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, chitosan 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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According to the present state of knowledge, well nucleating efficiency seems to play a decisive role in transcrytallisation [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 becausecharacterize real conditions in polymer processing.

**Experimental**

**Materials**

Isotactic polypropylene (iPP) Malen P F-401 (Orlen Plock 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 vacuum 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°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-