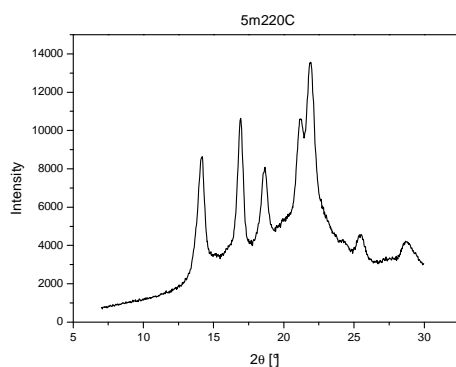
Figure 44 *Diffractogram of 5m220C*
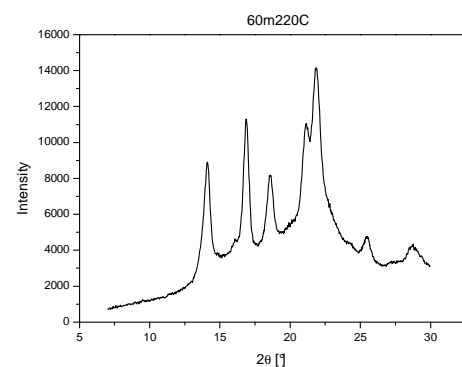
Figure 45 *Diffractogram of 60m220C*
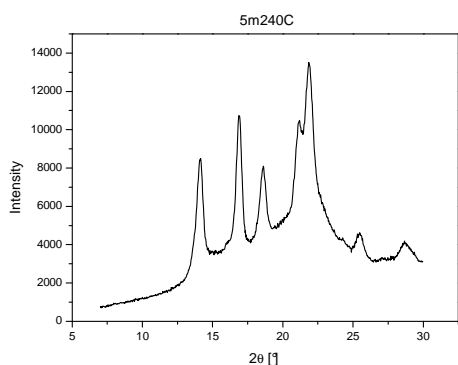
Figure 46 *Diffractogram of 5m240C*
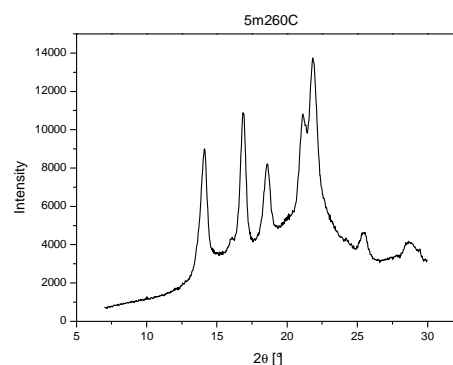
Figure 47 *Diffractograms of 5m260*
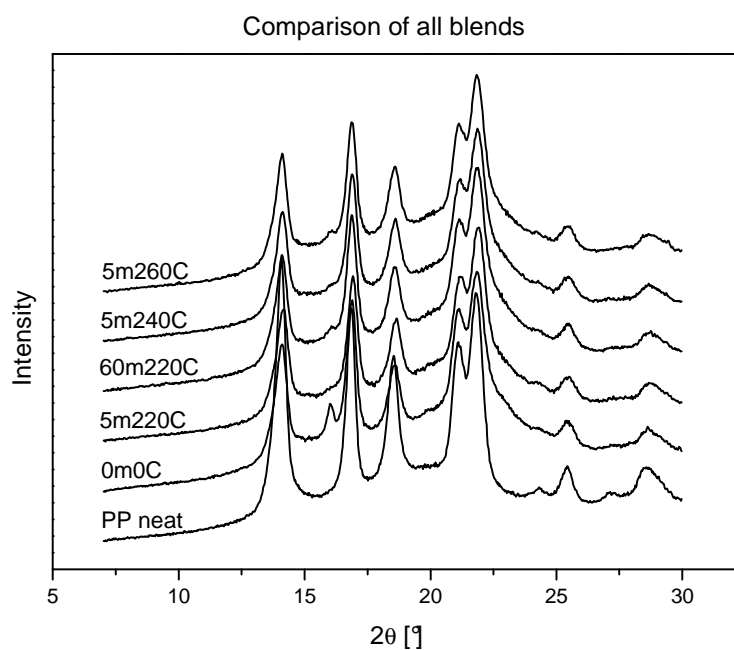
Figure 48 *Diffractograms comparison*

The β – form occurs in all blends. The largest occurence of β – form is in the case of 0m0C blend. In the following table the individual crystallinity of each sample was calculated from the diffractogram patterns.

sample	Crystallinity (%)		
	total	α-form	β–form
PP neat	*59*	*100*	*0*
0m0C	47	79	21
5m220C	46	93.5	6.5
60m220C	49	90	10
5m240C	**51**	94	6
5m260C	47	91.5	8.5

Table 6 *Crystallinity*
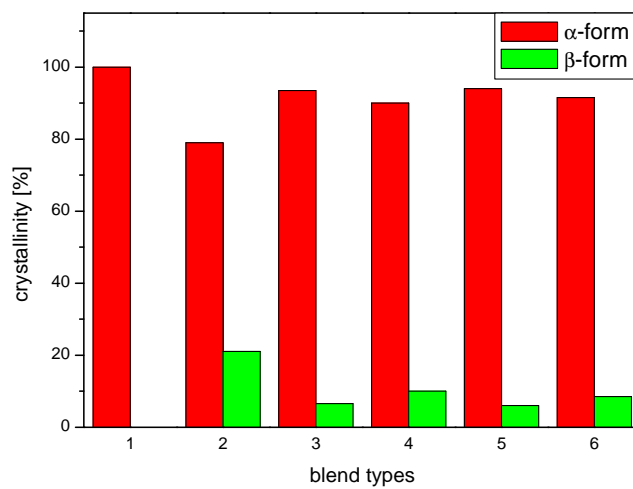
Blends nomenclature (fig. 49):

1 – PP neat

2 – 0m0C

3 – 5m220C

4 – 60m220C

5 – 5m240C

Figure 49 *Crystallinity comparison*

The largest crystallinity of all blends is presented in 5m240C. It is worth noting that this blend crystallized at the highest crystallization temperature; the lowest crystallization temperature showed 5m220C with the lowest crystallinity. The addition of the filler did not cause any difficulties in the PP crystallization, because the spectra show clear reflexions.

11 TENSILE TESTS

At least five specimens were tested for each composite blend. The yield stress, yield strain and modulus were measured. The modulus was not evaluated according to ISO 527-2 standard. It was calculated from the slope of linear part at 4-5 % strain. The measured and calculated values are ordered in the following table:

Tensile test			
sample	Yield stress (MPa)	Yield strain (%)	Modulus (MPa)
PP neat	**35.99**	**15.32**	437
0m0C	20.12	8.08	435
5m220C	21.96	7.49	**491**
60m220C	21.80	8.39	463
5m240C	20.49	9.03	383
5m260C	19.01	8.28	378

Table 7 *Measured values: yield stress, yield strain, calculated values: modulus*
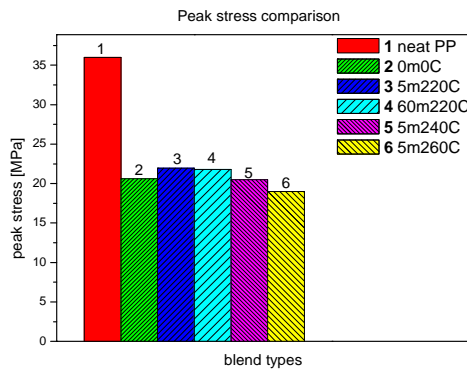
Figure 50 *Yield stress comparison*
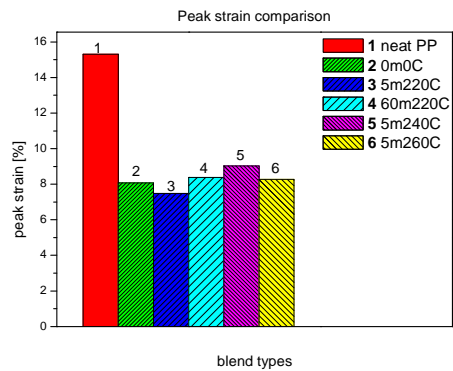
Figure 51 *Yield strain comparison*
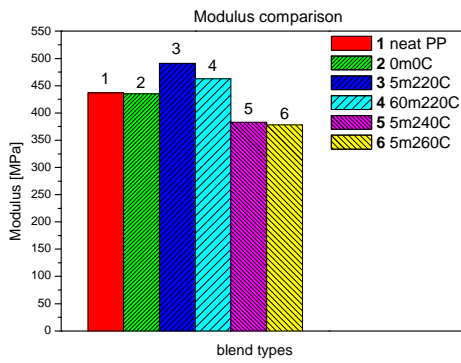
Figure 52 *Modulus comparison*

The yield stress values of blends vary between 19–22 MPa. The yield stress value of the neat PP was the highest. Moduli of the blends are lower than moduli of the neat PP except the 5m220C and 60m220C blends.

Yield strains of blends vary between 7.5 – 9 %. The yield strain of neat PP is 15 %.
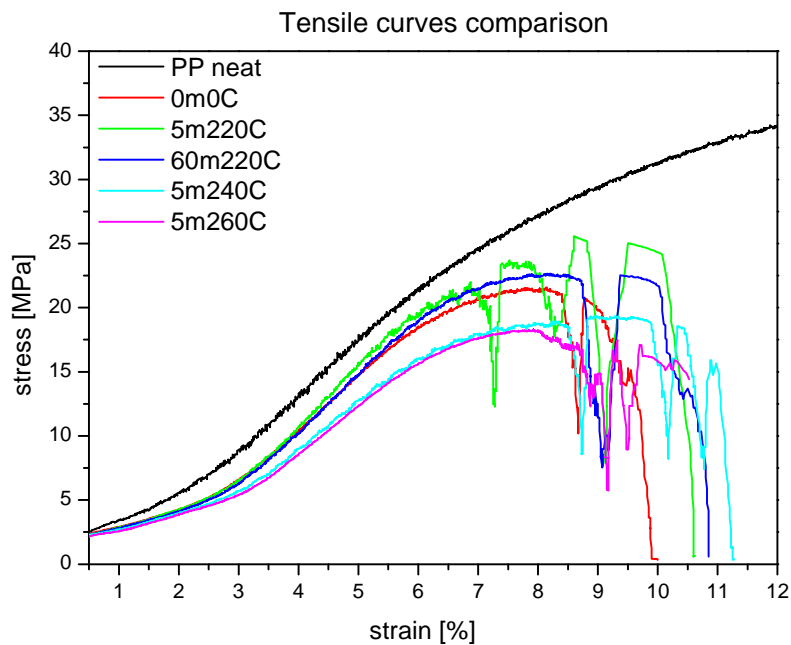
Figure 53 *Tensile curves comparison*

The addition of the wood flour in PP caused decrease of the yield strain, the samples are more brittle, and they broke at about 9-10 % of elongation. However, the preparation of test specimens and the specific measurements conditions this tensile test could be only informative and the results have to be proved by other measurements.

12 THERMOGRAVIMETRIC ANALYSIS

By the method of thermogravimetric analysis, the decomposition temperatures, decomposition rates and weight-losses of samples were investigated. In the following figures, the weight-losses (TG) and decomposition rates (dTG) of all samples are presented. The weight-losses are presented by the red curves, the decomposition rates by the black ones.

Figure 54 *TG and dTG curves for neat PP*

Figure 55 *TG and dTG curves for 0m0C*

Figure 56 *TG and dTG curves for 5m220C*

Figure 57 *TG and dTG curves for 60m220C*
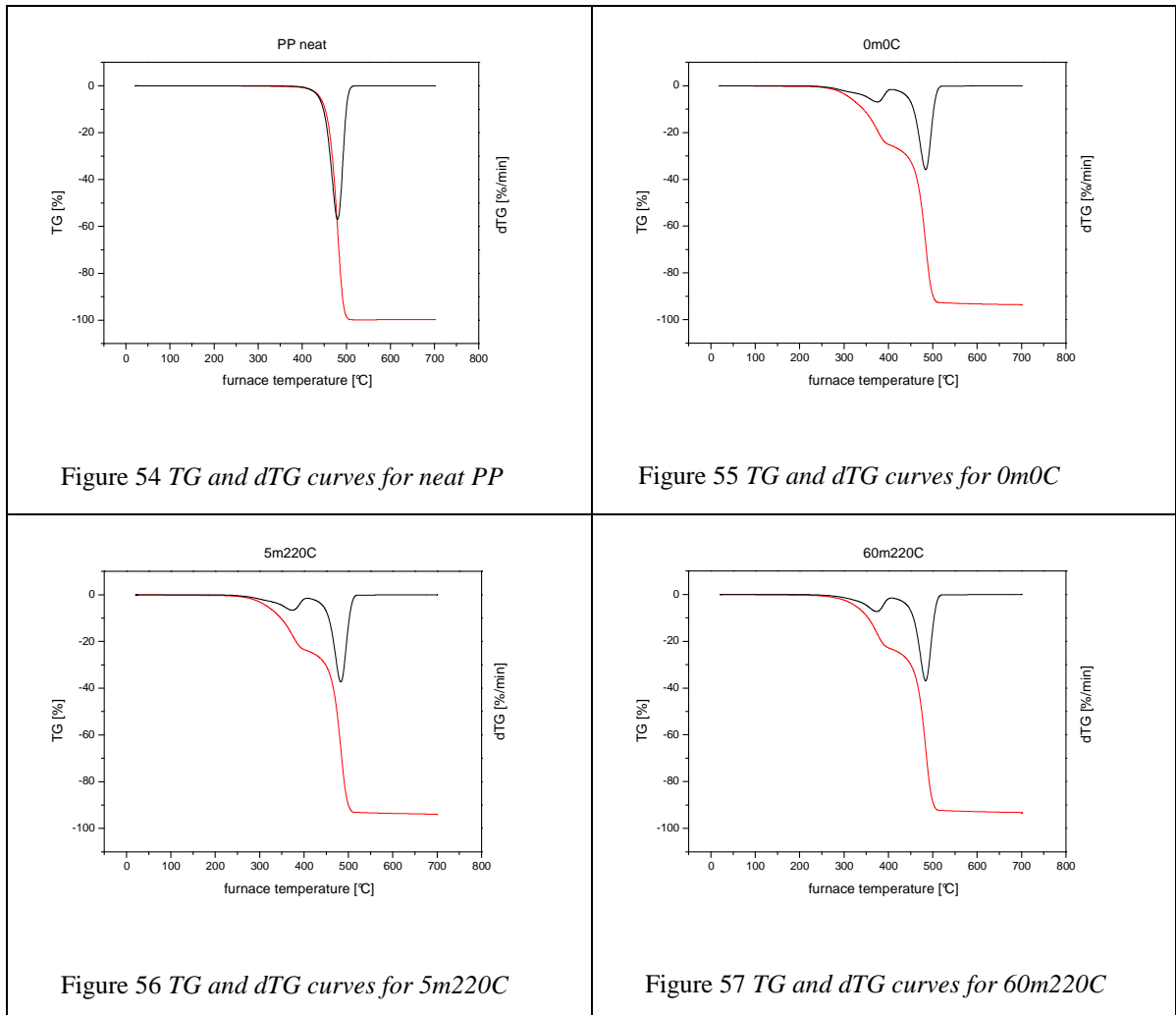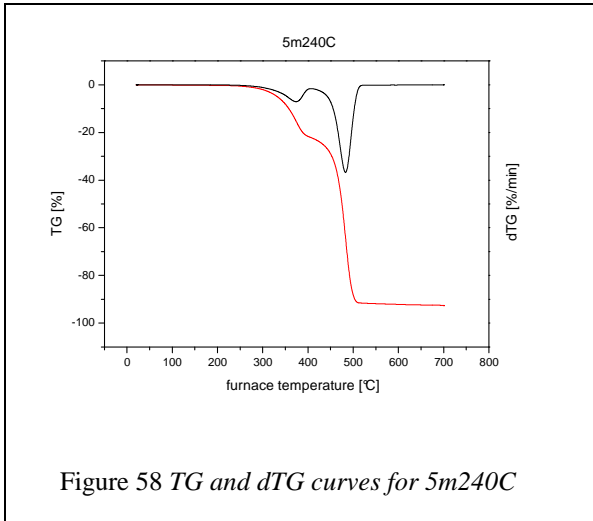
Figure 58 *TG and dTG curves for 5m240C*
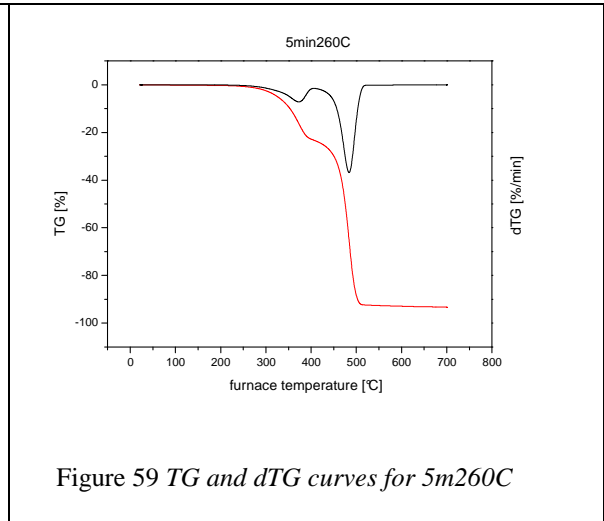
Figure 59 *TG and dTG curves for 5m260C*
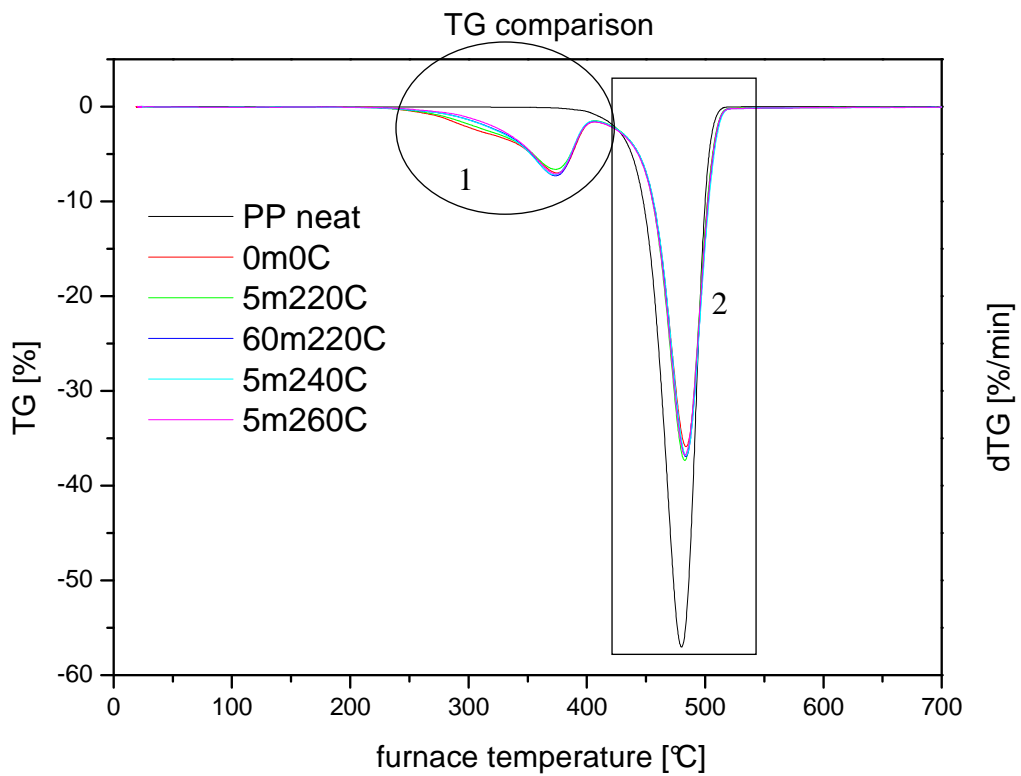
Figure 60 *TG comparison*

The circle region 1 (figure 60) displays the decomposition rates of wood flour and it is expanded in the following figure (figure 61). The squared region 2 displays decomposition rates of polypropylene and it is expanded in the figures 62 and 63.

Comparison of WF decomposition rates

PP neat
0m0C
5m220C
60m220C
5m240C
5m260C

TG [%]

dTG [%/min]

furnace temperature [°C]
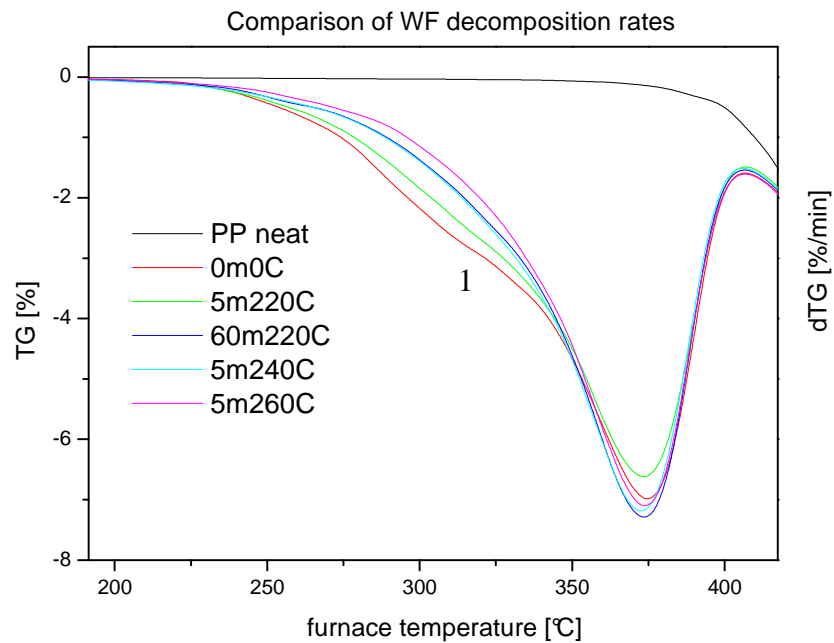
Figure 61 *Expanded curves of decomposition rates of WF*

In the figure above, it can be seen, that the decomposition of 0m0C and 5m220C blends proceeds in two steps, because the curves form two visible peaks. The maximum of the first one is about 300 °C; the second one has the maximum about 375 °C. Whereas, in the cases of the 60m220C, 5m240C and 5m260C blends, the peaks with the maximum about 300 °C are missing. It can be explained by the fact, that with increasing temperature of wood flour treatment (retification), the wood flour obtains better temperature stability.
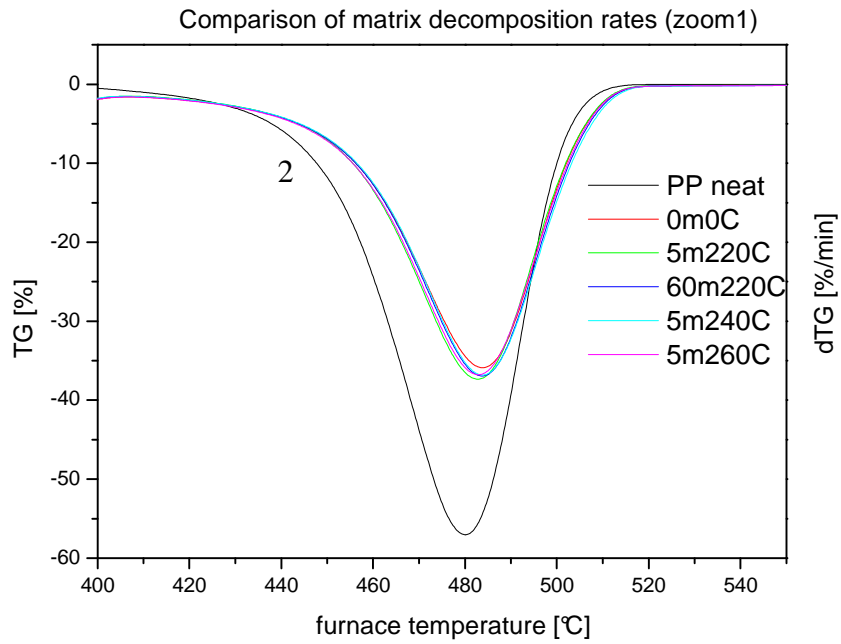
Figure 62 *Expanded curves of decomposition rates of matrix (zoom1)*
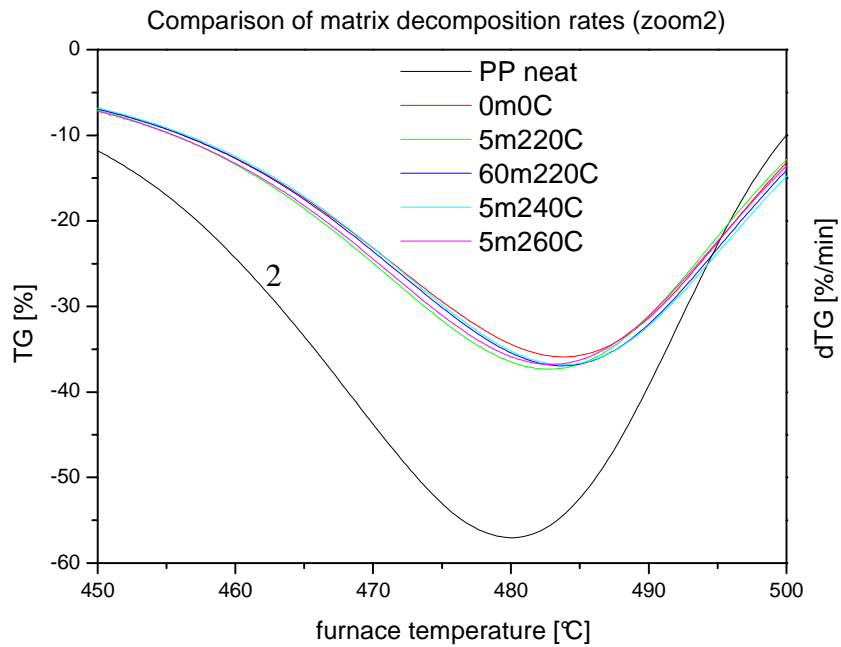
Figure 63 *Expanded curves of decomposition rates of matrix (zoom 2)*

Further, compared with the neat PP, the peak maximums of the decomposition rates of the blends are slightly shifted to higher temperatures.

13 SCANNING ELECTRON MICROSCOPY

On the scanning electron microscope, the surface area of broken samples from tensile test was investigated. This method was used to investigate adhesion (interaction) between particles and matrix.

In the following micrographs, there are five investigated blends.
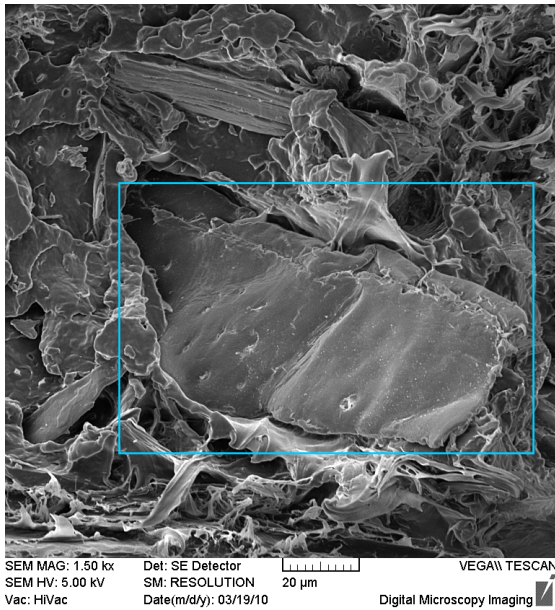
Figure 64 *Micrograph of 0m0C blend*
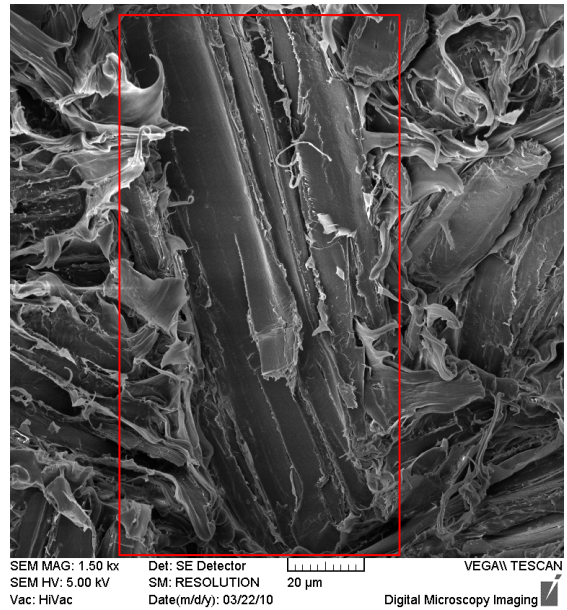
Figure 65 *Micrograph of 5m220C*
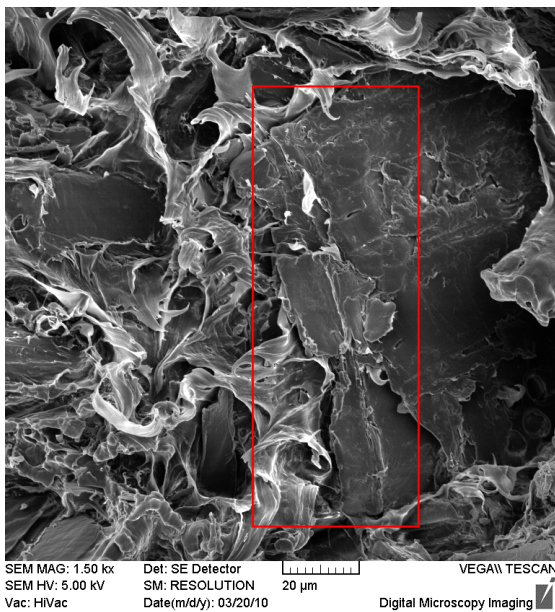
Figure 66 *Micrograph of 60m220C blend*
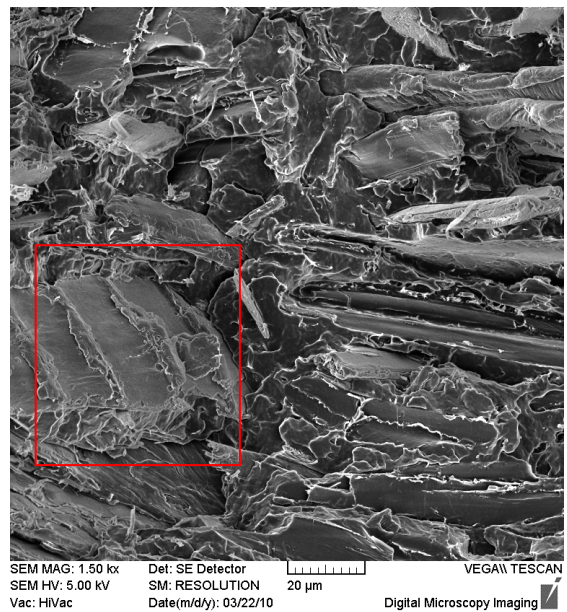
Figure 67 *Micrograph of 5m240C*
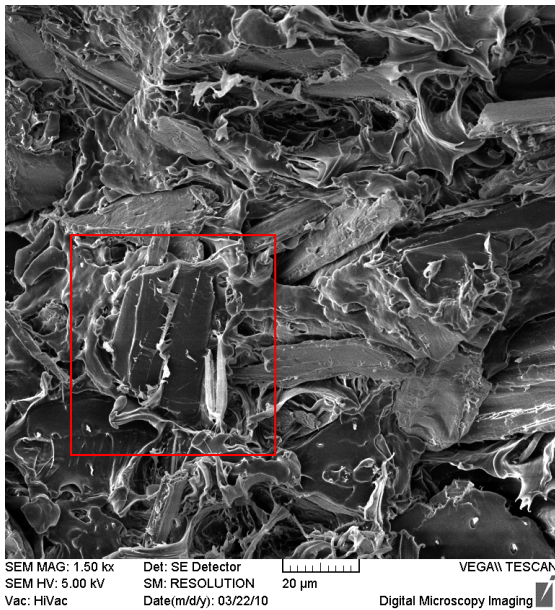
Figure 68 *Micrograph of 5m260C*

After Ichazo et al [2] with increasing interfacial interactions (adhesion), thickness of interface between polymer matrix and particles decreases. As can be seen in the figures above, this statement is not demonstrable in the cases of investigating blends in this work.

However, the adhesion between the matrix and the particles can be studied at the crack surface of the specimens broken within the tensile testing. Good adhesion should be demonstrated by the presence of the particles which are covered by plastic-deformed matrix.

As can be seen in the figure 64 (0m0C blend), there is a wood particle, which is completely smooth (blue frame). There are no parts of deformed matrix at the particle surface, therefore the adhesion is insignificant. On the other hand, as can be seen in the next figures, there are the wood particles or imprint of wood particles with low occurence of deformed matrix (red frames). It appears from this that the adhesion is better in the cases of filling with retified wood flour.

14 DYNAMIC MECHANICAL ANALYSIS

Dynamic mechanical analysis measures the mechanical properties of viscoelastic materials as a function of time, temperature and frequency. At this test, low extensions (deformations) were used for investigation of mechanical properties.

In the following figures, the dependence of the dynamic modulus (G*) on temperature is represented.
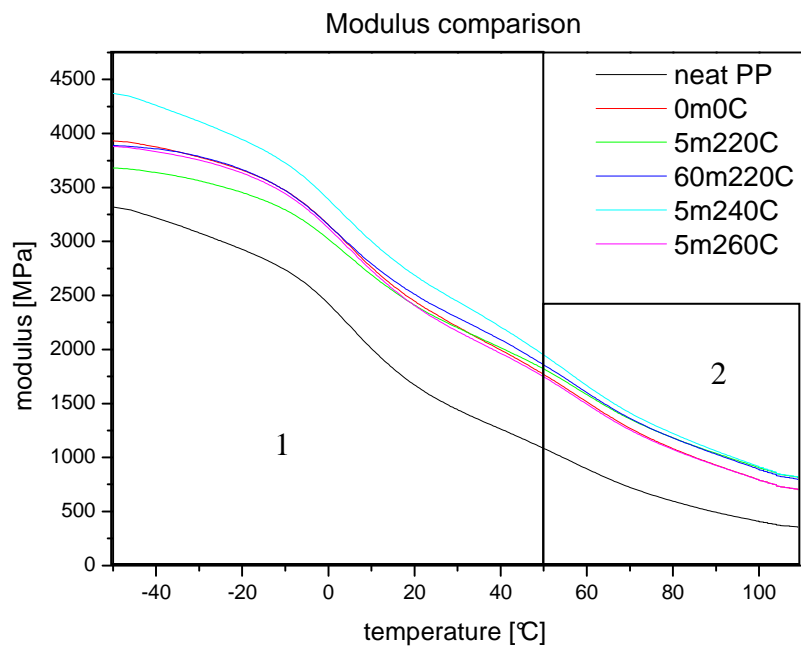
Figure 69 *Dependence of the dynamic modulus on the temperature*

For better illustration, the graph is divided in two areas, which are expanded in the following figures (70, 71). The first is marked by the number 1, the second by the number 2 (figure 69).
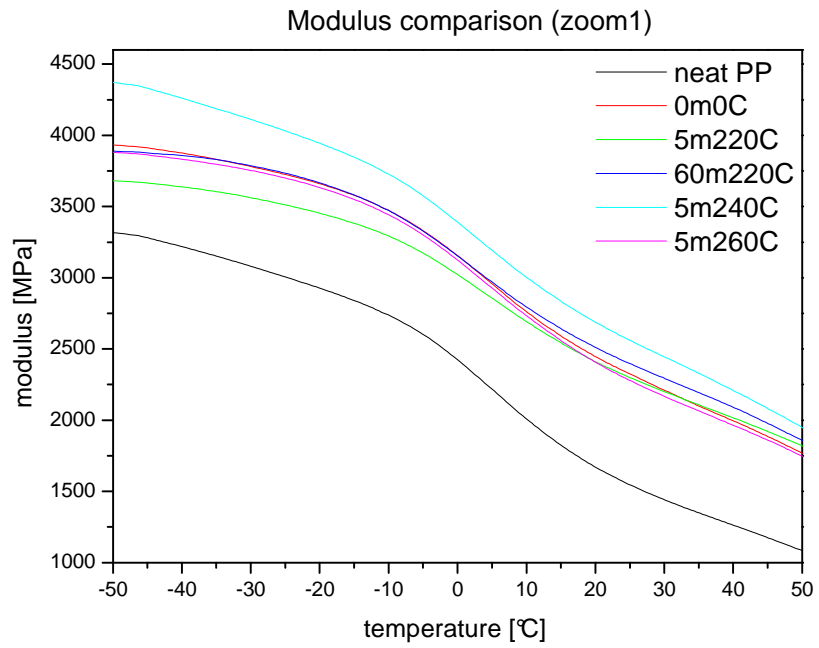
Figure 70 *Expanded area number 1 of dependence of modulus on the temperature*
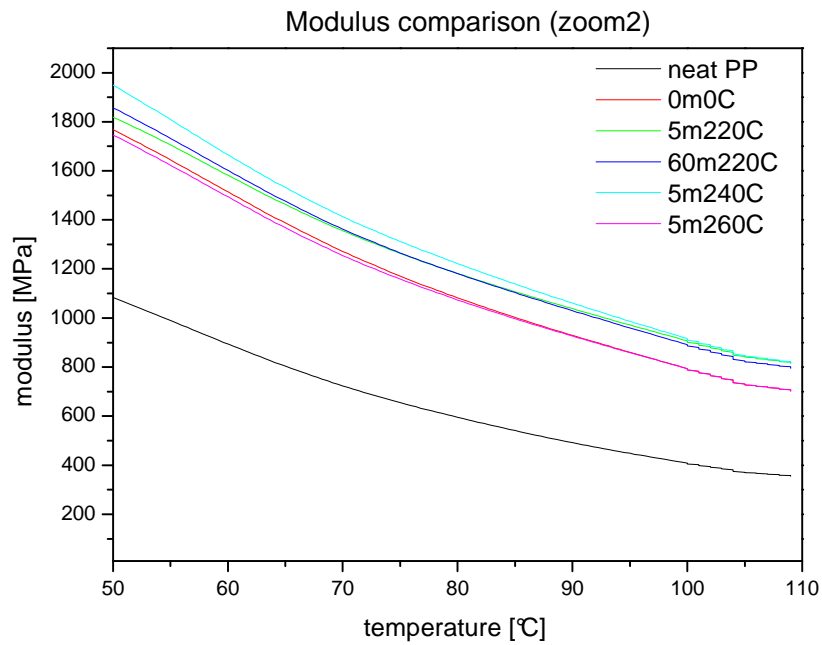
Figure 71 *Expanded area number 2 of the dependence of the modulus on the*

temperature

As can be seen in the figures above, with addition of the WF into PP the dynamic modulus increased. In detail, the highest modulus was measured in the case of 5m240C blend within the range of temperature. It is interesting to note that this blend possesses the highest crystallization temperature and also the highest crystallinity (see DSC and X-rays diffraction). In the first expanded area it can be seen that this blend is followed by 0m0C, 60m220C, 5m260C and last 5m220C, but the dynamic modulus of these blends changes with the increasing temperature (expanded area 2).

At the temperatures from -50 to almost 50 °C, the moduli of 0m0C, 60m220C, 5m260C and 5m220C have similar courses (expanded area 1). Then, at the temperatures from 50 to 110 °C they are divided into two pairs of blends (expanded area 2):

1. the pair formed by 5m220C and 60m220C blends;

2. the pair formed by 0m0C and 5m260C blends.

The moduli of the first pair are got closer to the modulus of 5m240C blend, especially at higher temperature from about 90 to 110 °C. The moduli of the second pair decreased. This blends behavior can be explained by the fact, that 5m220C and 60m220C blends have similar mechanical properties and the difference is caused by the time of retification process only. The 0m0C and 5m260C blends have also similar mechanical properties. Lower mechanical properties in the case of 5m260C blend could be caused by the highest temperature of retification process, when the wood could be slightly degraded.

In the following figures, the dependence of tan δ on temperature can be seen.
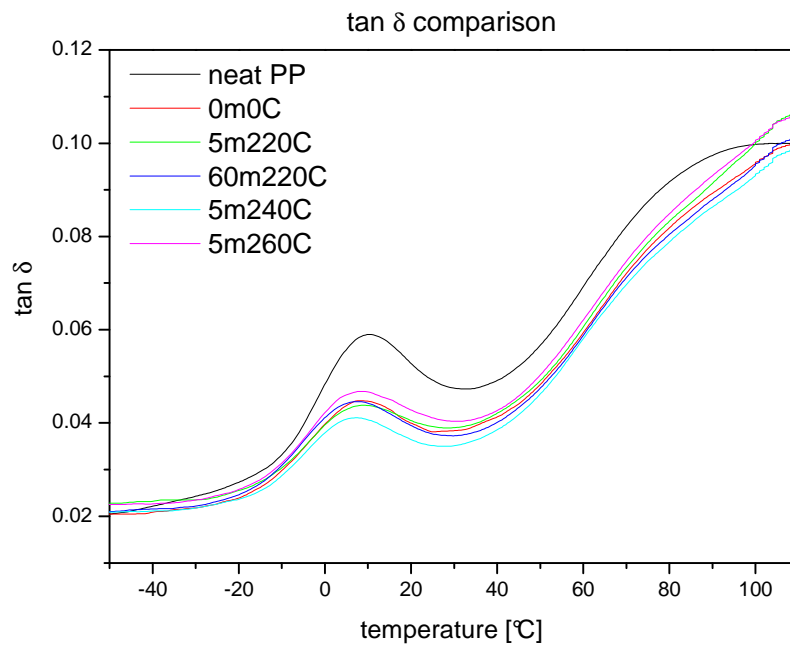
Figure 72 *Tan δ comparison of all blends*

As it was explained above, the maximums of peak represent the glass transition temperature (T_g). For better demonstration of results, the graph is expanded in the area of peaks and this area is represented in the following figure.
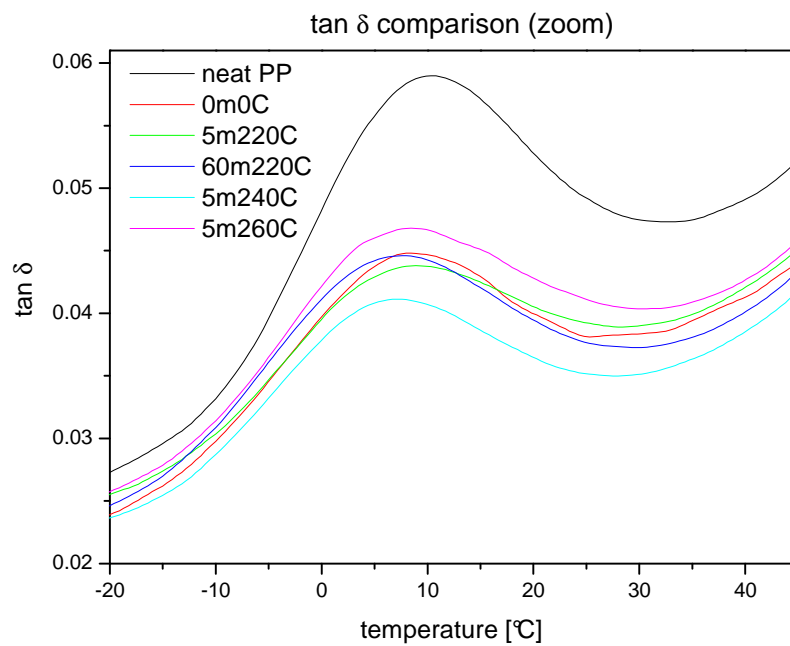
Figure 73 *Expanded area of peaks*

From the figure 73, it can be seen that the maximums of peaks are shifted lower from the maximum of the peak of the neat PP. It can be explained by the fact, that with addition of WF into PP, the glass transition temperature decreased. It is caused by the influence of the wood particles on the PP matrix properties. The influence on properties increases with better adhesion (interaction) between particles and matrix. This implies, that the 5m240C blend has the highest adhesion between the particles and the matrix, beacause the maximum of its peak (T_g) mostly differs from the maximum of neat PP. This is also confirmed by the highest crystallization temperature, the highest crystallinity measured by DSC and wide-angle X-ray diffraction and at least by the fact, that this blend has the highest dynamic modulus.

In the following table the glass transition temperature values of all samples are ordered:

sample	T_g (℃)
neat PP	11
0m0C	8
5m220C	10
60m220C	7
5m240C	6
5m260C	8

Table 8 *Glass transition temperature values of all samples*

The following figure 74 represents the differences of T_g between blends and PP neat. The figure 75 represents the crystallinity of all blends.
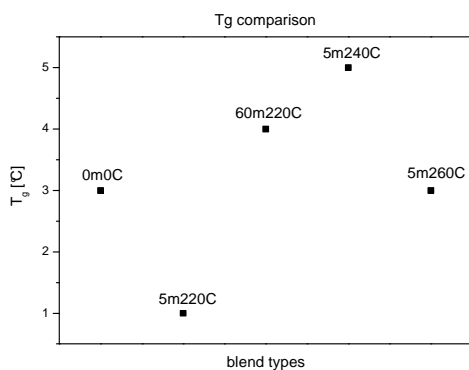
Figure 74 *Differences of T_g between blends and PP neat*
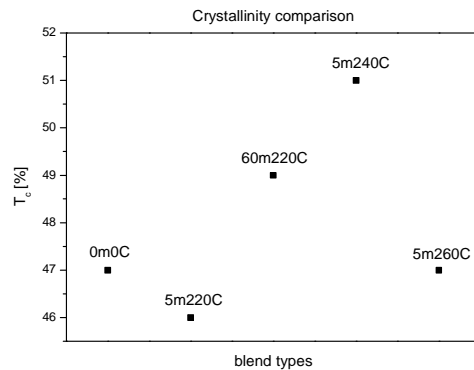
Figure 75 *Crystallinity of all blends*

From the figures above it can be seen that the 0m0C and 5m260C blends have the similar properties; as the glass transition temperature and the crystallinity. The 5m240C showed the largest difference from the T_g of neat PP; in connection with the results from all the measurements this blend can be pronounced to be the best in particle/matrix adhesion. The 5m220C blend presents the poor adhesion because of its low crystallinity and a small difference between T_g of this blend and neat PP. The difference between the mechanical behavior of 5m220C and 60m220C blends arises from the time of retification process.

CONCLUSION

This master thesis deals with the polypropylene wood flour composites. PP was filled by the same ratio of both and thermally treated wood flour. The properties of these five various blends and the neat PP were investigated by rheology, DSC, WAXD, tensile testing, TGA, SEM and DMA measurements.

Rheology measurements shows, that the 5m240C blend has the highest viscosity in whole range of measured shear rate. DSC demonstrated that the addition of wood flour into polypropylene causes increase of crystallization temperature; wood flour acts as a heterogeneous nucleation agent especially in the cases of blends with retified wood flour. The highest crystallization temperature occurs in the case of 5m240C blend. The melting temperature range between 161–164 °C and the highest temperature was measured in the case of 5m220C blend.

WAXD results indicate that filling polypropylene with wood flour causes the crystallinity increasing. The highest crystallinity was investigated in the case of 5m240C blend. Additionaly, in all PP/WF blends the β-form occurs.

Tensile tests show that the moduli of PP/WF blends are generally lower than in case of neat PP, except 5m220C and 60m220C blends. Further, with filling PP with wood flour, yield strain and elongation at break decrease. The tensile test is only informative, for better explication of results it could be used many other measurements.

From TGA results that 60m220C, 5m240C and 5m260C blends have better temperature stability than 0m0C and 5m220C, because of their higher temperature of wood flour treatment (retification).

SEM micrographs show, that there is a little improvement of adhesion in the cases of blends filled with retified wood flour.

From DMA, there are two main results. First one is, that at low deformations, blends have higher values of moduli than the neat PP. The highest modulus was measured in the case of 5m240C blend. Simultaneously, this blend has the best adhesion between particles and matrix because the glass transition temperature of this blend mostly differs from the neat PP.

From the results above it can be said that there are some differences between the PP filled with untreated and treated wood flour. In case of treated wood flour the adhesion is better, which is confirmed by higher crystallinity, higher crystallization temperatures, higher moduli at small deformations range and at least lower glass transition temperatures.

Generally, interfacial interactions are very weak in untreated wood flour filled composites, because of the differences in chemical nature. As a consequence adhesion must be improved practically always to achieve acceptable properties. The thermal treatment of wood flour increases the adhesion and can be rated as a suitable step for PP/WF composite preparation.

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LIST OF ABBREVIATIONS AND SYMBOLS

DMA   Dynamic mechanical analysis

DSC   Differential scanning calorimetry

EMSE   École Nationale Supérieure des Mines de Saint-Étienne

HDPE   High density polyethylene

HDT   Heat deflection temperature

LDPE   Low density polyethylene

MA   Maleic anhydride

MaPOs   Maleated coupling agents

MAPP   Maleic anhydride modified polypropylene

MOR   Modulus of rupture

NOW   New Option Wood

PMPPIC   Polymethy1ene polyphenylisocyanate

PP   Polypropylene

PS   Polystyrene

PVC   Polyvinylchloride

SEM   Scanning electron microscopy

Tc   Crystallization temperature

Tg   Glass transition temperature

TGA   Thermogravimetric analysis

Tm   Melting temperature

UV   Ultraviolet

WAXD   Wide angle X-ray diffraction

WF   Wood flour

WFs   Wood fibers

WPC   Wood plastic composites

Xc   Crystallinity

α   Monoclinic crystalline form

β   Trigonal crystalline form

γ   Orthorhombic crystalline form

θ   Angle of X-ray diffraction

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