Structure and Properties of Polymer–Wood Composites Based on an Aliphatic Copolyamide and Secondary Polyethylenes

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ABSTRACT: Composite materials based on an aliphatic copolyamide and a secondary polyethylene, as thermoplastic matrices, and wood chips as filler were obtained and characterized. The influence of different factors (polymeric matrix type, fractional composition and geometrical characteristics of wood filler, processing parameters and ratio polymer/wood) on the properties of polymer–wood composites (PWCs) was studied. It was demonstrated that the packing factor F has an essential influence on the properties of PWCs: increasing F values determines an improvement in mechanical properties of these materials. Mechanical properties, thermal behaviour, morphological and diffusion characteristics of the analyzed composites were evaluated through specific methods and reported herein. Morphological and DSC data confirmed the presence of strong interface interactions between polymer and wood. The diffusion characteristics of PWCs showed that the diffusion coefficient D essentially depends on filler content in composites. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 1700–1710, 2006

Key words: composites; thermoplastics; polyamides; polyethylene; mechanical properties

INTRODUCTION

During the recent years, the field of composite materials has rapidly grown in terms of both industrial applications and fundamental research. In fact, because it is very costly to develop new homopolymers, a large part of the research has consisted of attempts to produce polymeric materials with improved properties by the combination of already existing polymers with various fillers, that is, to obtain polymer composites.

Lately, high interest has been shown in organic fillers, which are often production waste, are able to undergo biodegradation processes, and have low costs.[1–19] Polymer–wood composites (PWCs) based on thermoplastic polymers and wood chips are a kind of polymeric material that uses organic fillers.[3–10] PWCs bring together the properties of polymers and wood and processable in goods by methods that are typical for polymers: extrusion, pressing, and molding.[7–12] PWCs have been studied intensively as an innovative alternative to already known materials that may contribute to the reduction of vegetal biomass waste and prevent pollution with plastic waste.[2,4]

In previous investigations,[7–19] it has been shown that the properties of PWCs depend on several factors: the physical and mechanical characteristics of the polymer matrix, the fractional composition of the wood particles, the presence of chemical interactions between the polymer and wood chips, and the processing conditions. From this point of view, to obtain a PWC with high performance, it is necessary to use polar thermoplastics or polymers having functional groups that are able to interact with the functional groups on the wood surface. On the other hand, the polymer must have high mechanical characteristics, such as those of polyamides or polyethyleneterephthalate.

However, the presence of a wood component in composites raises some difficulties from a technological point of view because lignocellulose thermodegradation begins around 200°C, whereas the temperature needed to process high-melting engineering thermoplastics is much higher (240–270°C for polyamides and about 300°C for polyethyleneterephthalate).

Therefore, for this study, a low-melting-point aliphatic copolyamide (CoPA) was chosen as the matrix for a PWC, and a secondary polyethylene having functional groups able to interact with wood[16] was used for comparison. The influence of the polymeric matrix type, the fractional composition of the wood filler, and

TABLE I
Properties of the Polymers

Characteristic	Value	
	CoPA	SPE
Chemical composition	Copolyamide 6/6.6/6.10	Recycled low-density polyethylene
Granulation (mm)	0.3–0.5	2–4
Density at 23°C (g/cm^3)	1.11	0.92
Crystallinity (%)	58	37
Melt flow index (g/10 min)	11.9	0.55
Interval of melting temperature (°C)	125–135	108–120
ΔH_m (J/g)	41.5	108.1

the polymer/wood ratio on the properties of the PWCs were studied.

EXPERIMENTAL

Raw materials

As polymer components, we used

- A low-melting-point CoPA, which was supplied by the Institute of Macromolecular Chemistry "Petru Poni" (Iasi, Romania).
- A secondary low-density polyethylene (SPE) obtained by the recycling of polyethylene films from agriculture.

The characteristics of the polymeric components are listed in Table I.

As the wood component, pine chips were used. The chips were separated on vibrosieves with size fractions of less than or equal to 0.2, 0.2–0.5, 0.5–1, 1–2, 2–3, 3–5, 5–7, and 7–10 mm (hereafter, the size of the fraction is marked by its upper limit). The yield of each fraction was defined by weighing. Wood fillers with various sizes were used for composites based on SPE, whereas composites based on CoPA contained particles with size fractions of 2 mm or less.

The values of the packing factor (F) of the wood filler were determined by vibrational compacting of the wood chips in a glass measuring cylinder with a diameter of 80 mm. The portion of chips by weight (P) was placed in the cylinder, and its volume (V) was measured after vibrational compacting. The value of F was calculated as follows:

$$F = \frac{P}{V\rho_f} \tag{1}$$

where ρ_f is the density of the wood filler particles.

The measurement of the geometrical dimensions of the filler particles was carried out with optical microscope (MBS-9; Moscow, Russia); their weight was determined with a Sartorius 4431 microbalance (Gottingen, Germany). Ten particles of each fraction were taken for measurements. ρ_f was calculated with the weight and geometrical dimensions with the following equation:

$$\rho_f = \frac{\sum\limits_{i=1}^{n} m_i}{\sum\limits_{i=1}^{n} l_i b_i h_i} \tag{2}$$

where m_i, l_i, b_i, and h_i are the weight, length, width, and thickness of a particle i and n is number of particles ($n = 10$ in our case). Calculations had a given value of ρ_f of 0.496 g/cm^3 for particles of each fraction.

Preparation of the composites

The influence of the processing conditions on the properties of PWCs has already been studied.[7,11,12] For a homogeneous mixture of a polymer with wood chips and for a uniform repartition of polymer on a wood chip surface, it is necessary to use a two-stage compounding method.[7,11]

In the first stage, dry wood chips and polymer were mixed in a predetermined ratio; then, the mixture was homogenized in an extruder with a forming head temperature of 160°C. The homogenization of the polymer–wood mixture in extruder at a temperature higher than the polymer melting point resulted in wood particles covered with a polymer layer. The polymer–wood mixture was transformed by extrusion into pellets 2–3 mm in size. Subsequently, these pellets served as a semifinished product for the further pressing.

In the second stage, the pellets were pressed in a steel compression mold at 150°C for 3 min under a pressure of 20 kg/cm^2. After pressing, the mold was replaced in the cold press, where it was cooled to room temperature under the same pressure.

Measurements of the mechanical properties

Tensile strength (σ_t)

σ_t measurements (ASTM 638-90) were performed on a mechanical tensile machine (FU-1000; Rauenstein, Germany) at room temperature and a crosshead speed of 20 mm/min. Samples were blade-shaped with length of 150 mm, a width of the testing part of 10 mm, and a thickness of 4 mm and were pressed from polymer–wood pellets in a special mold.

Bending strength (σ_b)

Three-point bending tests (ASTM 790-90) were carried out at room temperature at a crosshead speed of 3 mm/min and tested with a span of 75 mm in a PM-400 testing machine (Ivanovo, Russia). The composite samples with dimensions of 80 × 10 × 5 mm were cut from the molded plates of the PWC.

Impact testing

Impact testing (unnotched Izod; ASTM D 256-90) was carried out with a Dinstat impact-testing machine (Darmstadt, Germany). The samples for testing, with dimensions of 15 × 10 × 5 mm, were cut from the molded plates.

At least five samples were tested for each type of measurement.

Differential scanning calorimetry (DSC)

The thermal characteristics of the composites were determined with a Mettler TA Instrument DSC 12E calorimeter (Atkinson, NH). Samples were maintained for 3 h at 80°C *in vacuo* for water removal before testing. Samples were heated at a rate of 10°C/min at atmospheric pressure under a purge of dry nitrogen. The melting point and melting heat (ΔH_m) of the composites were determined from the endothermal peak area.

Diffusion characteristics

The diffusion characteristics of the PWCs were determined by the immersion of the samples in water at ambient temperature and the measurement of the increase in their weight after well-determined time intervals (ASTM D 570-86). The sample dimensions were 50 × 50 × 5 mm.

After an interval of immersion, the sample was taken out the water, dried with a filter paper, and weighed in an analytical balance (±0.001 g). Then, it was immersed in water for the next interval. The period of a manipulation of the sample out of water was no longer than 1 min. The weight increase due to water sorption [ΔP (%)] was calculated as follows:

$$\Delta P = \frac{(P_t - P_0) \times 100}{P_0} \quad (3)$$

where P_0 and P_t are the weights of the sample before and after exposure to water, respectively. From a diagram of ΔP versus time, the equilibrium sorption (P_m) was defined.

A diffusion coefficient (D; cm^2/s) corresponding to the initial period of sorption was defined from the slope of curve P_t/P_m versus $\tau^{1/2}/h$ (where τ is the time
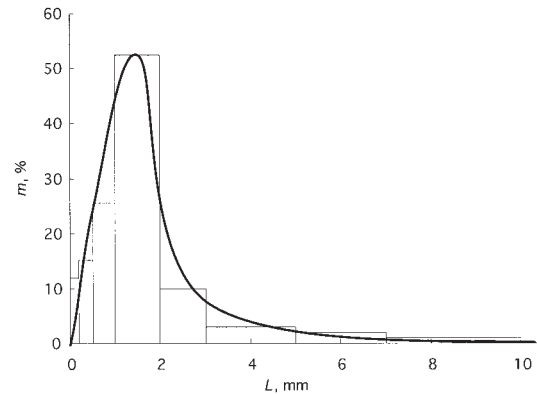

Figure 1 Differential curve of weight distribution of the wood filler particles.

of sorption and h is the thickness of the sample) and was calculated with eq. (4):[20–22]

$$D = \frac{\pi}{16}\left[\frac{\Delta(P_t/P_m)}{\Delta(\tau^{1/2}/h)}\right]^2 \quad (4)$$

IR spectra

We used both a transmitting method and a method of multiple reflection in the surface layer to characterize the samples through IR spectrometry (Zeiss Jena, Germany). IR spectra were obtained on a Specord M-80 instrument (the wavelength ranged between 4000 and 200 cm^{-1}) with 1% w/w composite/KBr pellets.

Morphological observations

A transmission electron microscope (type BS 340, Tesla, Czech Republic) was used to observe the morphology of the composites. The surface of samples were prepared by successive treatments of abrasion (from coarse to fine) and by polishing with a special paste in the last stage. For obtaining the image, a replication method was used.

Optical observation of the PWC morphology was performed with an optical microscope (IOR type MC1, Bucuresti, Romania).

RESULTS AND DISCUSSION

Influence of the characteristics of the wood filler on the PWC properties

Geometrical characteristics of the wood filler

The data of the sieve analysis resulted in a differential curve of the filler fraction distribution, as presented in Figure 1. This describes the weight part of the particles (m) of each fraction with fraction size (L) in the bulk of the filler. The highest yield in the chip processing had an L of 1–2 mm (more than 50%). The distribution

curve was asymmetric and had a typical shape for a normal logarithmic distribution. In accordance with literature data,[23] the systems, which were obtained by grinding, crushing, and pounding, showed this type of distribution.

One of the most important characteristics of filled polymer composites is the packing factor of filler F. The value of F depends on the particle shape and on the possibility of skeleton or chain structure formation. The F parameter is a limit of system filling, and it is equal to the highest possible filler volume fraction at a given type of packing:

$$F = \frac{V_f}{V_f + V_P} \tag{5}$$

where V_f is the volume occupied by the filler particles at the highest possible filler fraction and V_p is the volume occupied by the polymer (space among filler particles).

For statistically packed monodispersed spherical particles of any size, the F value is equal to 0.64.[24] In the case of deviation of particle shape from the spherical one or of the volume filler skeleton structure formation, the F value decreases due to increasing V_p. The use of polydispersed filler particles results in an increase in F.[25] As a rule, real fillers have F values smaller than 0.64. Thus, the particle shape, fractional size, and spatial distribution of particles influence the characteristics of the composite through the value of F.

It is possible to increase the content of a wood filler in a composite if the limit of system filling is shifted, that is, by an increase in the value of F. Such a possibility is given by the usage of a fractions mixture, for example, of coarse, middle, and fine particles. In this case, the middle-size particles occupy the space between the coarse ones and the fine particles. Maximal filling of the polymer matrix space provides the optimal relationship between fractions. Methods of regulating the fractional composition of wood filler were described in literature.[26] In accordance with this, fillers with $F = 0.71$ were prepared with a mixture of fractions having L values of 7, 1, and 0.2 mm, respectively.

Figure 2 shows the dependence of F versus L of the wood filler. The value $F = 0.58$ for the smaller fraction (0.2 mm) was close enough to the theoretical value of 0.64 for the spherical particles. The value of F rapidly decreased with increasing L, which was caused by the increase in the dimensional anisotropy of the particles along with their increasing size. The evaluation of the geometrical size and shape of the wood particles of various fractions was done by a microscopic method. Adduced sizes of particles were calculated from eqs. (6)–(8):[27]
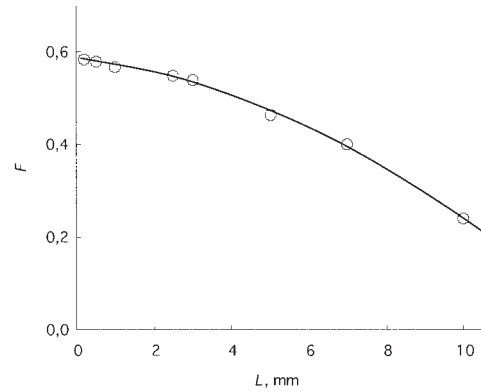

Figure 2 Influence of wood particle size on F values.

$$l_r = \frac{\sum\limits_{i=1}^{n} m_i}{\rho_f \times \sum\limits_{i=1}^{n} b_i h_i} \tag{6}$$

$$b_r = \frac{\sum\limits_{i=1}^{n} m_i}{\rho_f l_r \times \sum\limits_{i=1}^{n} h_i} \tag{7}$$

$$h_r = \frac{\sum\limits_{i=1}^{n} m_i}{\rho_f l_r \times \sum\limits_{i=1}^{n} b_i} \tag{8}$$

where l_r, b_r, and h_r are the adduced values of the length, width, and thickness of the filler particles, respectively.

The results of the calculations were used to establish the dependence of the reduced values of l_r, b_r and h_r of the wood particles on L (Fig. 3). With increasing L, the thicknesses of the particles decreased. For small fractions, all three dimensions were comparable, and the shape of the particles came close to the cubic shape, whereas the coarse particles had a pronounced flake shape (their l_r and b_r exceeded their thickness by more than one order of magnitude). Accordingly, in the case of random distribution, the flakes had loose packing with low values of F. Hence, for the wood filler, the size of the particles and their shape were interrelated, and this resulted in the value of F.

The influence of F values on the PWC properties is presented in Table II. For the PWCs, a SPE polymeric matrix (polymer/wood mixing ratio = 60/40) and
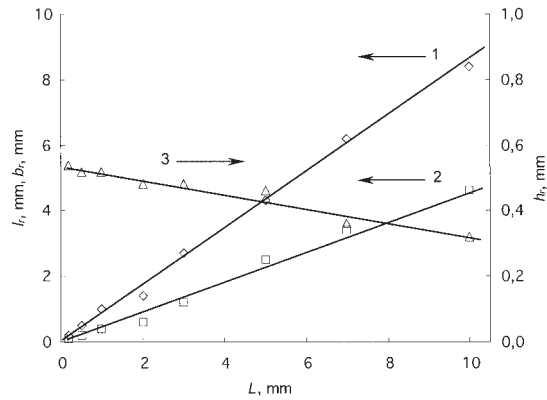
Figure 3 Dependence of adduced values of (1) l_r, (2) b_r, and (3) h_r of wood particles on the size of the filler L.

various wood chip sizes (1.00 and 0.20 mm and a mixture of particles) were used. For all samples, the following parameters were determined: σ_t, water sorption (ΔP), and swelling (ΔS) for 24 h and operating torque of the extruder screw (M).

As presented in Table II, the PWC with $F = 0.71$ (corresponding to the mixture of particles) determined the higher values for the measured parameters. For the composite with $F = 0.71$, σ_t increased by 50% compared to that of the PWC with $F = 0.57$ (with $L = 1$ mm). The water resistance sharply increased: ΔP and ΔS were three to four times lower. A decrease in M showed the improvement of PWC processability due to the increase in the polymer layer thickness between the wood particles, along with an increase in F, for a constant polymer/wood ratio.

This may be easy to understand if we consider eq. (9):

$$R = L\left(\sqrt[3]{\frac{F}{\phi}} - 1\right) \tag{9}$$

where R is the distance between particles and ϕ is volume content of the filler in the composite. The increase in F determined the increase in R; that is, the polymer layers between wood particles became thicker, which was equivalent to a decrease in wood content.

TABLE II
Characteristics of SPE–W Composites with Different Values of F

L (mm)	F	σ (MPa)	ΔP (%)	ΔS (%)	M (gm)
1.00	0.57	5.2	3.4	2.5	1200
0.20	0.58	5.9	2.4	2.0	1350
Particles mix	0.71	7.9	0.9	0.6	1000

TABLE III
Influence of Processing on Parameters of the Wood Filler

Composite	C (wt %)	ϕ (vol %)	ρ (g/cm³)	ρ_f (g/cm³)	K_c
Polymer–wood mixture	40	55	0.685	0.496	1
Extruded PWC	40	44	0.857	0.785	1.57
Pressed PWC	40	34	1.020	1.167	2.33

Influence of PWC processing on the wood filler characteristics

Compared with mineral fillers, wood fillers have a characteristic that should be taken into account when composite formulation and optimal processing parameters are established. The capillary–cellular structure of wood results in its easy deformability under squeezing stresses. During pressing, ρ_f is modified from 0.5 to 1.45 g/cm³.[28] The processing of PWCs in an extruder and their subsequent pressing can essentially change the wood filler characteristics. For calculation of ρ_f and ϕ in the composite formulation, the following equations may be used:

$$\rho_f = \frac{\rho - \rho_p(1 - \phi)}{\phi} \tag{10}$$

$$\phi = \frac{C\rho_p}{C\rho_p + (1 - C)\rho_f} \tag{11}$$

where ρ, ρ_p, and ρ_f are the densities of the composite, polymer, and filler, respectively, and ϕ and C are the volume content and the weight of filler in the composite, respectively. The combined solution of eqs. (10) and (11) gives eq. (12):

$$\phi = \frac{\rho_p - \rho(1 - C)}{\rho_p} \tag{12}$$

All of the calculated data presented in Table III were determined for wood composites with an SPE matrix.

For composites containing 60 wt % SPE and 40 wt % wood filler with $\rho_f = 0.496$ g/cm³, ϕ, calculated according to eq. (11), was 55 vol %. ρ of this composite calculated from eq. (10), which implied that the additive combination of the densities of the components, ρ_p and ρ_f, was equal to 0.685 g/cm³, whereas the experimental measurement of the density of the extrudates showed a value of $\rho = 0.857$ g/cm³. In this case, ϕ in the secondary low-density polyethylene–wood (SPE–W) composite, prepared by extrusion, according to eq. (12), was $\phi_e = 44$ vol %, and the density of the filler (ρ_{fe}), calculated from eq. (10), was 0.785 g/cm³.

Hence, the effect of the shear stresses on the composite melt during its processing in the extruder led to and increase in ρ_{fe} from 0.496 to 0.785 g/cm³ and to a

decrease in ϕ from 55 to 44 vol % at a constant weight content of 40 wt %. The increase in ρ_{fe} was a result of the compression of filler particles and a decrease in its L, which in its turn, led to an increase in R between the wood particles.

This effect, in accordance with eq. (9), caused an appropriate increase in the F/ϕ relationship, equivalent to the decrease in ϕ. The difference in the weight and volume values of the filler content for composites filled with plant filler was reported previously in the literature.[29]

During the pressing of the extrudates of the SPE–W composites, the highest ρ (1.020 g/cm³) was reached at the highest degree of compression (K_c = 2.33, where K_c is the compression coefficient) of the filler particles. In this case, the calculations gave a value of the density of the filler in a composite obtained by pressing (ρ_{fp}) = 1.167 g/cm³ for ρ_{fe} and ϕ = 34 vol % (at 40 wt %). These data are also listed in Table III.

It was possible to define a K_c that for the extruded composites was equal to ρ_{fe}/ρ_f = 1.57 and for the pressed systems was ρ_{fp}/ρ_f = 2.33. This coefficient indicated an increase in ρ_f during the processing of the PWCs.

On the basis of these data, we concluded that it was necessary to take into account this effect when processing the composites containing wood filler. This allowed the introduction in the composite formulation of a much higher amount of filler than that obtained by the calculations.

Properties of PWCs with different polymer matrices

Mechanical properties of the composites

σ_b was studied for two types of composites, one with a SPE matrix and the other with a CoPA matrix. For composites based on SPE, wood particles with various sizes were used. For the composite based on CoPA, the wood particle size was 0–2 mm.

The dependence on σ_b of the composites versus wood filler content and fractional composition is given in Figure 4 (curves 1–3 are for SPE-based composites, and curve 4 corresponds to CoPA-based composite).

An increase in the content of small fractions (0.2 and 2 mm) led to a decrease in σ_b (curves 1 and 2), which was caused by the increasing influence of the interfacial polymer–wood boundary, which weakened the composite strength. A decrease in the composites strength as a result of the introduction of a filler is well known for the case of the mineral fillers, where the adhesion interaction in the polymer matrix–filler is weak.[30]

However, for the wood filler with a particle size of 5 mm, a particular characteristic of the dependence on σ_b versus C was observed (curve 3). Evidently, in this
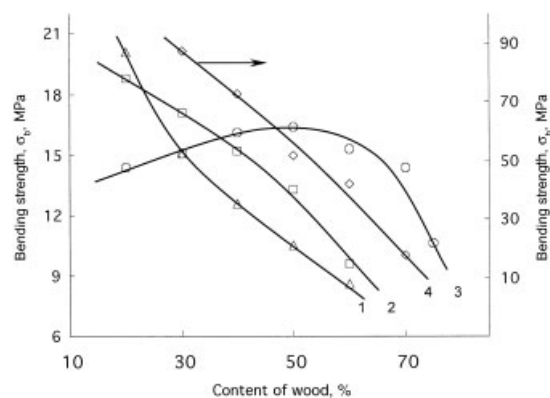

Figure 4 σ_b of SPE–W composites with different wood particle sizes, (1) 0–0.2, (2) 1–2, and (3) 3–5 mm, and (4) CoPA–W composites with a wood particle size of 0–2 mm.

case, a skeleton of wood filler was formed, and it reinforced the polymer matrix under the influence of bending stress. The increase in σ_b was a result of a change in the particle shape along with an increase in their size: for 5-mm particles, l_r and b_r were significantly higher than for 0.2- and 2-mm particles. As consequence, they had a pronounced flake shape (see Fig. 3). This effect promoted the reinforcing skeleton formation by providing the overlap of particles. If the filler content was higher than 50%, the values of σ_b decreased, apparently because of the appearance of defects caused by imperfect wetting of the filler surface by the polymer melt.

For the copolyamide–wood (CoPA–W) composite (curve 4), the dependence of σ_b on the filler content had approximately the same shape as that of the SPE–W composite with particle sizes of 1–2 mm (curve 2). The difference was in the values of σ_b, which were significantly higher (ca. four times higher at an equal content of wood) for the CoPA–W composite. These data were in good correlation with the higher mechanical characteristics for polyamidic matrices than for SPE (e.g., σ_t of PA6 was four to six times higher than high density polyethylene, HDPE[31]).

σ_t and impact strength (a_n) of the CoPA–W composites depended on the filler content and are shown in Figure 5. The $\sigma_t \propto C$ dependence (curve 1) was similar to σ_b (see Fig. 4, curve 2), whereas a_n had maximum value at about 50% wood content. Obviously, the formation of the reinforced skeleton of wood filler affected the value of a_n, in contrast to σ_t. This was caused by the mechanism of breaking, which was different. The measurement of σ_t was accompanied by the development of an extreme deformation in the material that was defined by a possible structure reorganization and reorientation of macromolecules as a result of the overcoming of intermolecular bonds. By the indtroduction of wood particles in a polymer matrix, the orientation processes were hindered (the
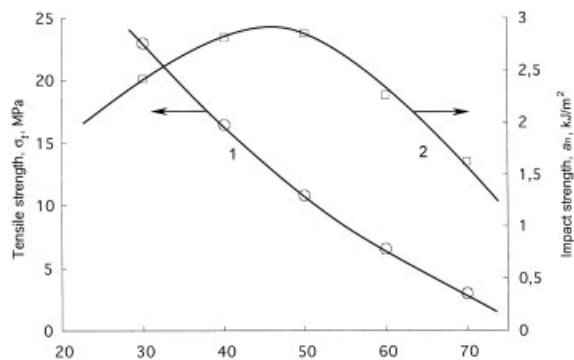
Figure 5 Dependence of the (1) σ_t and (2) a_n of CoPA–W composites on the wood filler content.

value of elongation decreased from 300% for pure CoPA to 2–3% for the CoPA–W composites with a wood content higher than 30%).

It is known that the inclusion of a stiff filler in a polymer matrix can induce an increase in the toughness of a composite. Still, it leads to a sharp decrease in the elongation at break. When a high adhesion exists between the filler and matrix, such an effect is foreseen even at a small content of filler. If adhesion is weak, the elongation can decrease more slowly, but it becomes very small at a high filler content.[32,33]

Simultaneously, a boundary region polymer–wood is developed in a composite. This is the most weak element of the system, wherein the breaking mainly takes place. In fact, the value of σ_t decreases monotonically with an increase in the filler content.

The a_n testing for the composites is accompanied by crack formation on the inside of the material due to the high rate of loading. If the rate is high enough, the deformation develops through the crack growth along with breaking of the intermolecular bonds.

The presence of filler inclusions in a polymeric matrix can induce a reinforcing effect, which determines an increased impact resistance due to the fact that microcrack development is blocked by filler particles. So, for further growth, an additional stress is required.

This principle has been applied to obtain impact-resistant polymers (e.g., impact-resistant polystyrene containing elastomer particles, which suppressed cracks due to an elevated relaxation rate).

In our case, the CoPA–W composite was considered a stiff matrix of CoPA that contained tough inclusions of wood. For wood contents higher than 50%, the value of a_n decreased. This may have been associated with the appearance of additional defects in the composite structure due to the loss of continuity in the polymer matrix.

Polymer–wood interactions

In Figure 6, IR spectra of the pure components (CoPA and wood) and the CoPA–W composite with a wood

content of 20% are shown. The wood spectrum (curve 1) was characterized by the presence of three main regions:

- One with a maximum at 910–960 cm^{-1}, associated with the deformation motion of —CH groups.
- Another one with a maximum at 1020–1050 cm^{-1} determined by the cyclic ethers of cellulose.
- A peak at 3310 cm^{-1}, attributed to the valence vibration of —NH— groups.

These data were in accordance with the features of the chemical structure of wood.[34] Because the natural polymers in which wood consisted have polar pendant groups (—OH, —O— and —COOH),[33] it was obvious that the surface of the wood filler had reactive groups that could participate in chemical and/or physical intermolecular interactions with reactive groups of the polymer matrix.

The IR spectrum of pure CoPA (Fig. 6, curve 2) showed the presence of the following peaks: 3301 and 3063 cm^{-1} (N—H chemical bonds), 2919 cm^{-1} (C—H bonds), 1635 cm^{-1} (amide I), 1542 cm^{-1} (amide II), 1273 cm^{-1} (amide III), 946 cm^{-1} (amide IV), and 690 cm^{-1} (amide V). The presence of IR absorbing —C=O (1635–1645 cm^{-1}) and —NH (1550 cm^{-1}) groups was revealed in the same diagram.

As for the CoPA–W composite (curve 3), the spectrum showed changes that occurred for the peak at 3330 cm^{-1}, which was attributed to valence vibrations of the bounded NH groups. With the introduction of a wood component in CoPA, the profile of the curve changed, resulting in a wide region, which included a new, low-intensity peak at 3450 cm^{-1}, which appeared
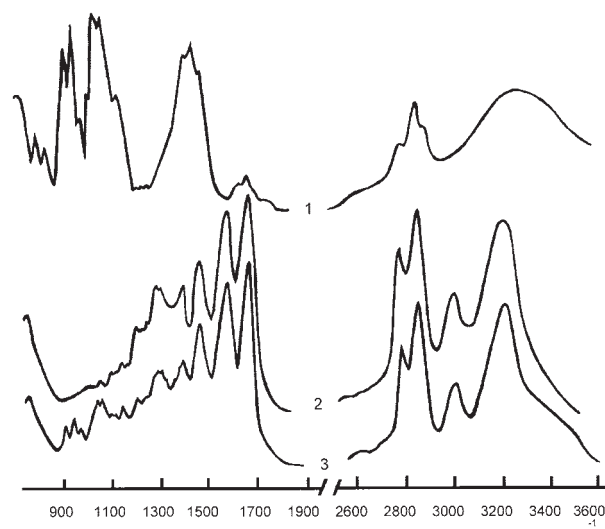

Figure 6 IR spectra of (1) the wood component, (2) pure CoPA, and (3) the CoPA–W composite.

TABLE IV
Data of DSC Measurements for the ΔH_m
of the CoPA and SPE Composites

Composites with various wood contents	ΔH_m (J/g)	
	CoPA–W	SPE–W
Pure polymer matrix	41.5	108.1
5% wood PWC	—	99.8
30% wood PWC	38.2	93.3
40% wood PWC	30.6	—

in the spectrum. Repartition of the peak intensities at 1280, 1380 and 1460 cm^{-1} were also observed.

All of these changes could be explained by the partial destruction of intermolecular hydrogen bonds in CoPA and the formation of new hydrogen bonds at the interfacial polymer–wood boundary. At the same time, a new type of bond between polar groups from CoPA (C=O, —NH—) and the functional groups of wood (—OH, C—O—) was formed. The presence of these interactions was confirmed by IR spectroscopy data. The existence of such interactions between SPE and the wood filler surface was previously reported.[16]

The results of a calorimetric study confirmed these conclusions. The measurements of ΔH_m of the CoPA–W and SPE–W composites showed that the introduction of wood into the polymer matrix (CoPA or SPE) led to a decrease in ΔH_m, and this decrease was greater with increasing wood content (Table IV).

The interactions between the polymer and wood led to the binding of some macromolecular chains to the wood surface. This determined a decrease in the polymer rate of crystallization (i.e., ΔH_m) near the surface of the wood because the polymer chains bound to wood were excluded from the crystallization process that took place during the cooling after composite manufacturing.

Morphological study of the composites

The images of the wood-based composites submitted to study showed a random distribution of the wood filler in the polymer matrix. The images presented in Figure 7(a,b) were obtained with an optical microscope, whereas the image in Figure 7(c) was obtained with an electronic microscope, for a SPE–W composite having 30% wood with $L = 2$ mm.

From Figure 7(a), it is obvious that particles had an anisotropic shape, which was confirmed by the data presented in Figure 3, where l_r, b_r, and h_r of the particles are shown. The technology for composite manufacturing provided the distribution of wood chips along with the presence of polymer layers between the particles.

When the magnification of the microscope increased, the disclosure of the wood intimate structure

became possible [Fig. 7(b)]. The capillary–cellular structure of wood was revealed, and that justified the low value of density (0.496 g/cm^3 according to our previous calculations) and wood deformability under pressure during PWC manufacturing (see Table III).

Figure 7(c) shows the electron microscope image of the polymer–wood boundary region. It was easy to observe the close contact between those two components, without any discontinuity, despite the presence of some small elongated pores in the polymer phase close to the polymer–wood interface, which are also visible in this image. This was a proof of the strong adhesion forces that appeared at the contact zone between the polymer and wood due to interface interactions.

Diffusion characteristics of PWC

One of the most important characteristics of a composite, from an applicative point of view, is water resistance, which defines the ability of a composite to maintain its properties during exploitation toward water and/or atmospheric moisture without further treatment to protect the surface.

Therefore, a definition of diffusion parameters for a water sorption process gives one the possibility of modifying the composite formulation to improve its service properties.

Water sorption of the PWCs based on CoPA, with various amount of wood, was studied (Fig. 8). ΔP [the value of ΔP was calculated according to eq. (3)] values, depending on τ toward water, is presented in Figure 8(a). ΔP was minimal for composites with wood contents of 30 and 40%. The increase in filler content up to 60 and 70% led to drastic changes in the curve shape: the rate of ΔP sharply increased, and the values of P_m increased as well. The curve corresponding to the PWC with 50% wood (located between these two groups of curves) was closer to PWCs with low contents of wood.

On the basis of these results, kinetic curves of sorption were calculated [Fig. 8(b)]. The initial parts of the curves were linear, which means that Fick's law for the process of water diffusion in the PWCs was fulfilled in short time intervals. D was calculated from the slope of the linear parts of the curves, according to eq. (4), which resulted from Fick's law.

The values of D, depending on the wood content, are shown in Figure 9. As shown, when the wood content exceeded 50%, the value of D increased two orders of magnitude. The composite showed percolation behavior with the presence of a percolation threshold at about 55% filler in the PWCs. This may have indicated a drastic change in the composite structure and the appearance of a great amount of cracks and pores due to the discontinuity of the polymer matrix and facilitated access of the diffusant to the
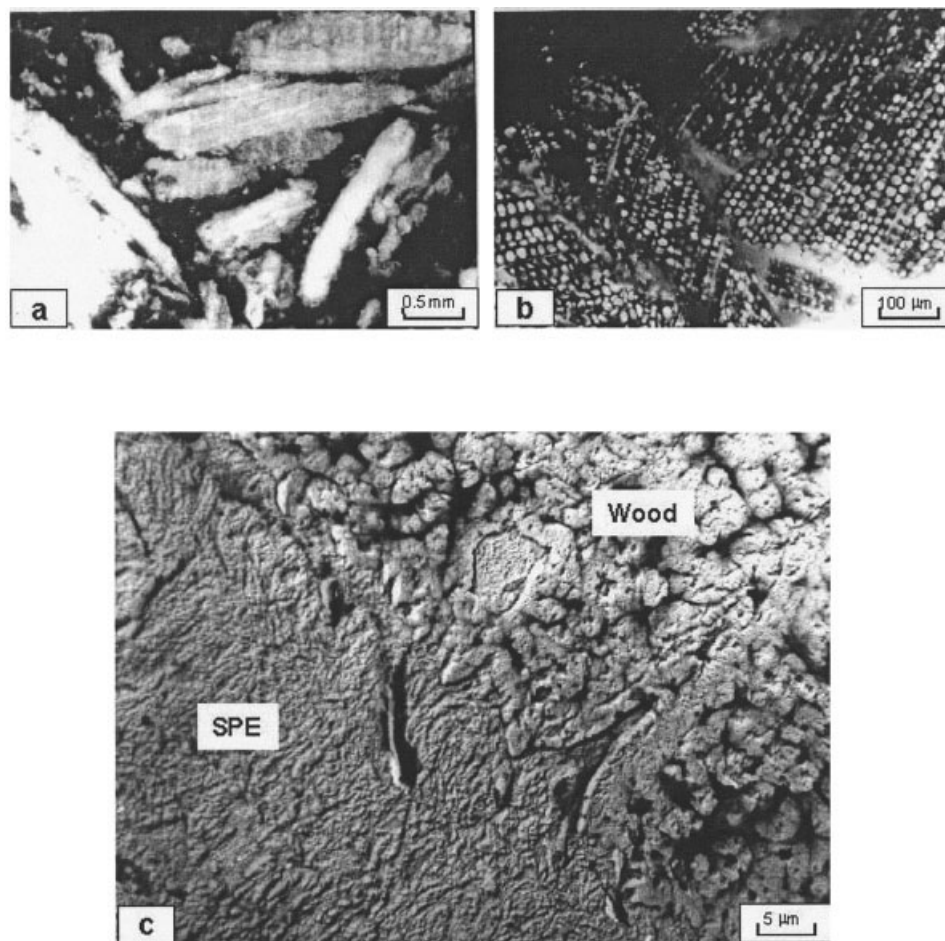
Figure 7 Microstructure of SPE–W composites at different magnifications obtained with (a,b) an optical microscope and (c) an electron microscope.

hydrophilic filler. Also, the arising pores were additional centers of sorption that sharply raised the value of P_m and contributed to the increase in D.[35] These data were in good correlation to the dependence of a_n on wood content (curve 2, Fig. 5), where the maximal strength was reached for 40–50% wood. During further filling of the composite, the value of a_n sharply decreased, which was natural when we considered that the defects (pores and cracks) appeared in the structure of the composite and promoted the break of the material.

Hence, in the region corresponding to 50–60% wood, the continuous and free-of-defects structure of the polymer matrix was destroyed. This region was defined by value of F that was a limit of the system filling and indicated the maximal content of filler, when the polymer matrix maintained its continuity. The introduction of a higher amount of filler than the value of F destroyed the continuity of the polymer matrix, which led to the appearance of pores. For the wood filler with $L = 2$ mm (used in CoPA–W composites), the value of F was 0.56. Consequently, the composites should contain less wood to provide high performances. This allows us to conclude that the optimal composition of the PWCs was reached when the CoPA/wood ratio was 50/50.

CONCLUSIONS

The data presented in this article led us to the following conclusions:

1. The geometric characteristics of the wood filler and its fractional composition defined the density of the filler packing, which was characterized by the value of F. The increase in F of the wood filler led to improved characteristics for the PWCs.
2. PWC processing influenced the parameters of the wood filler inside the composite. The compression stressed in the extruder, and pressing led to the deformation of wood particles and a significant increase in their density, which allowed us to introduce a higher content of wood into the polymer.

3. The study of mechanical characteristics showed different behaviors of the composites in terms of σ_t and a_n. σ_t monotonically decreased with increasing filler content, whereas a_n was characterized by extremes at 40–50% wood content. This was caused by different mechanisms of composite breaking.

4. The SPE–W and CoPA–W composites showed different interfacial interactions between the wood filler and polymer matrix, as reflected in their IR spectra and ΔH_m values, depending on wood content.

5. Morphological investigations demonstrated the presence of close contact between the wood and polymer matrix at their interface, which was evidence of good polymer–wood adhesion interactions.

6. Measurement of water sorption in the CoPA–W composites showed that in the initial period of sorption, the kinetics influenced the fulfillment of Fick's law. The value of D indicated percolation behavior with the presence of a percolation threshold about 55% wood content in the PWCs. This effect was due to the change in the composite structure along with an increase in wood content, namely, to polymer matrix discontinuity and the appearance of pores at filler contents higher than 55%.
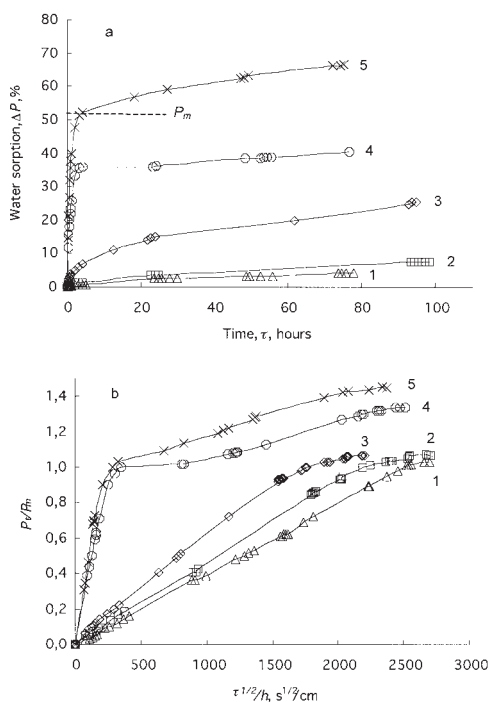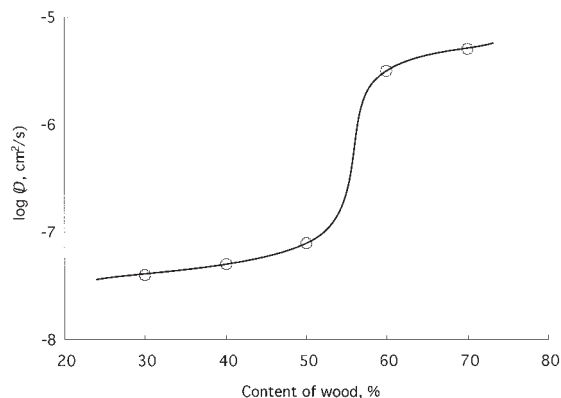

Figure 9 Dependence of D on the content of wood filler.

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Figure 8 (a) ΔP of PWC based on CoPA containing various contents of wood filler and (b) kinetic curves of sorption. Contents of the wood filler = (1) 30, (2) 40, (3) 50, (4) 60, and (5) 70%.

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