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DETERMINATION OF NUCLEATING ABILITY OF WOOD FOR NON-ISOTHERMAL CRYSTALLISATION OF POLYPROPYLENE

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Composites made from an isotactic polypropylene matrix and wood (pine or beech) have been prepared and tested. To improve adhesion between components, the wood modification was performed by esterification with maleic, propionic, crotonic, succinic and phthalic anhydrides. The surface of wood fillers was also modified by chemical treatment with NaOH as well as by extraction process. Non-isothermal crystallisation of polypropylene in wood composites is studied by DSC, and the basic parameters of crystallisation are determined. We discovered that the composites containing chemical treated wood fillers showed the tendency reduction the nucleation efficiency of polypropylene. The ability of wood filler to induce nucleation in polypropylene matrix is dependent on the kind of chemical modification of surface wood

Keywords: *chemical modification, crystallisation, nucleation, polypropylene, wood*

Introduction

In recent years, significant efforts have been made to manufacture thermoplastic composites using such natural fibres as wood, flax fiber, jute fiber and wheat straw [1–4]. Lignocellulosics are favored as new generation reinforcing materials in thermoplastics since they represent renewable natural sources. Much interest has been shown in the development of wood fiber reinforced polymers due to low cost, renewability, biodegradability, low specific gravity, abundancy and high specific strength and stiffness of wood fiber [5, 6].

However, the highly hydrophobic nature of certain thermoplastics, such as polyolefines, causes compatibility problems with the hydrophilic lignocellulosic materials and is one of the major reasons for limited use of wood fiber as reinforcement. Various strategies are available in order to improve compatibility between the lignocellulosic filler and the matrix: chemical modification of the lignocellulosic filler [7–9], the use of compatibilizers [10, 11] and grafting of polymers onto the lignocellulosic material [12]. These operations can act as an interfacial coupling in a composite system and also influences the nucleation and crystallisation process of polymer matrix and the formation of transcrystalline layers.

It is know that the presence of a solid surface in contact with semicrystalline polymers (e.g. polyethylene, polypropylene) during crystallisation from the melt favors heterogeneous nucleation [13, 14]. Heterogeneous nucleation of spherulites is the commonly encountered mechanism of initiation of crystallisation of polymers. This is in contrast to homogeneous nucleation which is believed to take place as a result of random fluctuation of order [13]. In semicrystalline thermoplastic matrix composites, the nucleating efficiency of filler is thought to have a critical influence in polymer processing. Composites materials with high nucleating ability cause the shortening of injection molding cycle time.

Recently, efforts have been made to characterize the effect of fibres like carbon, glass, aramid, Kevlar, nylon, PET, PTFE, flax, hemp on the crystallisation kinetics and morphology of the matrix [13, 15–19]. However, results reported in many studies are often contradictory. Mucha and Krolikowski [20] found that talc and carbon acted as nuclei in polypropylene crystallisation. However, chiotosan or wood flour caused visible changes of the crystallisation rate of polymer matrix and disturbs the creation of polypropylene spherulitic structure. In many paper, the induction time, nucleation rate and nucleation density were important factors in characterize quantitatively the nucleating ability of fibres. Wang and Liu [15] showed that the inverse proportion relation between induction time and nucleation rate which is held valid for PTFE and carbon fibres systems is not applicable to Kevlar and PET fiber. In past years, much experimental work has been devoted to characterize nucleation ability of different fillers in PP composites, based on the comparison of the interfacial free energy difference function $\Delta\sigma$ at the surface and that in bulk

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[13, 15, 20]. According to the present state of knowledge, well nucleating efficiency seems to play a decisive role in transcrystallisation [15, 20–23] and also is accompanied with an improved adhesion between fillers and PP matrix. The nature required of foreign surfaces to be active in heterogeneous nucleation and the mechanism of the process is not fully understood.

In an earlier study [18, 19], the relationship between supermolecular structure of iPP in composite systems (PP/flax and PP/hemp fibres) and kinetic parameters of crystallisation was investigated. The purpose of this study is to investigate the effect of various chemical surface treatments on the nucleation ability of pine and beech wood fiber in polypropylene by using differential scanning calorimetry (DSC). The use of DSC method is very straightforward since this technique allows us to study the nucleation process and crystallisation kinetics. Although numerous articles have been published describing the study of polypropylene-lignocellulosic composites, little efforts have been devoted to the study of the parameters of crystallisation in these systems. Until now, investigations of the influence of chemical modification of wood on the nucleation efficiency of the PP during non-isothermal crystallisation in composites with pine and beech wood have not been carried out. The investigations during non-isothermal conditions are very significant because characterize real conditions in polymer processing.

Experimental

Materials

Isotactic polypropylene (iPP) Malen P F-401 (Orlen Płock S.A.) was used as a matrix of the composite system. It was characterized as follows: isotactic content – 95%, melting point – 166°C and melt flow index – 2.4–3.2 g/10 min.

The experimental material comprised two most common Polish timber species pine wood (*Pinus silvestris* L.) as a softwood species and beech wood (*Fagus silvatica* L.) as a hardwood species. The size of wood sawdust ranged from 0.5 to 1.0 mm.

Chemical modification of wood

Before chemical modification the wood was dried at 70°C for 24 h in a vaccum oven. Seven different types of chemical treatment of wood were prepared:

Mercerization process

Wood was treated with an aqueous solution of NaOH (17.5%). The pine wood and the beech wood was immersed in the solution during 60 min at room temperature. After alkali treatment wood was washed several times with distilled water (a final pH of 7 was maintained).

Esterification reactions

In this work, to improve the interaction between wood and polypropylene, the various kinds of anhydrides was used. Chemicals used for modification treatments of wood were: maleic, propionic, crotonic, succinic and phthalic anhydrides.

Part of NaOH treated wood was immersed in 1 M solution of anhydrides in xylene and then heated at reflux temperature (140^{o}C) during 8 h. The accurate procedure of chemical modification of wood, separation wood from xylene solution and extraction process is given in our previous articles [24, 25].

In wood particles, chemical modification is mainly achieved through the reaction of the hydroxyl groups in the materials. The esterification process was confirmed by the obtained FTIR spectra and calculated as mass percent gain [24, 25].

Extraction process

Extraction with ethanol/benzene (2:1) mixture were carried out by mixing the solution with the wood. The waxy substances, fats and resins of wood can be eliminated by this extraction [26].

Preparation of wood – PP composites

The iPP and wood composites were obtained by the extrusion method in ‘Fairex’ single-screw extruder. In first step, the mixture of polypropylene and 50% of wood was mixed in a drum blender for 30 min. A die measuring 4 mm in diameter was attached to the extruder. During the extrusion, the temperatures of the four processing zones were chosen as: 140, 180, 190, and 195°C and the die temperature was 190°C. The screw’s rotational speed was ranged from 25 to 30 rpm. Mixing temperature was controlled at less than 200°C to avoid decomposition and degradation of wood fibers. The extrudate was cooled with 20°C water after exiting the die, and then pelletized into granules. Next, the granules were dried in an oven for 24 h at 60°C. Name of the eighth composite materials are illustrated in Table 1.

Methods

DSC measurement

The composites with wood fibres content 50% were prepared for DSC analysis.

Differential scanning calorimetry measurements have been carried out on Netzsch DSC 200. The in-

Table 1 Name of the composite materials

Abbr.	Compounds
PP/W	PP and unmodified wood
PP/W-pr	PP and wood modified by propionic anhydride
PP/W-ma	PP and wood modified by maleic anhydride
PP/W-cr	PP and wood modified by crotonic anhydride
PP/W-su	PP and wood modified by succinic anhydride
PP/W-ph	PP and wood modified by phthalic anhydride
PP/W-me	PP and mercerized wood
PP/W-ex	PP and wood after extraction

strument was calibrated with indium standard for temperature and heat change. The samples were melted at a heating rate of 10°C min^{-1} to 200°C and maintained at this temperature for 5 min in order to eliminate the thermal history of the material. In the second step, the samples were cooled from 200 to 40°C at cooling rate 5°C min^{-1}. This procedure was repeated two times and second segment were supplied to calculation part. The experiments were carried out in nitrogen atmosphere. The kinetic parameters of crystallisation of polypropylene matrix in presence of wood like the crystal conversion and half crystallisation time were determined. The melting (T_m) and the crystallisation temperatures (T_cp) of composites were obtained from the maximum of the endothermic and exothermic peaks, respectively.

Based on the determined values for the enthalpy of crystallisation (H), the extent of crystallisation (crystal conversion), α was calculated:

$$\alpha = \frac{\int_0^{\mathrm{t}} (\mathrm{d}H/\mathrm{d}t)\mathrm{d}t}{\int_0^{\alpha} (\mathrm{d}H/\mathrm{d}t)\mathrm{d}t}$$

From the curves of α *vs*. time, the half-time of crystallisation ($t_{0.5}$) was determined as time when crystal conversion was 50%.

The term half-time crystallization is usually evaluated for isothermal crystallisation, but we assumed that the nucleation efficiency of wood may be estimated on the basis rate of total transformation of melt into crystalline phase, which is regulated, for example, by time when this transformation achieved 50%. Then in our case the half-time crystallization is defined as time from start of exothermic peaks (for non-isothermal condition) to point when crystal conversion was 50%. This time we named as half-time crystallization, similar as term the 'half-time crystallisation' which is applied for isothermal measurement.

WAXS measurement

The structure of iPP in composite materials was analyzed by means of wide angle X-ray scattering (WAXS) using CuK_α radiation. The X-ray diffraction pattern was recorded in angle range of 2θ=10–30°. Deconvolution of peaks was performed by the method proposed by Hindeleh and Johnson [27], improved and programmed by Rabiej [28]. After separation of X-ray diffraction lines, the contents of β-phase (k) by using the Turner-Jones formula [29].

Results and discussion

Melting and crystallisation temperature

In our earlier publication [18, 19] we investigated the influence of flax and hemp fibres on crystallisation and supermolecular structure of PP. It was shown that chemical modification of lignocellulosic fibres diminished the crystallisation rate and the density nucleation. Moreover, the increased rate of crystallisation for unmodified fibres/PP composites was therefore attributed to enhanced ability of creation of hexagonal phase of PP.

The quantitative results of crystallisation and heating behavior are presented in Figs 1 and 2. The temperature of crystallisation gives information for the nucleation ability which can be changed by the modification of wood.

During nonisothermal crystallisation, the heterogeneous activity of wood can be the shifting of DSC exothermic peak towards higher temperature. The strong increase of crystallisation temperature by 5–9°C was found at the PP/pine wood composites as well as at the PP/beech composites in comparison to pure PP. Consequently, it can be suggested that the wood act as heterogeneous nucleation agents for PP. Moreover, it is detectable, that values of T_cp are dependent of the chemical treatment of the wood. An increase of crystallisation temperature by about 1–4°C

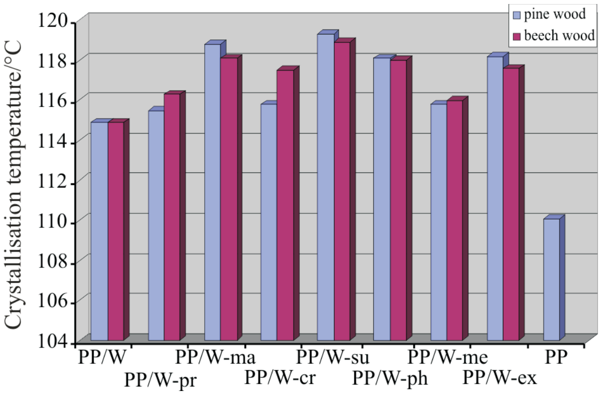

Fig. 1 Crystallisation temperatures for pure iPP and wood/PP composites

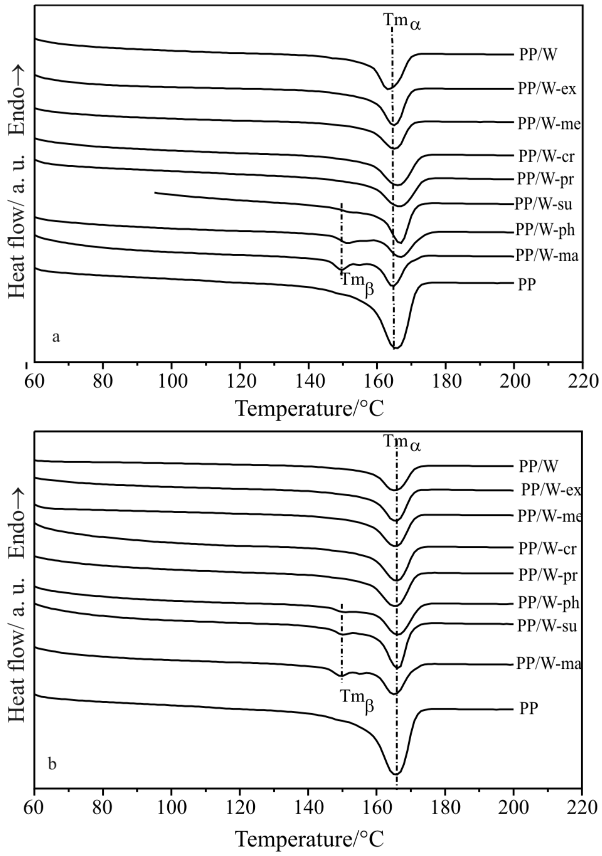

Fig. 2 DSC melting curves of pure iPP and iPP in different composites after non-isothermal crystallization: a – PP-pine wood; b – PP-beech wood

observed in composites with chemical modified wood in comparison to unmodified wood. As can be seen (Fig. 1), the highest activity for heterogeneous nucleation of PP exhibits pine wood modified by maleic and succinic anhydrides and beech wood treated by succinic anhydrides. In this case, the shifting of T_{cp} peaks is highest.

Typical DSC curves pertaining to the heating mode are shown in Figs 2a and 2b, which exhibits the melting temperatures. The qualitative melting behaviour for PP matrix and composite is similar.

The all composites materials (containing pine and beech wood) have similar values in range of 165–167°C. The small changes of T_m in composites are obviously due to perfection of spherulite structure of the polymer. It is known that the main peak at 165°C is caused by melting of the monoclinic (α-PP) phase, whereas the hexagonal (β-PP) phase melt at about 150°C. DSC curves for some composites are constructed as the sum of two curves: one for the melting of pure α-PP of certain crystallinity and the other for the melting of pure β-PP of certain crystallinity. It can be seen (Figs 2a and b) that when the composites contained wood modified by maleic, phthalic and succinic then peaks of the β-phase was noted. On the other hand, it is of interest to note that this kind wood (W-ma, W-ph and W-su) may be heterogeneous nucleating agent of hexagonal phase of PP.

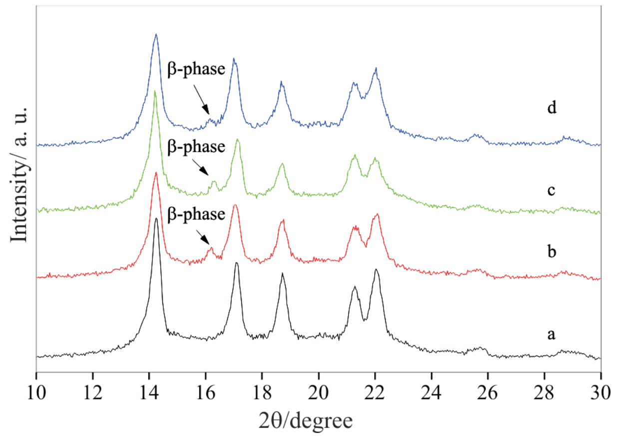

Fig. 3 X-ray diffraction patterns of polypropylene composites: a – with unmodified pine wood; b – with maleic anhydride, c – with phthalic anhydride, d – succinic anhydride

However, these results were confirmed by WAXS investigation. Figure 3 shows series WAXS patterns of selected of composites.

These experiments confirmed that formation of the hexagonal phase arises when the wood are modified by maleic, phthalic and succinic anhydrides. The amount of this hexagonal form is ca. 4–6% only. In other material composites only the monoclinic phase is registered. The differences in polymorphic structure for various modifications of the wood suggest that the formation of β-form is connected with different abilities of wood surface nucleation and with the crystal growth rate. It was shown in several studies, that certain salts of aliphatic acids (like succinic, pimelic or suberic) are active nucleating agent for β-iPP. The role of active β-nucleating agents added to polypropylene on the crystallisation process have been a subject of many studies [18, 30–38], but the mechanisms of formation of particular forms and transformations of one phase into another still remains unsolved.

The polymorphic transformation is a characteristic feature of β-isotactic polypropylene, which transforms from the metastable β-phase to the thermodynamically more stable α-form via a recrystallisation process. Varga [30, 31, 38], on the basis of a DSC study showed that the formation of the α phase from the β is preceded by an endothermic effect identified as melting of the β-form. According to his statement the molten hexagonal form recrystallised into the monoclinic phase. This recrystallisation process during the melting of the β-phase is connected with thermodynamic instability of the β-phase. Recently, Cho [36, 37] observed that recrystallisation process is due to the formation of a very small amount of α-form crystals within the β-phase. In addition, it is responsible for βα-recrystallisation during second heating, which occurs in spite of the presence of β-nucleating agent

Garbarczyk presented [39] that one of the reasons for a formation of the given form are perturbations in the mobility of the chains during crystallisation which make it difficult for polymer chains to reach the arrangement with the lowest potential energy (α-form). The phase transformation process consists of a number of intermediate stages based on rotations and transitions of the iPP chains. Therefore, the β modification can be considered as one of the stages on the way of transformation from melt to crystal monoclinic lattice. This suggestion corresponds well with Varga proposition [30, 31] where melting corresponds to the first stage of the transition, which we termed as expansion of inter-chain spacing [18]. In other words, when samples containing the β-form have a suitable level of internal energy, then a slight increase in kinetic energy is sufficient to convert the hexagonal arrangement into the more stable monoclinic one.

In our DSC experiments the recrystallisation tendency of β-phase in the composites is very difficult to observation. Probably, this effect is not seen because very small amount of the hexagonal form (4–6% only). Moreover, the α- and β-peaks are partially overlapped, therefore, it is difficult to determine the recrystallisation process. However, the completion of melting of β-phase and start of the recrystallisation of β- to α-modification occur simultaneously and the βα recrystallisation is superimposed with the onset melting α-form crystals [35]. These parameters are important to correct interpretation of recrystallisation process in case of very small amount of β-phase.

The crystal conversion of polypropylene matrix

From exothermic DSC runs crystal conversion and half-time of crystallisation were determined. Figures 4a and b shows the variation of measured crystal conversion of PP in presence of various wood filler.

The crystal conversion is significantly decreased for composites with mercerized wood and wood after extraction process. A strong effect of the enhancement of rate crystallisation is observed in the composites modified by anhydrides (earlier wood was mercerized). Similar effect has been observed in case of all kind of anhydrides. Moreover, the results given in Figs 4a and b indicate that nucleating ability of wood surfaces modified by all anhydrides is higher than that in the bulk although clearly the differences are not great ad the values do not appear to permit adequate discrimination between different composite materials with wood modified by anhydrides. As an example, in Figs 4a and b the crystal conversion is reported, evidencing that unmodified wood possesses highest nucleating ability. It is also worth noting that PP/pine wood composites have a crystal conversion value comparable to that of PP/beech wood composites. It is also worth noting that PP with unmodified and chemical modified wood have values of crystal conversion significantly higher than of the bulk. We conclude that the nucleating ability is in the following order: unmodified wood>wood modified by anhydrides> wood mercerized by NaOH>wood after extraction, based on the course of crystal conversion *vs.* time crystallisation curves.

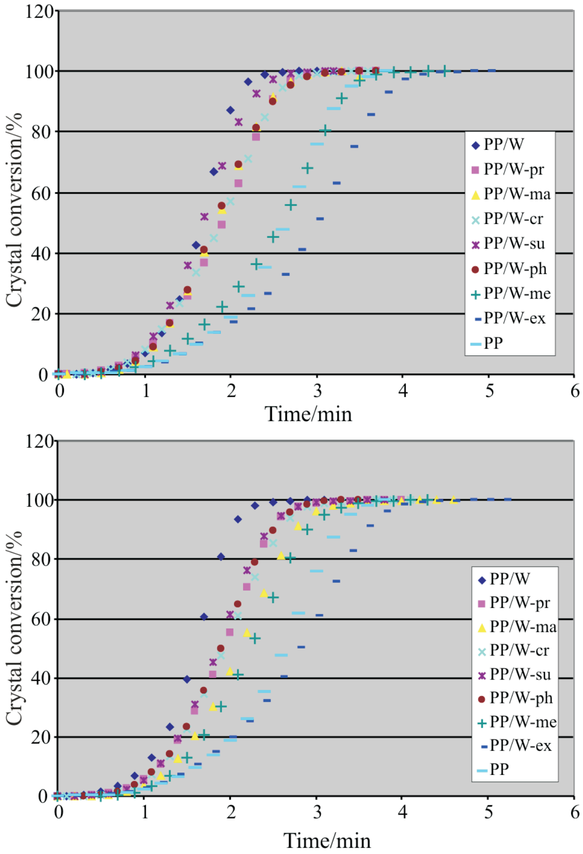

Fig. 4 Crystal conversion of pure iPP and in composites with wood fillers: a – pine wood; b – beech wood

The half-time of crystallisation of polypropylene

The value $t_{0.5}$ is also a useful criterion to compare the nucleating ability of wood fillers. Values of half-time of crystallisation depend on composites type are given in Fig. 5.

In all cases, the composites show a very noticeable decrease in half-time of crystallisation as compared with the pure polymer which is attributed to a nucleant effect of wood on PP crystallisation. It is quite clear that the nucleation is much greater along the wood surface that in the bulk. However, it was

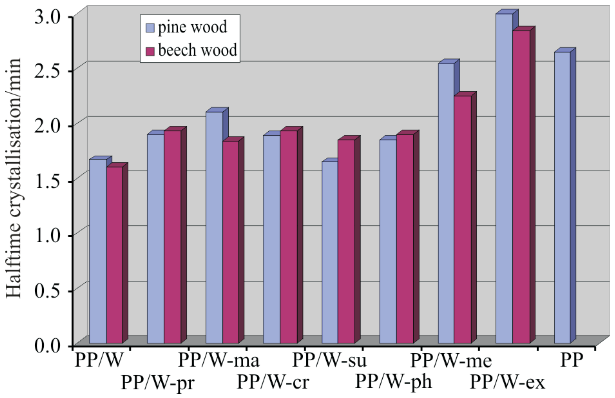

Fig. 5 The half-time of crystallization of pure iPP and in composites with wood fillers

shown that pine as well as beech wood exhibit comparable nucleation ability towards iPP.

It is evident that the unmodified wood has a much better nucleating efficiency because of its lowest of $t_{0.5}$ value (~1.6 min). With respect to the considerable changes in half-time of crystallisation values, treatment of wood filler produced increase of 15–25% for PP/wood modified by anhydrides and 40–90% for PP/mercerized and extracted wood.

Half-time of crystallisation is also affected by the kind of applied chemical treatment. Generally, the $t_{0.5}$ of PP/W-ex and PP/W-me is significant higher up to 60 % in comparison to the composites modified by anhydrides. Reduction in the hydrophilic character of wood in results of chemical treatment can be attributed to increase the nucleating effect. For PP the changes of half-time crystallisation, influenced by the presence of wood fillers, are decreasing in order PP/W-ex>PP/W-me>PP/W-modified by anhydrides >PP/W. It was shown that the chemical modification of wood has an influence on nucleating process of polypropylene. A possible explanation for the effect of kind of chemical modification of wood on the bulk nucleation is as follows. The presence of modifier containing functional groups from anhydrides drastically promotes the nucleation, as compared to wood after extraction and alkalization. It should also be added here that the all wood fillers were treated by alkali before chemical modification by anhydrides. From these results we see that it is possible to predict the crystallisation behavior of polypropylene at a wood surface from how that polypropylene matrix crystallizes in the presence of a different wood surface modified by chemical treatment.

Theoretical aspects in many publications indicate that the nucleation of polymers on substrates is complex and suggested factors have included, among others, crystalline morphology of the substrate, surface topography of filler, the chemical compositions of the surface, the wettability and surface energies of the substrates.

Our results indicate that the unmodified wood has the strongest nucleating ability. It seems that wetting or adsorption of PP molecules on the lignocellulosic materials is not a critical factor. Our results are in contrast to those of Mucha and Krolikowski [20], who observed disturbances the creation of PP spherulitic structure and delays crystallisation process in hydrophilic chiotosan or wood flour/PP composites. They noted the best nucleating efficiency for hydrophobic fillers like talc and carbon black. In our experiment, predominant nucleating effect exhibited strongly hydrophilic wood (unmodified). It has been pointed out that surface topography and chemical compositions of substances in wood rather dominates the nucleating process.

Hata *et al*. [40] have demonstrated that geometrical morphology of the surface plays an important role for nucleation to develop. Moreover, the surface roughness may be critical to improve of nucleation because of the enhanced thermal-stresses at the peaks or valleys, when specimens are cooled from high temperatures to the crystallisation temperatures [15]. It is suggested that small ridges, valleys and grooves present on the unmodified surface of wood will cause the enhancement the nucleating ability. The wood after mercerization and extraction processes have smooth surface as a result of the removal of wax and fats. Such smooth surfaces declined the nucleation ability.

Moreover, Campbell and Qayyum [41] noted that high nucleation in composites system may be caused by the preferential adsorption of impurities in the melt onto wood filler surface. The high concentration of these impurities leads to the high level of nucleation. When in our work some amount of impurities, e.g. waxy substances, fats and resins removed by extraction and mercerization process, the level of active nuclei is reduced.

On studying the effect of nucleating ability of Kevlar, PET, carbon and PTFE fibres on transcrystallisation, Wang and Liu [15] have also suggested that the surface morphology of fibres is due to the enhance the nucleation process.

However, additional investigations are needed to clarify the role of wood surface chemistry and composition of wood on the nucleation activity of wood.

In spite of the large research effort devoted to the study of polymer crystallisation, the nature of the nucleating agents and mechanism through which foreign surfaces promote nucleation are still at the stage of much conjecture and active investigation.

Conclusions

Measurements have been carried out using a differential scanning calorimetry in order to investigate the nucleation ability of PP on different wood fillers.

The different nucleating activity for chemical modified wood filler was evaluated by crystal conversion, half-time of crystallisation and crystallisation temperature. The crystallisation of isotactic polypropylene from the melt in the presence of wood fillers has been shown to produce preferential nucleation at the wood surface leading to increase the crystallisation temperature, decrease of half-time of crystallisation and enhance of crystal conversion in comparison to bulk matrix. From our results we conclude that nucleation ability of polypropylene in composite materials is related to chemical treatment of surface wood. Predominant nucleating effect exhibited unmodified pine and beech wood. Composites containing chemical treated wood fillers showed the tendency reduction the nucleation efficiency of polypropylene. The ability of wood filler to induce nucleation in polypropylene matrix is dependent on the kind of chemical modification of surface wood. A noticeable increase in the half-time crystallisation of PP is observed by the addition of mercerized and extracted wood fillers to PP. These wood materials have an inhibiting influence on PP crystallisation which leads to a 40–90% increase in the half-time of crystallisation (in comparison with PP) and reduction in the crystal conversion due to their weak nucleating effect. During the crystallisation of iPP in the presence of wood modified by anhydrides, the accelerating nucleating effect was observed as compared to wood modified by alkali and wood after extraction process.

During nonisothermal crystallisation, it was found the strong increase of crystallisation temperature by 5–9°C at the PP/pine wood composites and as at the PP/beech composites in comparison to pure PP. It was shown that in the presence of chemical modified wood values of crystallisation temperature of PP were higher by about 1–4°C in comparison to unmodified wood. Moreover, when the composites contained wood modified by maleic, phthalic and succinic then endothermic peaks of the β-phase was noted.

For further investigations into this problem, polarized optical microscope methods to characterize the interphase will be developed. Based on the theory of heterogeneous nucleation, the transcrystallisation and the interfacial free energy difference function of PP on presented in this work different wood/PP systems will determine. Moreover, wide angle X-ray scattering technique will be using to explain the influence of creation of hexagonal phase of iPP in the presence of some wood filler. The results obtained by POM and WAXS methods can be regarded as a potential for more knowledge of nature and extent of interphases.

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