Structure–morphology–mechanical properties relationship of some polypropylene/lignocellulosic composites

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ABSTRACT

Natural lignocellulosic materials have an outstanding potential as thermoplastic reinforcement. Polypropylene composites were prepared using different types of lignocellulosic materials by melt blending of 70 wt% polypropylene (PP) and 30 wt% biomasses. The specimens were firstly evaluated for structural and morphological properties by infrared spectroscopy, X-ray diffraction, scanning electron and polarized optical microscopy. Depending on the biomass type, there were evidenced some particular shifts of the infrared bands and also crystallinity changes. An increase in crystallinity is explained by nucleating agent role of biomass. The morphological changes are directly related to variation in mechanical and rheological properties, an increase in Young modulus, melt viscosity and storage and loss moduli being recorded.

1. Introduction

In the last two decades, the use of lignocellulosic materials as fillers in the plastic industry has been progressively increased. Thermoplastics are combined with biomass fillers mainly to produce biomass/plastics composites. It is well known that the use of biomass (lignocellulosics) in combination with common thermoplastics in order to reduce cost and/or to improve performance is not new, a large number of papers being devoted to this field [1–4], but the increased concern for bio-based, eco-friendly products has renewed the interest to develop various kinds of composites.

Natural fibers and powders have been used as reinforcements replacing inorganic fillers and synthetic fibers in thermoplastic polymer matrix [5]. They have several advantages, the most important being their renewability and biodegradability. These natural fillers are also lighter, cheaper, and provide much higher strength [6] per unit mass than do most of the inorganic fillers such as calcium carbonate, talc, zinc oxide, and carbon black.

Other advantages of using a biobased component in thermoplastic composites are the decrease in the machinery wear (due to the fact that biobased resource is nonabrasive), its availability, sustainability, lower density per weight of raw material, making the final product light, flexible, recyclable and with good thermal insulation properties [7,8]. The low processing costs is another advantage of thermoplastic matrix composites, and also the design flexibility and easy of moulding the complex parts.

Thermoplastics, such as poly(ethylene) (PE) [9,10], poly(propylene) (PP) [11–14], poly(lactic acid) [15] and poly(vinyl chloride) (PVC) [16]) with a high melting flow index and low softening temperatures are commonly used to prepare composites with lignocellulosic materials (such as sisal, jute, and sugar cane bagasse, cellulose or wood) [17]. Temperatures above 180 °C results in decomposition of biomass, so processing temperatures, usually below this value are needed if a biomass material is used as filler [1], to avoid their thermal degradation.

Composites based on wood – high density polyethylene, both recycled and virgin, are mostly used in exterior building components [18]. However, composites made with wood – polypropylene are typically used in automotive applications and consumer products [19], and have also recently been investigated for use in building profiles [20].

The composite components are often selected based on their inherent properties, product need, availability, cost, and the manufacturer's familiarity with the material [19]. The differences observed between the various composites were explained by some specific adhesion mechanisms between matrix and filler (including interdiffusion, adsorption–wettability and chemical bonds).

In order to evidence the structural, morphological, mechanical and rheological properties of the obtained composites, different analytical methods are involved in their investigation. For example, by scanning electron microscopy, the dispersion in the thermoplastics matrix can be examined [21]. FT-IR spectroscopy proved

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to be a useful tool for determining the distribution profile of wood and plastic materials in different types of composites [22]. At the same time, FT-IR spectroscopy correlated with wide-angle X-ray analysis could investigate the so-called crystalline bands of isotactic polypropylene and also the crystallinity degree [23]. Polyolefins/filler interactions play a significant role in determining all properties, including the mechanical and rheological characteristics of composites. It is known that melt rheology is very sensitive in characterization of the formation of percolated structures of fillers in polymeric matrices. Also, the nature of the polymer matrix, distribution and orientation of the reinforcing biomass fillers, influences the mechanical behaviour of composites.

The present study reports the preparation and characterization of polypropylene (PP)/lignocellulosic material composites in order to evaluate the possibility of using of different bio-based materials as fillers and to establish their effect on the matrix properties.

2. Experimental details

2.1. Materials

An *isotactic polypropylene* (PP) J 1100 manufactured by SC ROMPETROL Petrochemical SRL (Romania) with basic stabilization, melting temperature of 170 °C and decomposition temperature range: 205–430 °C, was used. The melt flow index of the polymer was of 26–30 g/10 min (2.16 kg/230 °C) and density at 23 °C was of 0.905–0.917 g/cm³. As bio-based materials different lignocellulosics such as: *Eucalyptus globulus* sawdust (EG), Norway spruce (*Picea abies*) thermo mechanical pulp (NS), energy grass (EnG), *Brassica rapa* (BR), pine cones (PC) and grape seeds (GS) were used. They differ by the concentration of the main components namely hemicelluloses, cellulose and lignin. The amount of carbohydrates (hemicelluloses and cellulose) in *Eucalyptus globulus,* Norway spruce and grape seeds is about 65%, in energy grass and *Brassica rapa* ≈ 42%, and ≈ 35% in pine cones. The lignin content varies between 24.9% and 29.4% in all biomasses, except *Brassica rapa*, which has 17.9% lignin content in composition.

The biomass samples were dried at 80 °C for 24 h and grinded in a Retsch PM 200 planetary ball mill. The obtained powder was sieved and the fraction with maximum size of 160 μm was used for the composites preparation.

2.2. Preparation of composites

For composites preparation a ratio of 70 wt% polypropylene (PP) and 30 wt% lignocellulosic materials (biomass) was selected. This is considered the optimum biomass content to maintain and obtain satisfactory properties when replacing the synthetic polymers with the natural materials [24,25].

Before mixing, the components were dried in a vacuum oven for 24 h at a temperature of 80 °C. The composites were obtained by melt blending in the Brabender mixer chamber, at 175 °C, for 10 min at 60 rpm and their corresponding torque-time curves have been recorded during processing. After the processing step, each sample was pre-melted for 5 min and then sandwiched (in a Carver Press 4394) between two Teflon sheets for 4 min, under a pressure of 200 bars, to obtain plates with thickness of 1 and 4 mm, respectively. PP used as reference material was subjected to the same processing steps. The obtained composites and their notations are presented in Table 1, column 1.

A small amount of PP and composites (processed as mentioned above) was obtained as fine powder by mechanical scratching and milling.

Table 1
Processing characteristics of the studied samples.

Sample	TQ$_{1 \text{ min}}$ (Nm)	TQ$_{5 \text{ min}}$ (Nm)	TQ$_{\text{fin}}$ (Nm)
PP	10	9.2	8.6
PP/EG	8.5	6.1	6.1
PP/NS	7.2	3.9	3.9
PP/EnG	8.5	7	6.8
PP/BR	17.1	11.7	10.7
PP/PC	9	6.6	6.7
PP/GS	10	9.2	8.6

TQ$_{1\text{min}}$ – torque after 1 min of mixing; TQ$_{5\text{min}}$ – torque after 5 min of mixing; TQ$_{\text{fin}}$ – torque at the end of processing.

2.3. Investigations methods

2.3.1. FT-IR spectroscopy

The infrared spectra were recorded in KBr pellets on a Bruker Vertex 70 spectrometer, with a resolution of 4 cm^{-1}, and a number of 64 scans were used. For each sample, the evaluations were made on the average spectrum obtained from three recordings. Processing of the spectra was performed using the Grams 9.1 program (Thermo Fisher Scientific) (license for M-C Popescu).

2.3.2. X-ray diffraction (XRD)

The X-ray diffraction (XRD) diagrams were recorded on a Bruker D8 Advance X-ray diffractometer in Bragg-Brentano configuration, equipped with NaI scintillation detector and filtered with Cu Kα radiation (λ = 1.5406 Å) in 2θ range of 2–40° at a scan rate of 2°/min. The X-ray tube was operated at 30 kV and 36 mA. Processing of the diffractograms was performed using the Grams 9.1 program (Thermo Fisher Scientific) (license for MC Popescu).

2.3.3. Morphological study

Scanning electron microscopy – examination of the fracture surfaces of tensile specimens was done using a Scanning Electron Microscope (SEM, Hitachi/S-3500N, Japan) at an accelerating voltage at 20 kV. The SEM instrument was equipped with a Robinson detector. Samples for cross-sectional images were prepared by placing them into epoxy resins and polishing for high image quality. Before viewing, the fractured surface was sputter coated with Pt by an ion sputter (Hitachi/E-1030 Ion sputter) to increase the surface conductivity. Magnification is given on each photo.

Polarized light optical microscopy – the samples sandwiched between two glass lamellas, were first heated to 180 °C, pressed into thin film and then maintained at 180 °C for 5 min, using a Boetius microscope hot stage. Investigations on the morphological aspects of PP and PP/biomass composites were realized by optical microscopy studies by means of a Leica DM 2500 M microscope, with polarized light, and a magnification of 500×.

2.3.4. Mechanical testing

The processing behaviour was evaluated from the torque–time curves recorded during melt mixing on the Brabender mixer. The mechanical tests specimens have been cut from the obtained plates with thickness of 1 and 4 mm, respectively.

Stress–strain measurements were performed at room temperature on dumbbell-shaped samples (1 mm thickness), on an Instron Single Column Systems tensile testing machine (model 3345) equipped with a 5 kN load cell and activated grips, which prevented slippage of the sample before break, operated according to EN ISO 527:1996 [26]. The cross-head speed used was of 10 mm/min, and gauge length of 40.0 mm.

Impact tests have been performed according to EN ISO 179/2001 [27], on a CEAST Impactor, equipped with a Charpy type hammer having 15 J energy. Similarly with tensile tests, all un-notched