Phase transformation in composites based on poly(1-butene) and natural fillers

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ABSTRAKT

Tato diplomová práce se zabývá vlivem přírodních plniv na transformaci poly(1-buten). Jako přírodní plnivo byla použita dřevní moučka. Nejvýznamnější vývoj v PB-1 je fázová transformace z Formy II do Formy I, jenž nastává po krystalizaci z taveniny obsahující PB-1 a dřevní moučku. Studium těchto přechodů bylo provedeno různými experimentálními technikami, jako je široko-úhlá rentgenografie a diferenciální skenovací kalorimetie. Studium krystalizace odhalilo zvýšení teploty krystalizace s rostoucím obsahem dřevní moučky, tuto teplotu také ovlivňovala velikost částic dřevní moučky. Rychlost fázové transformace z tetragonální na stabilní hexagonální formu byla větší, o čemž svědčí zkrácení doby transformace. Změny v kinetice krystalizace byly připisovány zvětšení nukleace poly(1-butene) v přítomnosti plniva. Molekulární změny těchto kompozitních materiálů byly sledovány za pomocí reologie.

Klíčová slova: izotaktický poly(1-buten), fázová transformace, dřevoplastové kompozity, DSC, WAXS, reologie

ABSTRACT

This masters thesis deal with influence natural fillers upon transformation in poly(1-butene), as a natural filler used wood flour. The most important evolution in PB-1 is a phase transformation from Form II to Form I after crystallization from melt containing PB-1 and the wood flour. Study of these transitions was carried out by different experimental techniques, such as Wide-Angle X-ray Diffraction (WAXS) and Differential Scanning Calorimetry (DSC). Crystallization of study revealed increase in crystallization temperature with increasing content of wood filler, temperature a was also influenced by the particle size of wood flour The rate of phase transformation from tetragonal to stable hexagonal form was enhanced as evidenced reduce the time transformation. The observed changes in the crystallization kinetics were ascribed to the enhanced nucleation of PB-1 in the pres ence of wood filler. Molecular changes these composites were monitored by Rheology.

Keywords: isotactic poly(1-butene), phase transformation, Wood Plastic Composites, DSC, WAXS, rheology

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INTRODUCTION

Plastic composites reinforced with wood fillers (WF) are a group of new materials made from a combination of wood fillers and thermoplastic resins. WF reinforced composites are becoming increasingly popular in the furniture, automotive, and building industries. However, thermoplastic users are still seeking new ways to improve product performance. Wood fillers are advantageous because they are inexpensive, renewable, lighter, and less abrasive to processing equipment compared with inorganic fillers. In addition to the processing and physical properties, the long-term behaviour of these materials is a very important parameter, especially with respect to the design layout and the product liability.

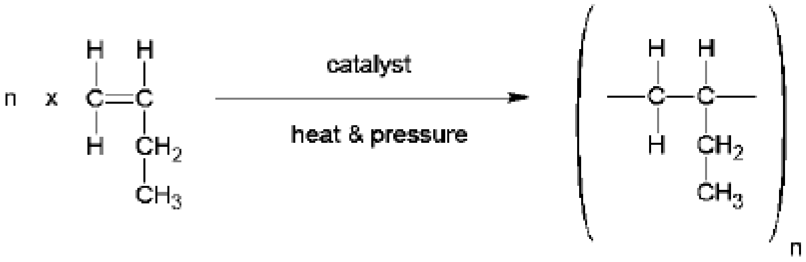
Poly(1-butene) was used in this experiment because phase transformation is very interesting and it is also very important property. Moreover, it is widely used and investigated at the Department of Polymer Engineering, Tomas Bata University in Zlin.

A general goal of this work was to create the blends of Poly(1-butene) and wood fillers and to study the phase transformation in composites based on poly(1-butene) and natural fillers. Phase transformation was studied by WAXS, DSC. Rheology was studied only in samples PB-1+wood [pine-untreated], because this measurement was carried out on stay in Laboratoire de Photochimie Moléculaire et Macromoléculaire, Université Blaise Pascal, Clermont- Ferrand.

I. BIBLIOGRAPHIC STUDY

1 ISOTACTIC POLY (1-BUTENE)

Poly (1-butene) is obtained by polymerization of but-1-ene, with stereo-specific Ziegler-Natta catalyst to create a high molecular, isotactic, semi-crystalline polymer [1].



But-1- ene Poly (1-butene)

Fig. 1 Synthesis of Poly (1-butene) by polymerization of butene-1-ene

Isotactic poly(1-butene) (PB-1) is a thermoplastic polyolefin with outstanding mechanical properties, like high creep resistance, low stiffness, good impact behaviour, and excellent elastic recovery. In addition, PB-1 is a resistant to a high number of chemicals and is very insensitive to environmental stress cracking in a wide melt flow ranges. Despite the excellent properties, applications of PB-1 are limited compared to those of the lighter polyolefins like polyethylene and polypropylene, mainly due to the slightly higher cost of the raw and due to the dimensional changes arising from crystal structure transformation, which complicates the production of goods with stable mechanical properties.

Isotactic PB-1 has a very complex polymorphic behaviour, since it can crystallize into various crystalline forms, depending on the preparation conditions [2].

1.1 Properties of PB-1

PB-1 displays excellent resistance to creep, abrasion, chemicals and environmental stress cracking –properties. In addition, the polymer has low stiffness, resists impact well (even at relatively low temperatures) and has excellent elastic recovery.

The crystalline fraction of a semi-crystalline polymer influences certain characteristics. Generally, increasing crystallinity raises stiffness, hardness, density, creep resistance, temperature resistance, abrasion resistance and lowers swelling by chemicals. The amorphous part determines characteristics like tensile and impact strength, crack propagation, and stress cracking resistance [3].

PB-1 displays excellent creep resistance. It does not require additional cross-linking or any other modification. Upon solidification from the molten state PB-1 creates a durable network of entangled molecules between the crystalline domains. The PB-1 crystallites act as fixed multi-functional cross-links that are supported by entanglements where extensive slipping is prevented by the ethyl side groups of the polymers.

The very high molecular weight (Mw = ca. 500.000) and the relatively long ethyl side groups of the polymer chains provide what are effectively very strong cross-links and a high number of tie molecules which help to maintain the network also at high temperatures close to the melting point of PB-1 [4].

1.2 Transformation of PB-1

Isotactic poly(1-butene) crystallizes into several crystal modifications differing in their helical conformation and chain packing [5-13]. One of the most important aspects of the polymorphic behavior of this polymer is the slow spontaneous transformation, from the tetragonal form II to the twinned hexagonal form I, that characterizes melt-crystallized samples and has a very strong impact on materials properties. Form II, in which chains in a 11_3 helix conformation are packed in the low-density tetragonal unit cell is the kinetically favored modification commonly obtained by melt crystallization in quiescent conditions at atmospheric pressure. At room temperature, this metastable modification slowly transforms into the most stable modification, form I, which is characterized by a 3_1 helix conformation [6, 7, 13]. The II - I transformation is accompanied by a considerable structural change which results in an extension of the chain conformation in crystalline strands of around 14 % and a decrease in the cross section of around 10 %. Form I exhibits higher density, melting temperature, melting enthalpy, and stiffness than Form II [7, 13-16].

It is well established that the transition from the tetragonal to the hexagonal phase is irreversible and that the initial crystal modification II can only be obtained by remelting the sample (monotropic polymorphism). The polymorphic transformation occurs over a wide temperature range, from Tg (-25 °C) up to 100 °C [8, 13], with a maximum rate at around 20 °C [9,13,17], at this temperature, completion of the transformation requires several days [8,9,15,18,19]. Despite the rewarding physical and mechanical properties of poly(1-butene), the slow transformation kinetics is the main reason that has so far restricted its commercial development.

2 WOOD

Wood, a renewable resource and naturally occurring material abundantly available has a wide range of applications as construction material, pulp, paper, fireboard products as well as source of energy and as raw materials for various industrially important chemicals. Two types of woods viz. hard and soft, are available. Softwood trees are lacking in strength, dimensional stability etc which restrict their uses. The softwood trees are generally used for fuel purposes. These softwoods can be converted into value added primary wood suitable for furniture, office equipment etc through impregnation with polymer in the capillaries, cavities, and void spaces of the wood cell [20].

2.1 Chemical composition

Dry wood is primarily composed of cellulose, lignin, hemicelluloses, and minor amounts (5% to 10%) of extraneous materials. Cellulose, the major component, constitutes approximately 50 % of wood substance by weight. It is a high-molecular-weight linear polymer consisting of chains of 1 to more than 4 b-linked glucose monomers. During growth of the tree, the cellulose molecules are arranged into ordered strands called fibrils, which in turn are organized into the larger structural elements that make up the cell wall of wood fibers. Most of the cell wall cellulose is crystalline.

Lignin constitutes 23 % to 33 % of the wood substance in softwoods and 16 % to 25 % in hardwoods. Although lignin occurs in wood throughout the cell wall, it is concentrated toward the outside of the cells and between cells. Lignin is often called the cementing agent that binds individual cells together. Lignin is a three-dimensional phenylpropanol polymer.

The hemicelluloses are associated with cellulose and are branched, low-molecular-weight polymers composed of several different kinds of pentose and hexose sugar monomers. The relative amounts of these sugars vary markedly with species [21].

Fig. 2 Scheme of structure wood

2.2 Wood for WPC

The chemical constituents of wood are cellulose, hemicellulose, lignin and a variety of low molecular weight waxes, tannins and rosins [22,23]. The cellulose constituent forms microfibrils that determine the level of reinforcement possible from the wood. The fiber lengths vary depending on the type of wood. Generally, deciduous wood fiber lengths are typically 1-1.5 mm and coniferous fibers are 3-3.5 mm. The commercially available sources of wood are sawdust, wood flour, wood fiber, and cellulose. Wood fiber can be obtained by chemical treatment of the wood (Kraft Process, which removes the lignin and low molecular weight waxes) or by thermo-mechanical wood treatment processes, which conserve the lignin and wax content. Recycled pulp fiber separation is achieved by mechanical agitation in water [22].

In mechanical pulping, the fibers are obtained from ground wood or small chips. The fibers separate as the heat softens the lignin and any remaining pulp is removed using screens [24].

Wood fiber has a length to diameter ratio of between 10:1 and 20:1. Fine mesh flour adds stiffness but reduces impact strength. Longer wood fibers contribute to strength but are more difficult to bind with the polymer. The properties of the wood plastic composite are dependent partly on the particle size of the wood. On increasing the particle size, an improvement in flow and flexural modulus is seen, however it may be more difficult to ensure that a homogenous blend is produced. The physical properties of the wood fiber vary depending on the kind of wood used. It is clear; therefore, that the choice of wood is important to the final properties of the WPC, for example the density of hardwoods can be almost twice that of softwoods so will result in a heavier product. Some wood fibers are more durable than others depending on the environmental conditions (wet, dry or alternating wet and dry) so the end application will have an influence on the type of wood fiber / flour selected. Also, the modulus is generally higher for hardwoods resulting in a stiffer WPC product [25].

Some of the most common sources:

- **Primary wood wastes**: these are post-industrial wood wastes from sawmills
- **Secondary wood wastes**: these are post-industrial wood wastes generated when wooden products, such as furniture, cabinets and doors are made

- **Post-consumer wood wastes**: this can include anything from construction and demolition debris to packaging, crates and pallets [26].

2.3 Effects of fiber characteristics on properties of wood plastic composites

[27] Properties vary significantly with fiber origin. Higher fiber size produces higher strength and elasticity but lower energy to break and elongation. The effect of fiber size on water uptake is minimal. Increasing fiber load improves the strength and stiffness of the composite but decreases elongation and energy to break. Water uptake increases with increasing fiber content.

Different wood species have different anatomical structures. These structural differences govern the use of these materials in WPC. For example, fibre dimensions, strength, variability, and structure are important considerations [28]. Melt flow index, heat deflection temperature, notched impact energy, flexural, tensile modulus, strength, torque and viscosity increase with increasing particle size.

Mechanical properties of the resultant WPC increase only at low weight percentages of wood filler. Tensile and flexural strengths reach a maximum at 15 wt% and 35 wt% wood particle contents, respectively, and gradually decrease with a further increase in wood particle content. Large wood content, considerable particle aggregation takes place, leading to lower strength due to the filler’s failure to sustain the stress transferred from the polymer to the matrix [27]

3 WOOD PLASTIC COMPOSITES

Traditionally, inorganic fillers such as fiberglass, calcium carbonate, and talc have been added to plastics to improve their performance or to reduce cost. More recently, wood flour has been added to plastic, leading to the development of Wood–Plastic Composites (WPC). Wood flour fillers are advantageous because they are inexpensive, renewable, lighter, and less abrasive to processing equipment compared with inorganic fillers. Wood filler in plastics is nothing new. Rolls-Royce used a gear lever knob made of wood filled plastic as long ago as 1916, less than a decade after the patenting of the first completely synthetic resins. But in the last 30 years, much better materials have been developed. They have higher wood contents, better interface properties, improved processing technologies and effective additives [29].

3.1 History

WPC was born as a modern concept in Italy in the 1970s, and popularized in North America in the early 1990s. By the start of the 21st century it was spreading to India, Singapore, Malaysia, Japan and China [30]. WPC may be one of the most dynamic sectors of today’s plastic industry with an average annual growth rate of approximately 18 % in Northern America and 14 % in Europe [31]. It has been reported that 460 million pounds of WPC were produced in 1999. Statistics show that the production of these composites in 2001 has increased to 700 million pounds [32].

Fig. 3. Compounded pellets (bottom) made from wood (upper right) and plastic (upper left).

3.2 Manufacture of WPC

The ability of thermoplastics to melt and re-harden has been exploited in many different processing methods. The most commonly used methods to produce plastics and wood-fiber filled plastic parts are extrusion and injection molding (IM) [32–34]. The extrusion process produces continuous linear profiles by forcing a melted thermoplastic through a die. The IM process produces three-dimensional items with minimal post-manufacturing stages. Although different, both processes follow the same basic steps: melting, shaping, and cooling [35]. Both processes also use screws to convey, pump, and blend the heterogeneous components [33]. Michaeli and Menges compared extrusion and IM using defined process parameters such as residence time, temperature, pressure; shear rate, shear stress, and cooling rate. Regardless of the processing data used, pressure and shearing in IM are significantly higher than in extrusion. Conditions that vary with processing method result in different final plastic product properties. Other investigators [35] found highly oriented layers in IM inorganic short fiber-reinforced thermoplastics. When forming, these layers align fibers with a specific orientation: in outer layers, fibers are oriented in the main flow direction, while in the core layer they are oriented perpendicular to flow. With extrusion, however, structural parameters such as orientation and boundary layers are less distinct.

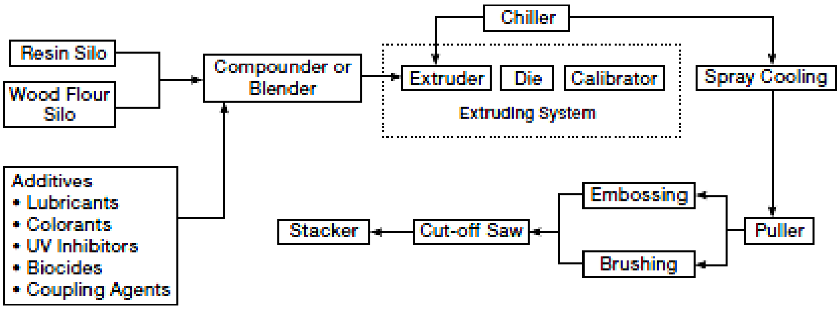


Fig. 4 The WPC manufacturing process, with extrusion forming [36]

3.2.1 Compounding

Melt blending wood and thermoplastics usually requires an input of physical energy, via high shear forces, for the polymer to melt (Morton-Jones 1989). Compounding is generally performed in melt blending equipment where sufficient heat will melt or soften the plastic, and allow for more dispersive mixing (Park and Balatinecz, 1997). Terms such as compounding, mixing, kneading and shearing are all used to describe the blending procedure based upon the specific equipment used. Wood flour is used extern sively because of availability, cost and ease of dispersion into the matrix. Fillers and larger particles require longer and higher intensity mixing to disperse the fibres (Pabediskas et. al. 1993). The methods in which the components of a thermoplastic composite are mixed vary depending upon the type of manufacturing process. Twin-screw extruders provide mixing capabilities during extruding or injection moulding process [37].

Once the materials are sufficiently mixed, the composite can then be formed into the final shape using forming technologies such as extrusion or injection moulding [38]

3.2.2 Forming

Most WPC are manufactured using profile extrusion, which creates long continuous elements, such as deck boards and window components. The wood-thermoplastic mixture (in pellet form) is conveyed into a hopper that feeds the extruder. As the material enters the first zone of the extruder, the heated screws and barrel melt or soften the thermoplastic. The molten material is then forced through a die to make a continuous profile of the desired shape. Molten WPC material is highly viscous, so the equipment needs to be powerful enough to force the material though the machinery and out of the die. As the material exits the extruder, it is cooled in a water spray chamber or bath to rapidly harden the thermoplastic matrix, embossed with a desired pattern, and cut to a final length. Extruders can have single screw or twin feed screws, which are counter- or co-rotating. These screws can be parallel, for mixing only, or conical, to increase pressure in the die to aid in consolidation.

Tandem extruders have one component for the compounding step and one for the shaping process. While extrusion methods create lineal elements, injection molding produces three-dimensional parts and components. The unique shapes and profiles that can be created with injection molding provide the potential for diversifying from the current WPC markets. The injection molding process involves two steps. The first is to melt-blend or compound the wood-plastic mixture, and the second is to force the molten WPC into a mold under high pressure. The molten material fills the cavity in the mold and solidifies as it is cooled. Injection molding is used to manufacture a variety of parts, from small components to large objects. Injection molding is a common method of production and is especially useful for making irregularly shaped pieces [39].

Fig. 5 An injection molder [40]

3.2.3 Additives

Additives are also often used in WPC. Additives are materials that are added in small amounts to enhance properties. For example, lubricants improve surface appearance and processing; coupling agents improve adhesion between the wood and plastic components. Other possible additives include colorants, light stabilizers, foaming agents, and thermosetting resins.

While the bulk of a WPC is wood fillers and thermoplastic polymer, a variety of materials are added in relatively small quantities. These additives are included for a variety of reasons.

- ***Lubricants*** help the molten WPC mixture move through the processing equipment
- ***Coupling agents*** improve the wood and polymer interaction. Wood is naturally hydrophilic (attracts water), while the thermoplastic polymers are hydrophobic (repel water). This basic chemical incompatibility makes it very difficult to bond polymers to wood. The use of coupling agents can help to overcome this incompatibility.
- ***Biocides*** can be added to protect the wood component of WPC from fungal and insect attack. Zinc borate is the most commonly used wood preservative added to

WPC. Fire-retardant chemicals reduce the tendency of the WPC to burn. UV stabilizers help protect the plastics from degrading in the sun.

- ***Pigments*** are added to provide a desired color to the product. UV stabilizers can help to protect the color, but some fading and whitening will occur with most WPC exposed to sunlight [41].

3.3 Properties of WPC

Some of the major advantages of WPC include their resistance against biological deterioration for outdoor applications where untreated timber products are not suitable.

There are several ways to improve overall properties of WPC, namely using right size of raw material, optimum mixture and preparation of the elements in the product, and adding small amounts of additives such as coupling agents, pigments, antimicrobials or light stabilizers during their production [42, 43,44].

Most of the physical and mechanical properties WPC depend on mainly on the interaction developed between wood and the thermoplastic 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 plastic allowing the formation of single-phase composite. Wood-Plastic Composites also have problems when they are exposed to UV rays, their natural wood or pigmented colour may tend to fade away. Therefore, depending on the final application, UV filters have to be added to stabilize their colours for a longer time.

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 [44].

3.3.1 Advantages

WPC are composite materials and have properties of both materials. They have stiffness and strength between those for plastic or wood, but the density is generally higher than either. The properties of WPC come directly from their structure: they are intimate mixes of wood particles and plastic. The plastic effectively coats the wood particle as a thin layer. The structure is shown at left. The high moisture resistance of WPC (water absorption of

0.7 % compared to 17.2 % for pine) is a direct result of the structure. Moisture can only be absorbed into the exposed sections of wood and is not transmitted across the plastic boundaries. The result is that WPC are extremely moisture resistant, have little thickness swell in water and do not suffer from fungal or insect attack. The properties of WPC can be tailored to meet the product requirements by varying the type of wood or the type of plastic. Pigments, UV stabilisers and fire retardants can all be added to the WPC raw material before extrusion to improve specific properties. WPC have: good stiffness and impact resistance, dimensional stability, resistance to rot, excellent thermal properties, low moisture absorption [45].

3.3.2 Disadvantages

The wood component within WPC does impart some positive attributes compared to plastic; however, the inherent problems with wood (moisture sorption and susceptibility to mold and decay) remain. Water can penetrate into WPC, albeit at a much lower rate and level compared to solid wood or other wood composites. Colour fade from sunlight is also accelerated when wood is added to thermoplastics, causing whitening or greying of the surface of the composite. WPC are also usually quite heavy and not as stiff as solid wood. This limits the potential use of WPC in many structural applications and creates the potential creep or sagging problems, especially in a warm environment. WPC is theoretically recyclable; it could be re-melted and reformed into new decking lumber. However, collection, cleaning and transportation of old WPC to a recycling centre for remanufacture are likely to be prohibitively expensive [46].

II. EXPERIMENTAL PART

4 MATERIALS AND EXPERIMENTAL TECHNIQUES

The aim was to prepare samples poly(1-butene) and wood filler with particles of different size and to investigate their phase transformation

4.1 Materials and sample preparation

Isotactic poly (1-butene) (PB-1) was provided by LyondellBasell. Polybutene-1 grade PB 0110M is a semi-crystalline homopolymer, which is used where creep, environmental stress crack resistance and elevated temperature performance are key requirements. Its relatively slow kinetics of crystallization allow for an excellent wetting behaviour. Its highly shear-sensitive flow behaviour means that it remains easily dispersible also in even more incompatible polymers like thermoplastic elastomers [47].

Technical data	
Density	0.914 g/cm^3
Melt flow rate (MFR)	0.4 g/10 min (190 °C/2.16kg)
Melt flow rate (MFR)	12 g/10min (190 °C/10kg)
Flexural modulus	450 MPa
Melting temperature	117 °C
Tensile Strength at Yield	19.5 MPa
Tensile Strength at Break	35 MPa
Tensile Elongation at Break	300 %

Table 1 Used material of PB 0110M [48]

4.1.1 Preparation of samples

Melt mixing was carried out in Haake MiniLab II MicroCompounder batch mixer of 7 cm^3 capacity at 111 rpm for 7 min at 190 °C. Six different blends were prepared containing 5, 10, 15, 20, 30, 50 wt% PB 0110M and the wood filler (Pine- untreated).

	Blend [UNF]	Plastic content [%]	Plastic type	Wood species	Wood content [%]	Compounding method
1.	Reference	100	PB 0110M	Pine- Sylvestre (natural)	0	Extrusion compounding
2.	PB1+5%WF	95			5	
3.	PB1+10%WF	90			10	
4.	PB1+15%WF	85			15	
5.	PB1+20%WF	80			20	
6.	PB1+30%WF	70			30	
7.	PB1+50%WF	50			50	

Table 2 Preparation of blends from wood [pine-untreated] and PB-1

Next samples were carried out in Haake MiniLab MicroCompounder batch mixer of 7 cm^3 capacity at 60 rpm for 4 min. at 160 °C. Six different blends were prepared containing 5, 10, 15, 20, 30, 50 wt% PB 0110M and the wood filler (Pine) Wood particles were dried in an oven before they were mixed with poly(1-butene).Wood was dried at 95 °C for 60 min.

	Blend [UNFN]	Plastic content [%]	Plastic type	Wood species	Wood content [%]	Compounding method
1.	Reference	100	PB 0110M	Pine- Sylvestre (natural) [**dried**]	0	Extrusion compounding
2.	PB1+5%WF	95			5	
3.	PB1+10%WF	90			10	
4.	PB1+15%WF	85			15	
5.	PB1+20%WF	80			20	
6.	PB1+30%WF	70			30	
7.	PB1+50%WF	50			50	

Table 3 Preparation of blends from wood [pine-dried] and PB-1

Others samples were prepared under the same conditions as the previous blends, but with other wood. Wood was a mixture of oak and ash and was separated by using separation machine. Particle about size of ***316 µm*** and ***50 µm*** were used for sample preparation.

	Blend	Plastic content [%]	Plastic type	Wood species	Wood content [%]	Compounding method
1.	PB1+10%WF	90	PB 0110M	Mixture of oak and ash **316 µm** [dried]	10	Extrusion compounding
2.	PB1+20%WF	80			20	
3.	PB1+30%WF	70			30	
4.	PB1+40%WF	60			40	

Table 4 Preparation of blends from dried wood about size particles **316 µm** and PB-1

	Blend	Plastic content [%]	Plastic type	Wood species	Wood content [%]	Compounding method
1.	PB1+10%WF	90	PB 0110M	Mixture of oak and ash **50 µm** [dried]	10	Extrusion compounding
2.	PB1+20%WF	80			20	
3.	PB1+30%WF	70			30	
4.	PB1+40%WF	60			40	

Table 5 Preparation of blends from dried wood about size particles **50 µm** and PB-1

4.2 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) measures the temperature and heat flows associated with transitions in materials as a function of time and temperature in controlled atmosphere [49].

Differential Scanning Calorimetry is a technique for measuring the necessary establish a zero temperature difference between a substance and an inert reference material, as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate.

This is type In-heat flux DSC, the sample and reference are connected by a low-resistance heat-flow path (metal disk). The assembly is enclosed in a single furnace. Enthalpy or heat capacity changes in the sample cause a difference in its temperature relative to the reference; the resulting heat flow is small compared with that in differential thermal analysis (DTA) because sample and reference ate in good thermal contact. The temperature difference is recorded and related to enthalpy change in the sample using calibration experiments [50].

4.2.1 Sample preparation

The success of the DSC experiments depends on the careful preparation of samples and the judicious selection of the appropriate experimental conditions (such as scanning rate and sample size). DSC samples are analysed in small metal pans, designed of optimal thermal conductivity and minimum reaction with the samples (for example aluminium), which are supplied by the instrument manufactured. Pans may be open, pin-hole, covered or sealed and are used in combination with reference pan of identical material. The samples with the weight about 5-10 mg were used.

4.2.2 Calibration

Other important instrument settings include the calibration parameters and purge gas conditions (such as flow rate and gas type). At the very start and end of each heating or cooling scan most instruments will not achieve perfect temperature control and this results in the so called ‘start-up loop’ phenomenon. To be sure of accurately observing a transition, it is recommended to program the instrument to start at least 30 °C below and to end at least 10 °C above the temperature of interest. This should ensure that the instrument has a steady baseline before and after any recorded transition. Most commercial DSC instruments cannot heat or cool accurately at rates in excess of 40 $°\mathrm{Cmin}^{-1}$, and in many cases 30 $\mathrm{K\ min}^{-1}$ is the practical maximum scan rate. Slow scan rates (< 1 $°\mathrm{Cmin}^{-1}$) may also be possible with certain instruments. Measurements under isothermal conditions are practical with most modern DSC instruments, although temperature control is not as good (typically ± 0.3 °C) as for other types of isothermal calorimeters [52].

4.3 Wide-Angle X-ray Scattering (WAXS)

Wide angle X-ray scattering is an X-ray diffraction technique that is often used to determine the crystalline structure of polymers.

The one-dimensional (1D) crystallinity index of the fibers was determined by taking the one-dimensional WAXS profiles from the 1D wire detector and, after all corrections have been made (beam intensity, collection time, subtraction of air background), curve fitting the intensity vs. 2θ (scattering angle) plot using a peak deconvolution package. Since the amorphous and crystalline peaks overlapped in the equatorial (or meridional) slice, it was necessary to find the peak parameters of the amorphous peak independently. The peak parameters of the amorphous peak for the on-line patterns were determined by the fitting of the one-dimensional equatorial slice of a two-dimensional WAXS pattern taken at a distance very close to the spinneret where crystallization had yet to begin. The amorphous peak was taken to be a single Gaussian peak based on experimental observations. The center position and full width at half-maximum (FWHM) f the amorphous peak from this fit were used in all subsequent fits for the on-line patterns where crystallization had taken place. For these on-line crystalline patterns, a peak representing the amorphous contribution was inserted with the above parameters, and its height was adjusted so that the tails of the amorphous peak fit very well with the experimental data. It is assumed that any scattering in these regions is only from the amorphous phase. As this time, various crystalline peaks were inserted, and their peak parameters (position, height, FWHM) were iterated to achieve a good fit with the experimental data. For the on/line study, these crystalline peaks were fitted with Lorentzian peaks, which fit the peaks most accurately. After fitting the pattern with an amorphous and several crystalline peaks, the 1D crystallinity index was determined as follows:

$$\chi_C = \frac{\sum A_C}{\sum (A_c + A_A)}$$

where A_C is the integrated area under neat the crystalline peaks and A_A is the integrated area of the amorphous peak of the one-dimensional slice. The upper range of the integration was approximately 40° 2θ. This 1D crystallinity index can be used to compare samples within the experiment for qualitative trends but should not be considered the absolute crystallinity of the sample. These results were compared with the two-dimensional (2D) crystallinity index as calculated by applying eq 1 to a radial integration of the WAXS profiles at a series of equispaced azimuthal angles from imaging plate after all corrections have been made [52].

The Philips X'Pert Pro 1 X-ray diffractometer is device to characterize crystalline materials. It is capable of performing various types of measurements and analyses. The diffractometer has a stationary, centrally placed, X-ray tube with (para focusing) line focus and (parallel beam) point focus employing two goniometers for each type of focus. The line focus is mainly used for general diffraction work and phase analysis. Furthermore, it is used for determination of stresses in (sub) surface layers and line profile analysis. The point focus is mainly used for texture measurements. All measurements are done at room temperature. An oven is available to perform measurements at elevated temperatures under gas protection if required [53].

Fig. 6 Philips X´Pert Pro 1 X-ray Diffracometer

A PEAKFIT v4 was used for the evaluation of crystalline part in the specimens. It is suggested to follow the disappearing of the peak at 11.8° 2θ (reflection plane 200) the form II rather than increase the peak at 9.9° 2θ (reflection plane 110) of the form I because, together with the phase transformation, a post crystallization phenomenon takes place during which part of the amorphous polymer crystallizes into the form I [54]. However, in this work, it was not possible to measure the identical specimen but a series of specimens prepared under controlled conditions. It was decided to follow evolution of the both peaks of forms I and II (at 9.9° and 10.8° 2θ) and calculate the ratio of heights both peaks and content of the form I from the total sum of both heights. The same approach has been used in several works by Azzuri et al. [55], Samon et al. [56] and Natta et al. [57]. The similar approach was used in work of Kaszonyiova et al. [58] or in case of isotactic polypropylene, which is also a polymorphic material [59,60].

4.4 Rheology

Rheology is the science of deformation and flow of materials. The Society of Rheology's Greek motto "*Panta Rei*" translates as "All things flow." Actually, all materials do flow, given sufficient time. What makes polymeric materials interesting in this context is the fact that their time constants for flow are of the same order of magnitude as their processing times for extrusion, injection molding and blow molding. In very short processing times, the polymer may behave as a solid, while in long processing times the material may behave as a fluid. This dual nature (fluid-solid) is referred to as viscoelastic behavior.

Hooke’s law describes the behavior of an ideal pure elastic solid:

$$\sigma = E.\varepsilon$$

where applied stress (σ) and induced strain (ε) are related by a unique modulus value E

The shear modulus (resulting from changing strain) is the ratio of the shear stress to the shear strain. It follows from the complex relationship similar the above that:

$$G^*(\omega) = \frac{\sigma^*}{\gamma^*} = G'(\omega) + iG''(\omega)$$

where G* is the complex shear modulus, G' is the in-phase storage modulus or elastic modulus. The imaginary component G" is the out-of-phase similarly-directed loss modulus; $G^* = \sqrt{(G'^2 + G''^2)}$. The frequency where these parameters cross over corresponds to a relaxation time (T) specific for the material.

It follows that:

$$\tan(\delta) = \frac{G''}{G'}$$

where tangent of the phase angle (tanδ) describes the balance between energy loss and storage in melt

As tan(45°)=1, a value for tan(δ) greater than unity indicates more „liquid“ properties, whereas one lower than unity means more „solid“ properties, regardless of the viscosity.

Dynamic viscosity (η^*) is related to the complex modulus by:

$$\eta^* = \frac{G^*(\omega)}{i\omega} = \eta'(\omega) - i\eta''(\omega)$$

where $\eta' = G''(\omega)/\omega$ and $\eta'' = G'(\omega)/\omega$. Then, the real component of the complex viscosity (η') describes the viscous dissipation in the sample, while the imaginary component (η'') represents the stored elastic energy.

4.4.1 Cole-Cole representation

An empirical rheological model used to fit dynamic data is the Cole-Cole distribution expressed by:

$$\eta^* = \frac{\eta_0}{1 + (i\omega\lambda_0)^{1-h}}$$

where λ_0 is the average relaxation time and h the parameter of the relaxation-time distribution. In the complex plane this model predicts the variation of the viscosity components (η'' versus η') to be an arc of circle (Figure 9). From this representation it is easy to determine the parameters of the distribution: η_0 is obtained through the extrapolation of the arc of the circle on the real axis and the distribution parameter h through the measurement of the angle $\Phi = h\pi/2$ between the real axis and the radius going from the origin of the axis to the centre of the arc of the circle.

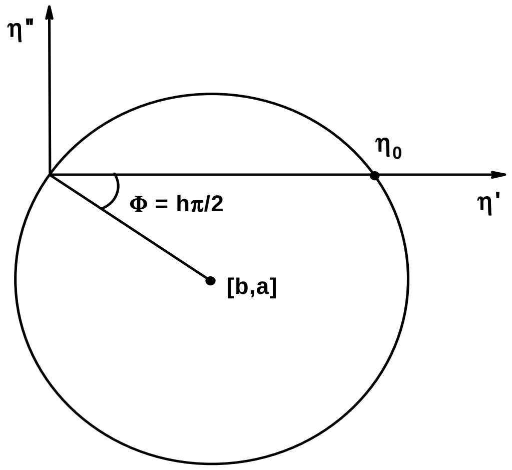


Fig. 7 Cole-Cole plot

5 RESULTS AND DISCUSSION

5.1 Differential Scanning Calorimetry

Phase transformation was studied by using a Perkin Elmer DSC-1.

5.1.1 DSC results – crystallization study

Samples were heated at 50 °C/min up to 170 °C and hold for 1 minute at 170 °C and then cooled at 10 °C/min from 170 °C to 30 °C. Second heating at 10 °C/min up to 170 °C and hold 1 min at 170 °C and cooled at 10 °C/min from 170 °C to 50 °C.

Generally, increasing wood filler content in the blend causes a pronounced increase of temperature of crystallization T_c and slight increase of temperature of melting $T_{m.}$ Increasing wood filler content in the blend causes a pronounced decrease of latent heat. The decrease of enthalpy with increasing Form I

Fig. 8 shows that of the highest temperatures of crystallization has WF [50 μm] and the lowest WF [untreated]. It follows that the particle size also influences the temperature of crystallization. With decreasing particle size increases the crystallization temperature. It can be observed, that drying wood has influence on temperatures of crystallization. Temperature of crystallization composites is around 80°C depending on the content of wood. With increasing content of wood, increases temperature of crystallization. PB-1 neat has temperature of crystallization 77, 3 °C. Little content of wood in the composite increases the crystallization temperature by 1 °C.

Crystallization temperature with the increasing time of transformation does not change.

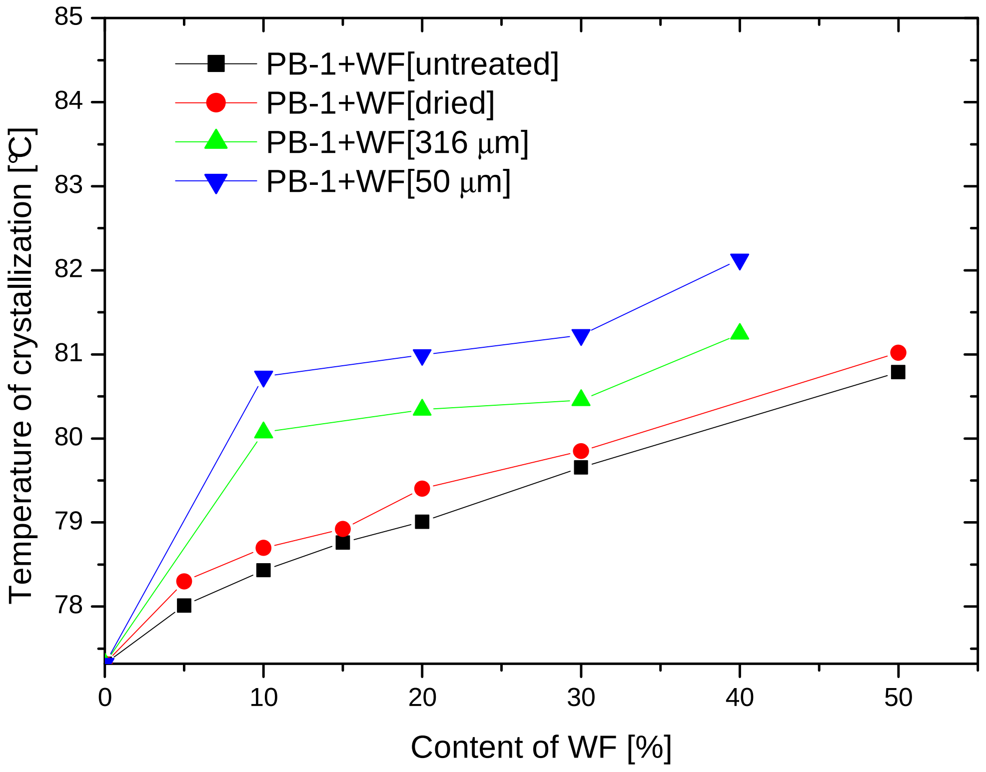


Fig. 8 Temperature of crystallization of all samples depending on the content of wood flour filler

The melting behavior of all samples is illustrated in Fig. 9. Temperature of melting in 0 day is about 115°C. Temperature changes are slightly, depending on the content of WF. Temperature of melting in 6 days is about 129°C. Difference between 0 day and 6 days are caused by phase transformation, when II form transformed to I form. At day 0 can be observed that temperature of melting are higher than at days 6. Form I has higher melting temperature than Form II.

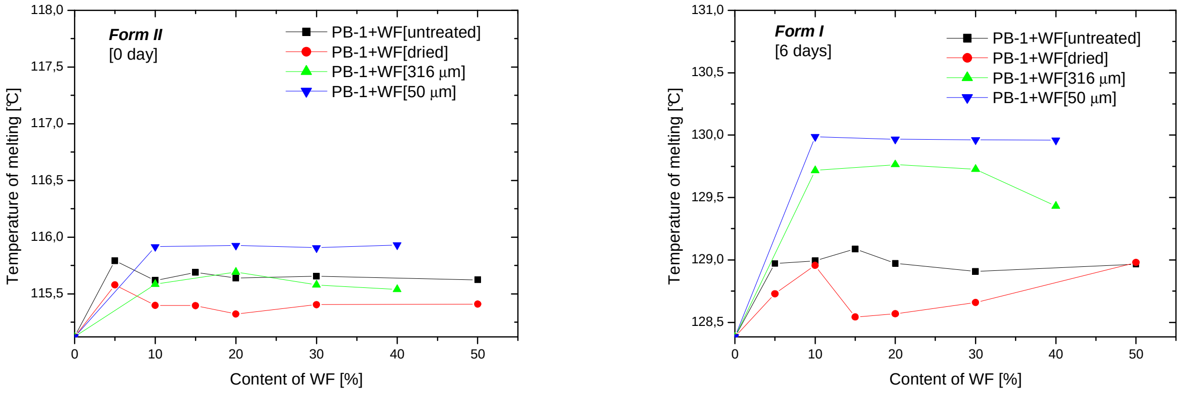


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Fig. 9 Temperature of melting all samples depending on the content of wood flour filler

5.1.2 DSC results - study of phase transformation kinetics

After melting PB-1 crystallizes to the tetragonal crystal Form II with 11_3 helix and then in time it transforms into stable twined hexagonal crystal Form I with 3_1 helix.

Comparing the integrated under both peaks of Form I and Form II the content of transformed Form I can be calculated – the extent of the phase transformation in time.

Form I was observed in the case of composites for all transformation times. The higher content of Form I suggest that the WF promote the crystal transformation through nucleation of Form I directly from amorphous phase. The higher values of the PB-1 composites compared to virgin PB-1 suggest lower amorphous content and it is well known that in the process of Form II to Form I phase transformation a slight extension of chain segment occurs.

It is interesting that Form II gradually transforms into Form I on aging at room temperature [61-67,68-71]. In the case of solution grown single crystals, morphological change induced by this transformation is not observed except for formation of small cracks. The Form I specimen that was obtained by transformation from Form II is the most stable [69].

From the figure 10 it was revealed that with increasing transformation time, the area under the lower temperature peak (116 °C, Form II) decreases and the area under the higher temperature peak (129 °C, Form I) increases. Shape of the curves is almost identical for all samples.

Gohil et al. [71] also suggested that the additional tensile stress induced due to the tightening of the tie molecules on the chain segments through the crystal amorphous interphase facilitates the local extension of the 11_3 helix to 3_1 helical conformations and enhances the nuclei formation which results in the higher rate of phase transformation. The crystallinity of the composites was found to be almost same for all the compositions, however, the transformation from Form II to Form I was found to increase with the content of WF. This suggests that the lowering in amorphous fraction is not the only factor in enhancing the rate of phase transformation. One of the other reasons for improvement in the rate could be the disordered crystallite of Form II [72].

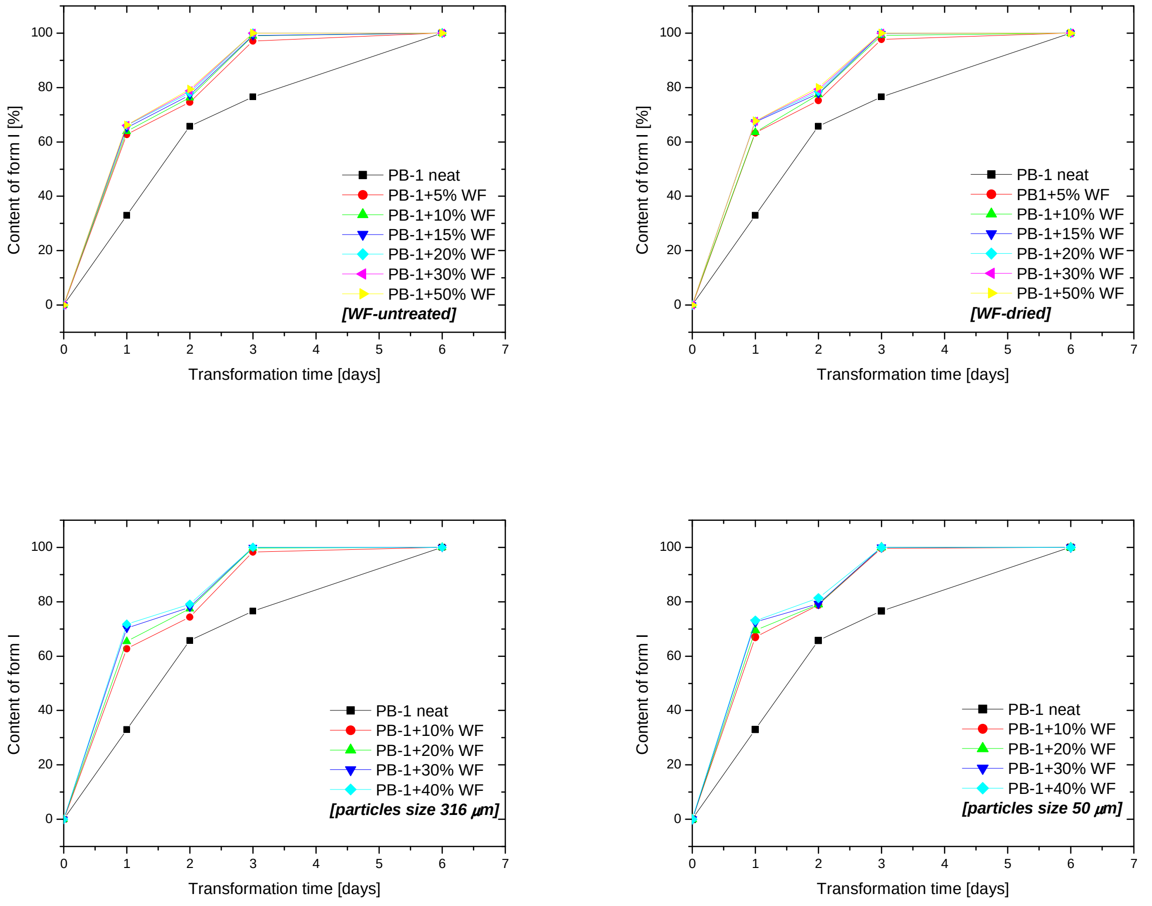

Fig. 10 Evolution of Form I in all composites for various transformation times

5.2 Wide-Angle X-ray Scattering (WAXS)

The Philips X´Pert Pro was used for samples investigation. WAXS patterns were recorded in the diffraction angular range 5 -30 °2θ.

The wide-angle X-ray scattering was performed in transmission mode to observe the evolution of the Form I and II in samples PB-1+wood (pine-untreated) as can be seen in following Fig. 11. It shows a virtually the same evolution of the Form I content at six different blends and PB-1 neat. It can be seen that content of Form I with increasing content of wood flour filler rises.

Until the day 4, the fastest gradual evolution seems to be similar for all samples depending on the content of WF. However during next 6 days their rate is same. Further observation at time of 12 and 22 days shows unexpected increase of the Form I content to over 85 %.

Form I was observed in the case of samples for all the transformation time. The higher values of Form I suggest that wood filler promote the crystal transformation through nucleation of Form I directly from amorphous phase.

At day 0 it can be observed that the higher values of content of Form I of the PB-1+WF composites compared to virgin PB-1 neat suggest lower amorphous content and it is well known, that in the process Form II to Form I phase transformation a slight extension of chain segment. The rate of phase transformation from tetragonal to stable hexagonal form was enhanced as evidenced reduce the time transformation. The observed changes in the crystallization kinetics were ascribed to the enhanced nucleation of PB-1 in the presence of wood filler.

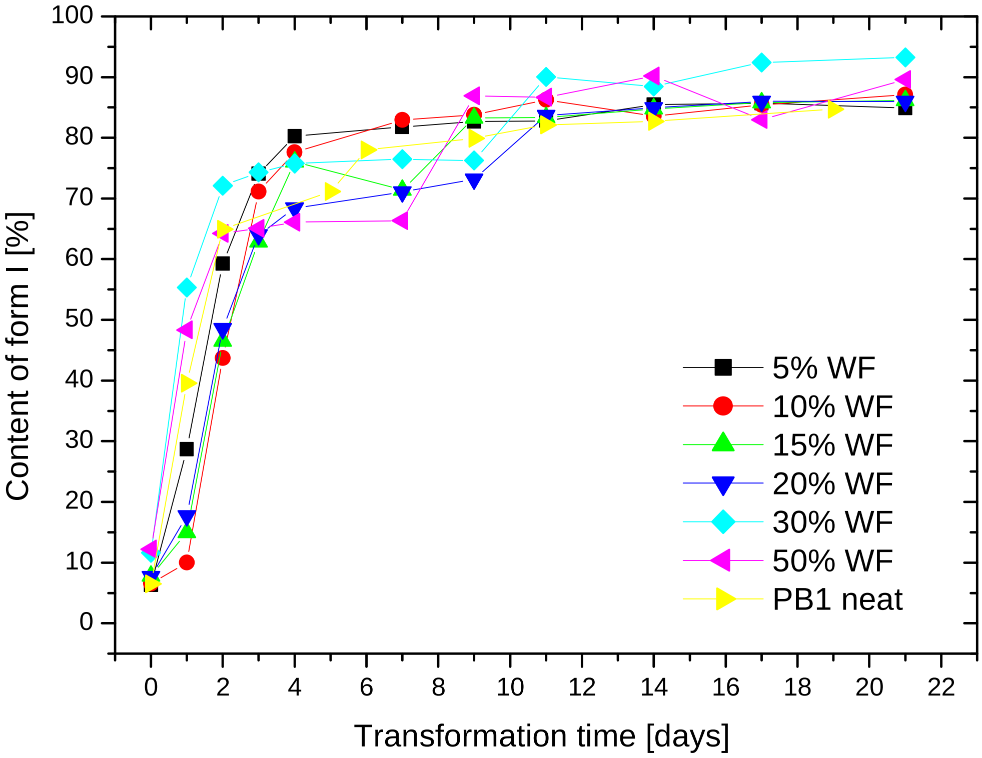

Fig. 11 Evolution of Form I content during transformation for PB-1+ WF [untreated]

Fig.12 shows that fastest addition is observed at transformation days from **1** to **9** and from day **11** the form content becomes constant at approximately **85 %.**

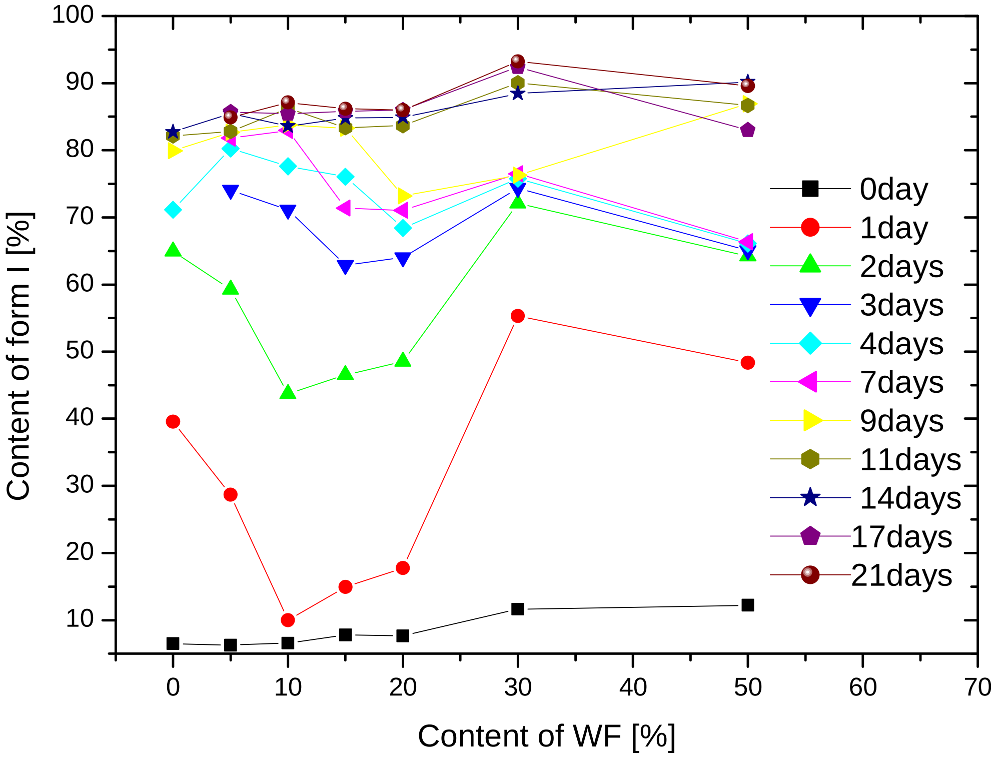

Fig. 12 Evolution of Form I content during transformation of PB-1 + WF [untreated] for different transformation times

Until the day 2, the fastest gradual evolution seems to be similar for all samples depending on the content of WF. This can signify that the dried wood flour affects the phase transformation. Further observation at time of 7 and 19 days shows unexpected increase of the Form I content to over 85 %.

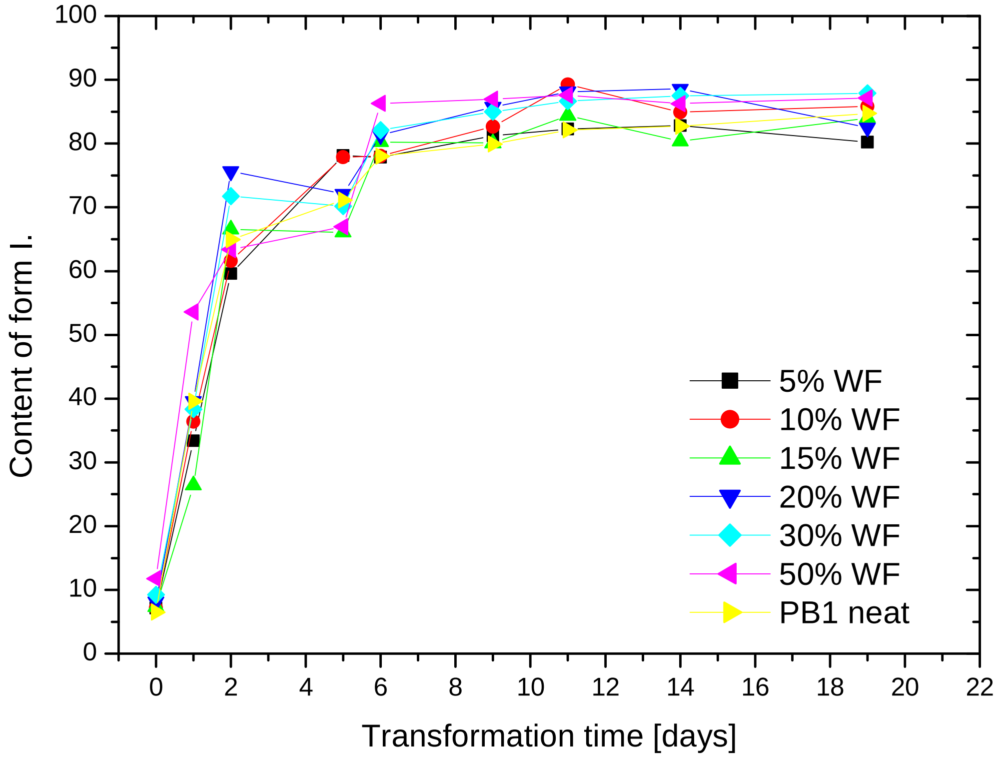

Fig. 13 Evolution of Form I content during transformation for PB-1 + WF [dried]

Fig.14 shows that fastest addition is observed at transformation days from **1** to **5** and from day **6** the form content becomes constant at approximately **85%.**

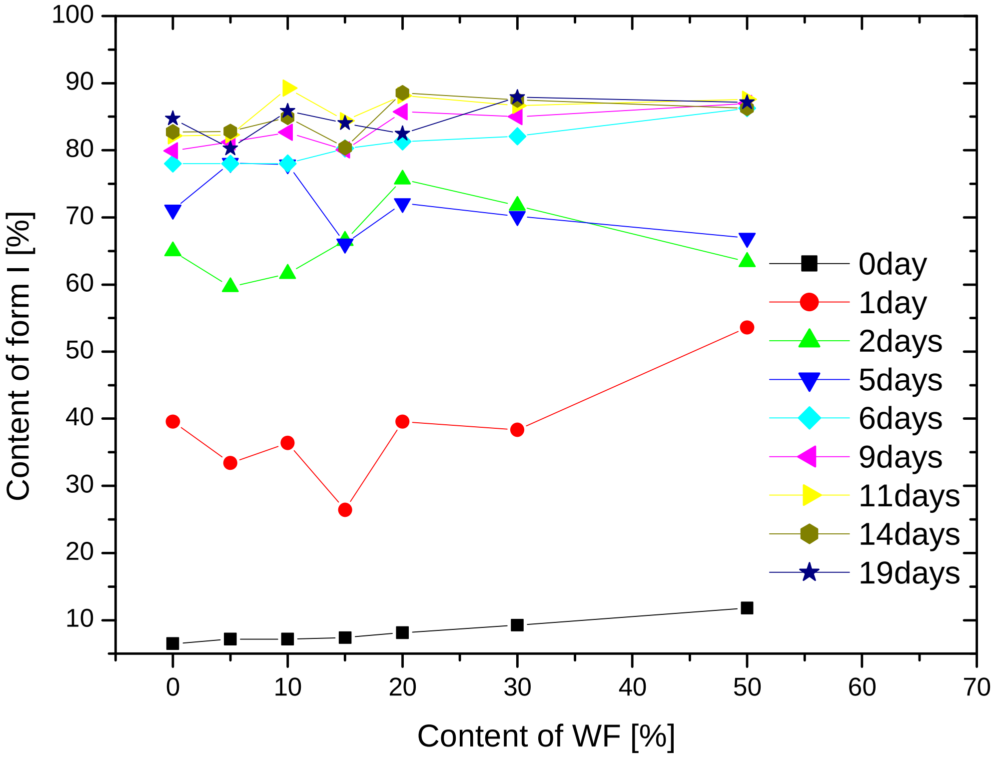

Fig. 14 Evolution of Form I content during transformation of PB-1 +WF [dried] for different transformation times

Until the day 2, the fastest gradual evolution seems to be similar for all samples depending on the content of WF. Further observation at time of 9 and 21 days shows unexpected increase of the Form I content to over 85 %.

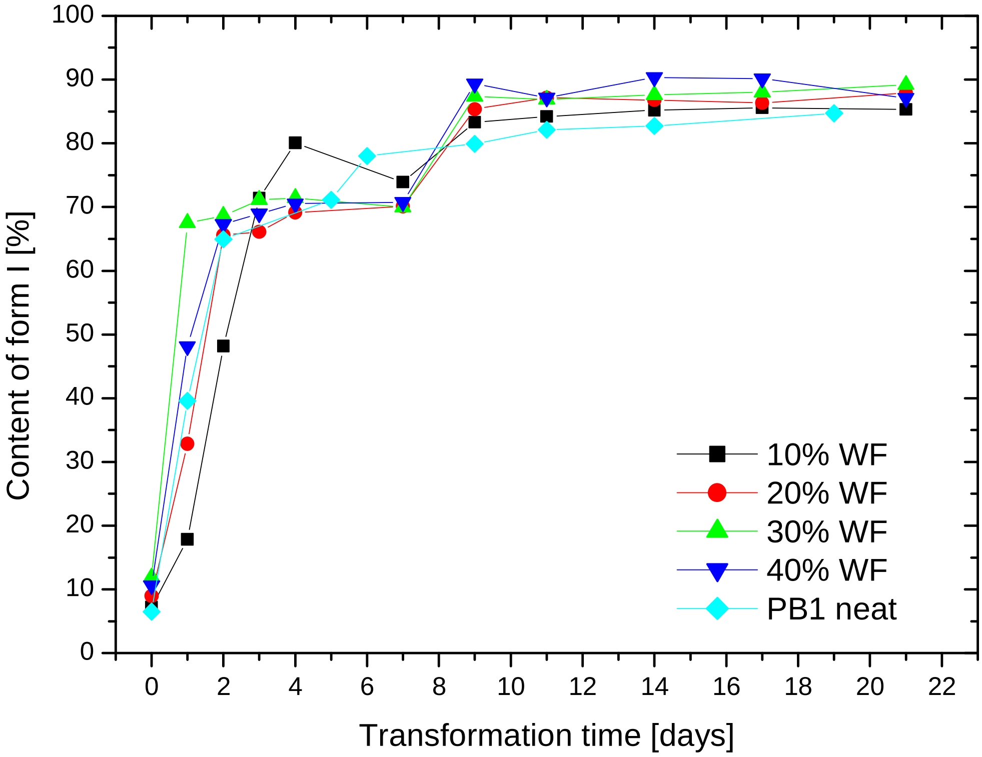

Fig. 15 Evolution of Form I content during transformation for PB-1 + WF [size particles **316 µm**]

Fig.16 shows that fastest addition is observed at transformation days from **1** to **5** and from day **6** the form content becomes constant at approximately **85 %.**

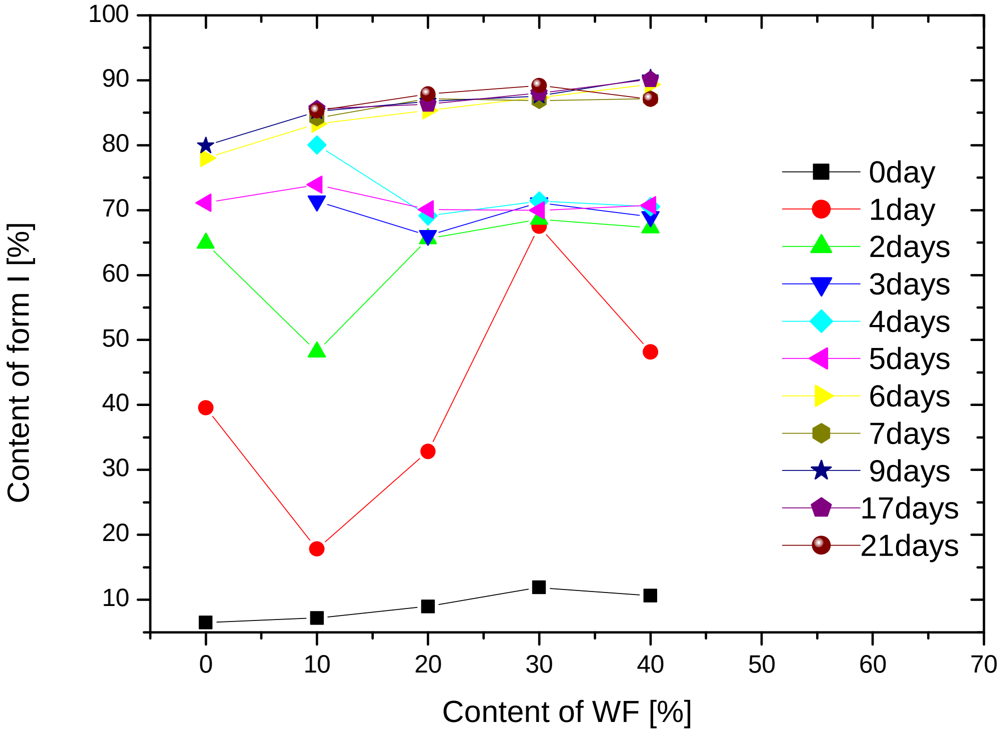

Fig. 16 Evolution of form I content during transformation of PB-1+WF [size particles **316 µm**] for different transformation times.

Wood filler about particles size 50 µm has higher content of Form I.

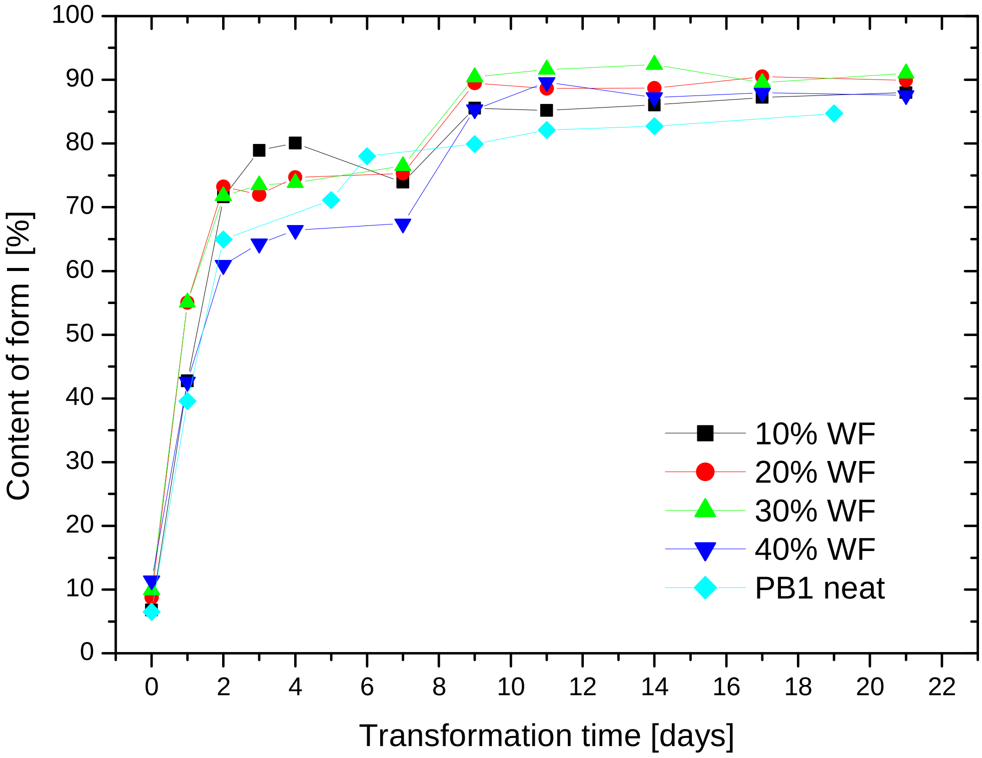

Fig. 17 Evolution of form I content during transformation for PB-1 +WF [size particles **50 µm**]

It can be seen that fastest addition is observed at transformation days from **1** to **7** and from day **9** the form content becomes constant at approximately **90%.**

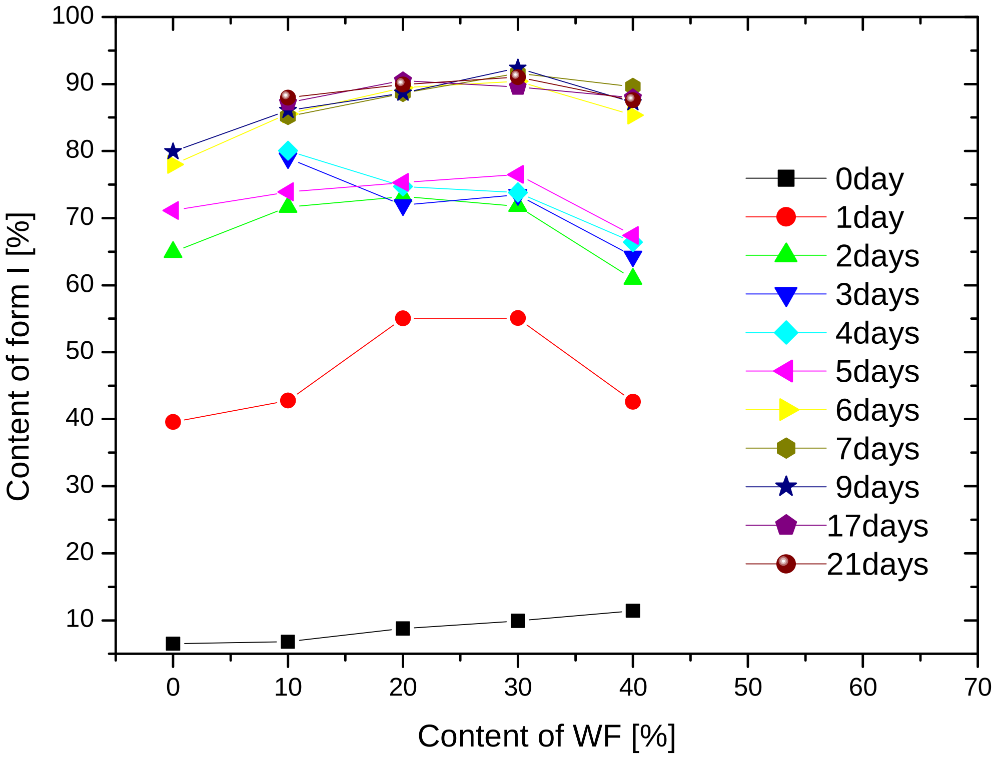

Fig. 18 Evolution of form I content during transformation of PB-1 +WF [size particles **50 µm**] for different transformation times.

The evolutions in selected days for samples with particles size 50 µm and 316 µm in all content of wood are illustrated in Fig. 18. Transformation is influenced by particles size. It was observed that smaller WF particles have positive effect on rate of phase transformation.

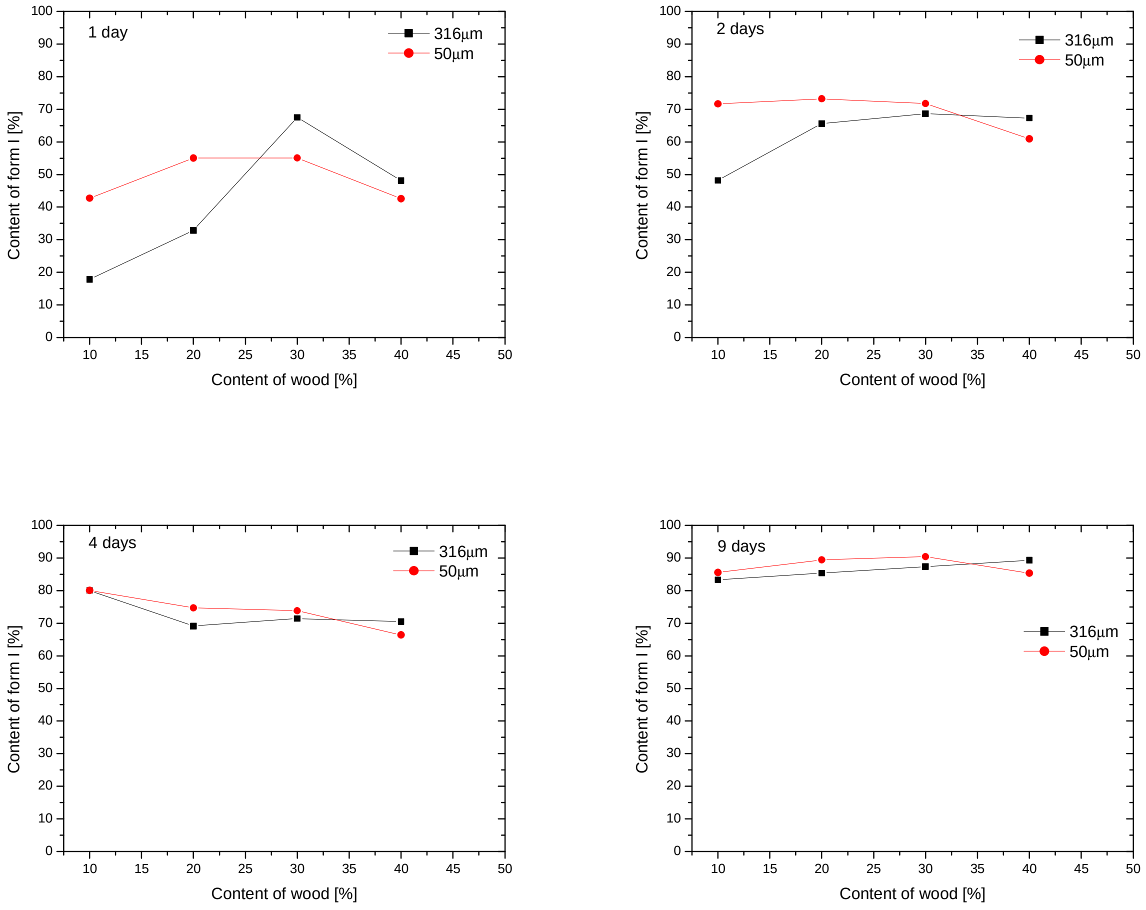

Fig. 19 Evolution of Form I content in the samples about size particles **316** and **50 µm** for all content of wood in selected transformation days

5.3 Rheology

Rheology was measured only in sample PB-1 +WF [pine-untreated]. This measurement was carried out on stay in Laboratoire de Photochimie Moléculaire et Macromoléculaire, Université Blaise Pascal, Clermont- Ferrand.

Molecular changes were monitored by melt viscoelasticity experiments in oscillatory shear mode using a rotational controlled stress rheometer ARES equipped with parallel plate geometry with diameter was 10 mm and the gap between the plates was 1.0 mm. In all cases, the values of the stress amplitude were checked to ensure that all measurements were conducted within the linear viscoelastic region. A frequency sweep extending from 0.1 to 100 rad/s was performed at different temperatures 190-210-230 °C. The temperature 190 °C was considered as a referential temperature.

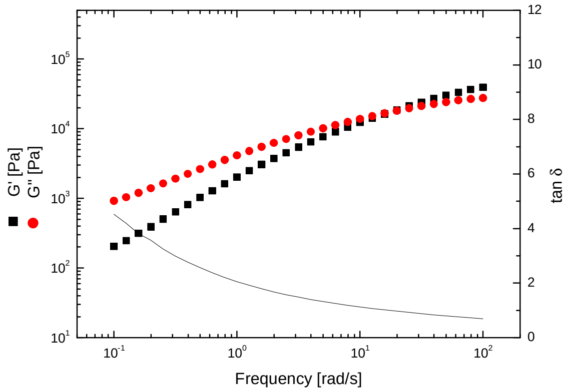

Fig. 20 Storage (G') and Loss (G") moduli as a function of frequency ω for **PB-1 granules**.

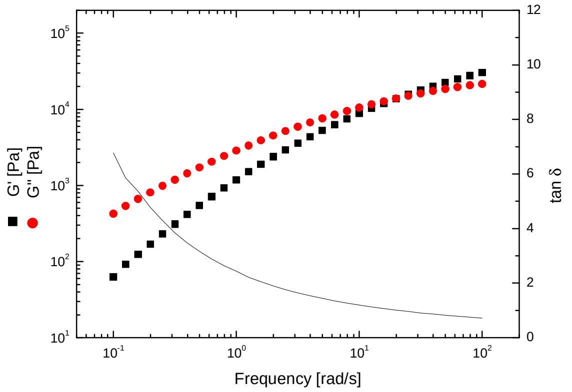

Fig. 21 Storage (G') and Loss (G") moduli as a function of frequency ω for **PB-1 reference**.

Values of storage and loss moduli of reference sample at PB-1 are lower than those of PB-1 granules. This is caused by thermal history of the reference sample. Thermal history influences mechanical resistance. Referential sample was mixed for 7 min at 190°C in Minilab. During mixing, a termooxidative degradation occurred. The decrease of M_w and polydispersity of PB-1 is calculated in chapter 5.1.1. At low frequencies, the *G´* values are lower than *G´´*. This is typical behavior of uncrosslinked polymer melt in terminal zone. The polymer melt’s behavior is more viscous than elastic. The crossover of *G´* and *G´´* is beginning transition zone.

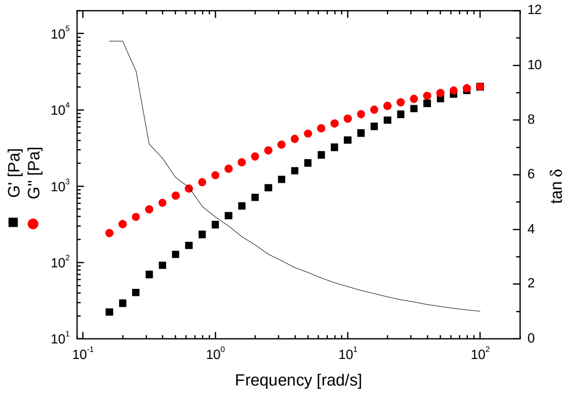

Fig. 22 Storage (G') and Loss (G") modules as a function of frequency ω for blend of

PB-1 +5%WF.

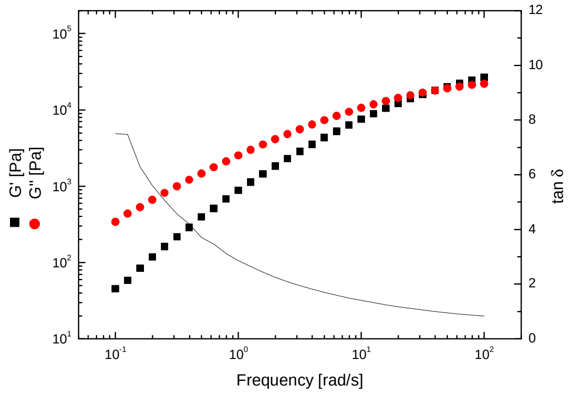

Fig. 23 Storage (G') and Loss (G") modules as a function of frequency ω for blend of

PB-1 +10%WF

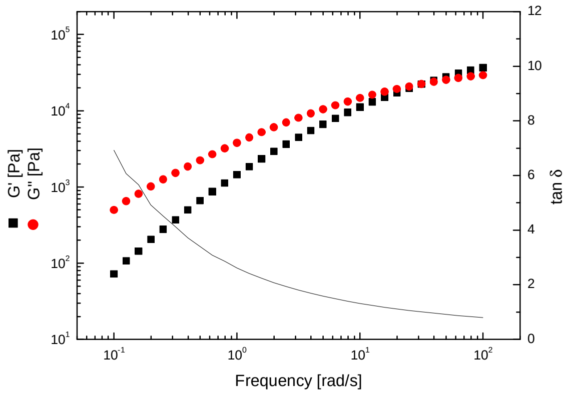

Fig. 24 Storage (G') and Loss (G") modules as a function of frequency ω for blend of

PB-1 +15%WF

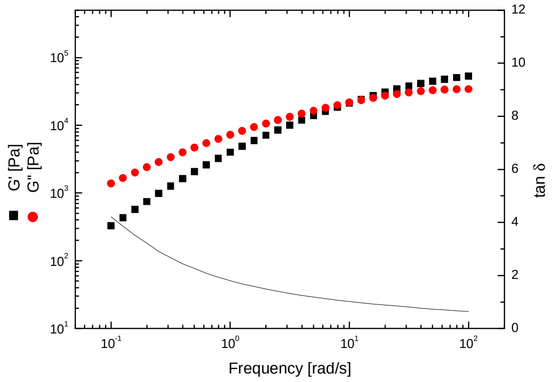

Fig. 25 Storage (G') and Loss (G") modules as a function of frequency ω for blend of

PB-1 +20%WF

Values of G´, G´´ of PB-1+5%WF and PB-1+10%WF are lower than those of PB-1 reference (Fig. 13, 14). Wood filler percentage higher than 15% in the blend leads to the moduli G´, G´´ higher than PB-1 reference.

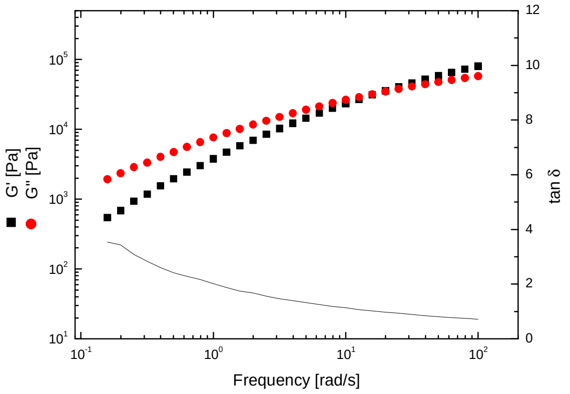

Fig. 26 Storage (G') and Loss (G") modules as a function of frequency ω for blend of

PB-1+30%WF

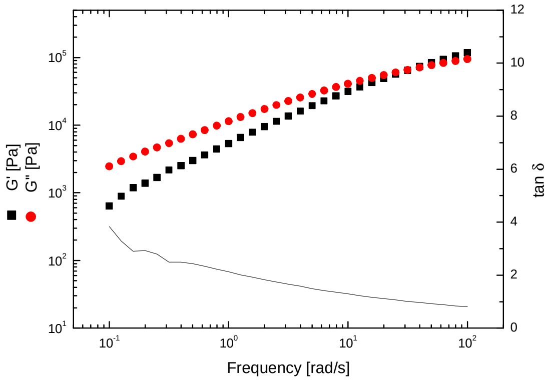

Fig. 27 Storage (G') and Loss (G") modules as a function of frequency ω for blend of

PB-1+50%WF

5.3.1 Cole-Cole representation

Cole-Cole plot of the imaginary vs. real part of dynamic viscosity, η'' vs. η', is a unitable rheological method of data presentation. For uncrosslinked polymer melts with monomodal distribution, Cole-Cole plot gives an arc article of circle. Its extrapolation to the real axis gives zero shear viscosity η_0 ($\eta_0 = k.M_W{}^{3,4}$) that is proportional to M_W. This can be used to calculate the decrease of M_w of PB-1 during microcompounding.

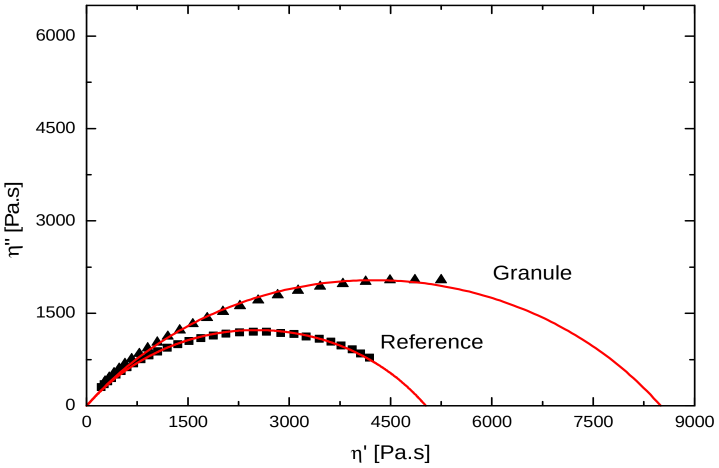

Fig. 28 Cole-Cole plot of **PB-1** granules and reference.

Fig.28 shows Cole-Cole plots of PB-1 granules and PB-1 reference. As the PB-1 reference was thermo-oxidized, it is obvious that its η_0 was decreased. It means that its M_W decreased too.

From the angle *Φ*, it is possible to calculate distribution parameter *h* that is a function of polydispersity.

The calculation of M_W decrease and distribution parameter *h:*

Figure for zero shear viscosity:

$$\eta_0 = k.M_W{}^{3,4}$$

Circle: $y = a + (a^2 - x^2 + 2bx)^{0,5}$

Zero shear viscosity: $\eta_0 = 2b$

Distribution parameter [h = f$\left(\frac{M_N}{M_W}\right)$] :

$$\phi = \frac{h \cdot \pi}{2}$$

$$tg\phi = \frac{|a|}{b}$$

$$\phi = arctg\left|\frac{a}{b}\right|$$

$$h = \frac{2}{\pi} arctg\left|\frac{a}{b}\right|$$

Numbers calculated from graph:

PB-1 granules	PB-1 reference
$R^2 = 0,991$	$R^2 = 0,989$
a = -3407	a = -1948
b = 4249	b = 2512
$\eta_{0granules} = 2b = 2 \cdot 4249 = 8498 Pa.s$	$\eta_{0reference} = 2b = 2 \cdot 2512 = 5024 Pa.s$

$$\eta_0 = k.M_W^{3,4} \Rightarrow$$

$$\Rightarrow k = \frac{\eta_{0\ granules}}{M_{W\ granules}^{3,4}} = \frac{\eta_{0\ reference}}{M_{W\ reference}^{3,4}} \Rightarrow \frac{M_{W\ reference}^{3,4}}{M_{W\ granules}^{3,4}} = \frac{\eta_{0\ reference}}{\eta_{0\ granules}} \Rightarrow \left(\frac{M_{W\ reference}^{3,4}}{M_{W\ granule}^{3,4}}\right) = \frac{\eta_{0\ reference}}{\eta_{0\ granules}} \Rightarrow$$

$$\Rightarrow \frac{M_{W\ reference}}{M_{W\ granules}} = \sqrt[3,4]{\frac{\eta_{0\ reference}}{\eta_{0\ granules}}} = \left(\frac{5024}{8498}\right)^{\frac{1}{3,4}} = \underline{\underline{0,86}}$$

$$h_{granules} = \frac{2}{\pi} arctag \frac{3407}{4249} = \underline{\underline{0,43}}$$

$$h_{reference} = \frac{2}{\pi} arctag \frac{1948}{2512} = \underline{\underline{0,42}}$$

$h_{granules} \rangle h_{reference} \quad \Rightarrow$ **polydispersity degression**

Sample		η0[Pa.s]	h
PB 0110M	Granules	8498	0,43
	Reference	5024	0,42

Table 6 Zero shear viscosity η_0 and distribution parameter *h* of PB 0110M granules and reference.

M_W decreased to 86% of initial M_W. The polydispersity decreased of the reference as well.

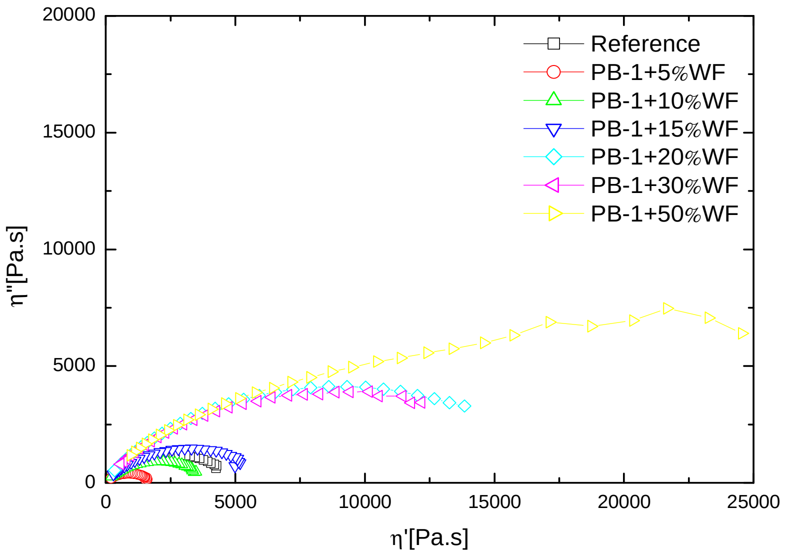

Fig. 29 Cole-Cole plot of blends PB-1+WF

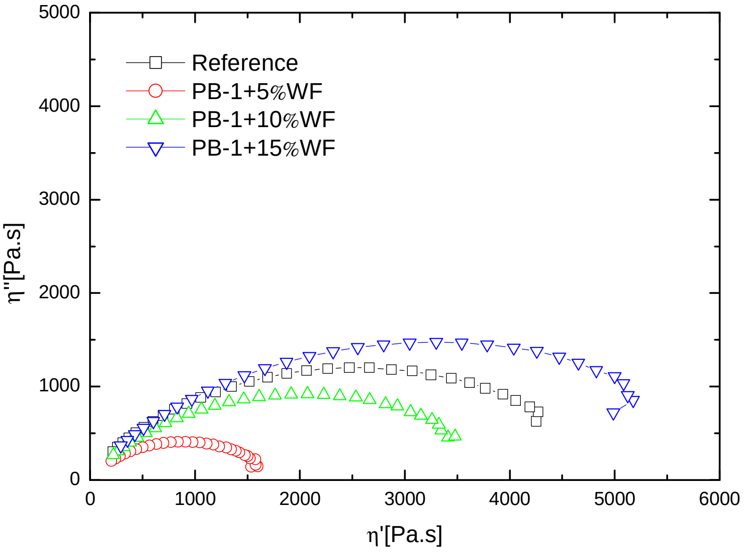

Fig. 30 Cole-Cole plot detail

Fig. 29 presents Cole-Cole plots of all blends. PB-1 +5%WF and PB-1 +10%WF have smaller arcs of circle than PB-1 reference. It means that these materials are more fluid. Therefore, wood acts as a lubricant agent. However, increasing content of wood has an opposite effect. Then, it acts as an apparent crosslink by Wan der Waals forces between wood particles and polymer chains.

5.3.2 Rheology of preparation samples

Rheology of preparation samples was measured by using MicroCompounder Haake MiniLab at 1 to 120 rpm for 8 min. at 170 °C.

Fig. 30 shows that with increasing WF content shear viscosity increases.

The rheological properties show that addition of WF increase viscosity. It is clearly seen at particle size 50 and 316. In case of dried WF there is no significant difference at low filling up to 30 %, but at PB-1+50%WF viscosity remarkably increase. It is caused by large WF content, considerable particles aggregation take place, leading to lower strength due to the filler’s failure to sustain the stress transferred from the polymer to the matrix.

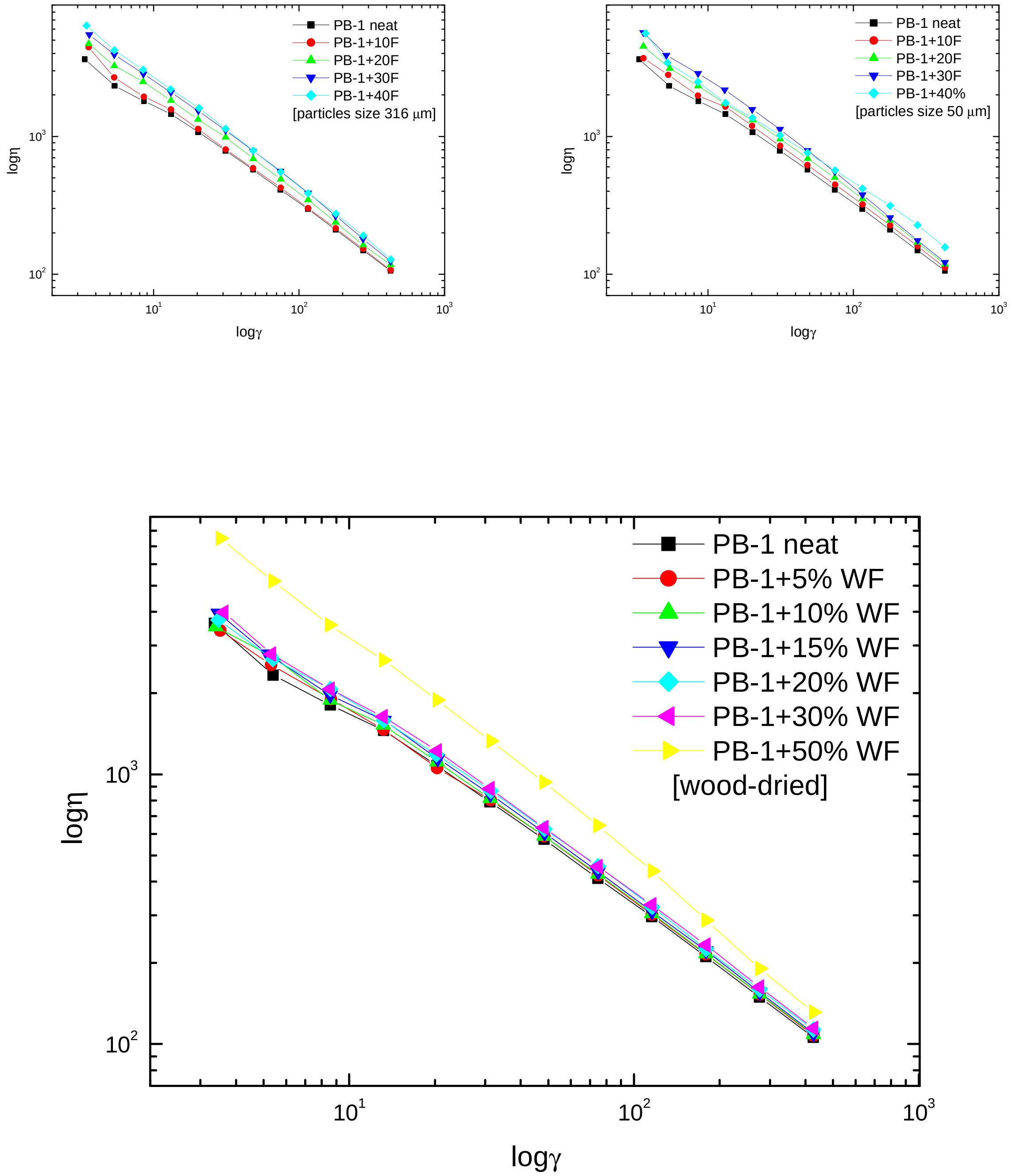

Fig. 31 Flow characteristics of preparation samples

CONCLUSION AND PERSPECTIVES

In the bibliographic are presented used materials, methods and the present state of knowledge concerning the phase transformation of PB-1. Next part describes of Wood-Plastic Composites. The experimental part contains the results of measurements, which are divided according to methods used.

The observations of the present investigation can be summarized as follows. Study crystallization shows that with increasing wood filler content the crystallization temperature increases and the heat latent of crystallization decreases. With increasing wood filler content the melting temperature does not change (only ± 1°C) and heat latent of fusion decreases. Crystallization temperature affects the particle size of wood flour. With decreasing particle size of WF, the crystallization temperature increases. Study the phase transformation the shows, that with increasing transformation time, the area under the lower temperature peak (116 °C, Form II) decreases and the area under the higher temperature peak (129 °C, Form I) increases. It follows the transformation from Form II to Form I was found to increase with the content of WF.

Further step was to study molecular changes. These results suggest that the mechanism for nucleation and growth of Form I was altered in the presence of WF. The observed increase in the rate of phase transformation for the composites was attributed to the decrease in the amorphous content and to the enhanced nucleation of Form I due to disordered crystallite morphology. Transition from phase II to phase I plays significant role in the physical and mechanical properties of PB-1 , these results demonstrate that the use of WF offers a novel route to enhance the transformation as the time required for the conversion of Form I was found to be decreased.

Melt behavior of the samples were investigated by rheometer ARES. Values of storage and loss moduli of reference sample at PB-1 are lower than those of PB-1 granules because of the thermal history of the reference sample. At low frequencies, the G' values are lower than G''. Wood filler percentage higher than 15 % in the blend leads to the moduli G', G'' higher than those of PB-1 reference. Cole-Cole plot was used to determine the difference between M_W reference and M_W granules. M_W reference decreased to 86 % of M_W granules. The polydispersity decreased of the reference as well. Cole-Cole plots of all blends shows that PB-1+5 % WF and PB-1+10 % WF have smaller arcs of circle than PB-1 reference. It means that these materials are more fluid. Therefore, wood acts as a lubricant agent. However, increasing content of wood has an opposite effect. The rheological properties show that addition of WF increase .viscosity. In the case of low filling up to 30 % no significant difference, but at PB-1+50 % WF viscosity remarkably increase. It is caused by large WF content, considerable particles aggregation take place, leading to lower strength due to the filler's failure to sustain the stress transferred from the polymer to the matrix.

Further research could be the use of additives, which could affect no only the phase transformation PB-1, but also properties of WF. Stabilization could bring further applicability of PB-1 based on its phase transformation.

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LIST OF ABBREVATIONS

PB-1	Poly(1-butene)
WPC	Wood-Plastic Composites
DSC	Differential Scanning Calorimetry.
WAXS	Wide Angle-X-ray Scattering
WF	Wood Filler
T_g	Temperature of glass transition
T_c	Temperature of crystallization
T_m	Temperature of melting
G^*	Complex dynamics modulus
G'	Elastic modulus
G''	Loss modulus
h	Parameter of the relaxation-time distribution
η^*	Dynamic viscosity
η', η''	Real and imaginary viscosity components
η_0	Zero shear viskosity
λ_0	Average relaxation time
ω	Frequency

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