New Thermoplastic Materials Reinforced with Cellulose Based Fibers

Carlos Andrés Rodríguez,[1] Jorge Alberto Medina,[1] Helmut Reinecke[2]

[1]*Centro de Investigación en Procesamiento de Polímeros, Departamento de Ingeniería Mecánica, Universidad de los Andes, Carrera 65B, 17A-11, Bogotá D.C, Colombia*
[2]*Instituto de Ciencia y Tecnología de Polímeros, CSIC Juan de la Cierva 3, E-28006 Madrid, Spain*

ABSTACT: The preparation of new cellulose fiber reinforced thermoplastics is described, and the mechanical properties and water absorption of these materials are measured.

In order to improve the compatibility between cellulosic and plastic materials, different amounts of coupling agents, such as organotitanate compounds, maleic anhydride copolymers and their combinations, are studied. As a filler, pine fiber, rose, carnation or coffee husk is used. Furthermore, the influence of the composition of the composites and the particle size of the filler on the material properties of the thermoplastics are investigated. The surface of the fractured samples is analyzed using scanning electron microscopy (SEM). © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3466–3472, 2003

Key words: composites; mechanical properties; fibers

INTRODUCTION

For the past two decades, natural fibers have been used as fillers and reinforcement in low-melting-point thermoplastics.[1] These organic filler particles have been shown to represent low-cost renewable reinforcements that enhance material properties such as stiffness and strength. Further advantages are their environmental friendliness and low density in comparison with conventional inorganic fillers. For all of these reasons, the development of composites reinforced with cellulose based fibers is a subject of intense research efforts and has led to extensive academic[2–5] and patent literature.[6–9]

Although much research has been conducted on this subject and there are numerous products available on the market, there are still valid reasons to continue investigating this field to understand better how the process parameters influence the final properties of the materials and to find new composites with improved performance.

The application of natural fibers as reinforcing materials in thermoplastics requires a strong adhesion between the fiber and the polymer matrix. Cellulose has a strong hydrophilic character due to three hydroxy groups in its monomeric unit, and polymers are generally hydrophobic. For this reason, means have to be found to overcome the poor compatibility between the two phases and to achieve a good interphase bonding.

In this article, the properties of thermoplastics reinforced with varying amounts of cellulosic fiber materials of different origins and sizes are studied. Furthermore, this study investigates how the quality of the filler-polymer interphase is influenced when using different coupling agents, such as maleic anhydride based copolyethylene, neoalkoxy titanates[10–11] or mixtures of them.

EXPERIMENTAL

Materials

The plastic materials used in this project as matrix components are a 1:1 mixture of an injection grade high-density polyethylene (HDPE) of melt index 6.4 and a recycled HDPE of melt index 0.4, and a recycled polypropylene (PP) of injection grade (melt index 1.6) purchased from Aproplast (Bogotá, Colombia).

As fillers, four lignocellulosic materials were tested: pine wood particles, rose and carnation fibers and coffee husks. The pine wood was purchased from Mantesa S.A. (Manizales, Colombia) as fine particles, and coffee husks were provided by the Cooperativa de Caficultores de Manizales (Colombia). Rose and carnation fiber wastes were purchased from Royal Farms and Flores San Juan, respectively, and were milled twice in a Condux mill C8150-106-2 of Bauknecht. The chemical composition of the filler materials with respect to their cellulose and lignin content was determined by ^{1}H-NMR spectroscopy, evaluating the areas of aromatic and aliphatic proton peaks. The relative

water content of the materials was determined by thermogravimetric measurements (TGA).

In order to obtain filler particles of different sizes, the organic material was separated using a column of sieves, following procedure D 1921 of the American Society of Testing and Materials (ASTM). Fractions with mesh sizes of less than 20, between 20 and 30, and between 30 and 40 were used for the preparation of the composites. The aspect ratio (length/width) of the particles as determined by optical microscopy follows a normal distribution with a maximum ratio of three.

Prior to the blending process, the lignocellulosic material was dried to 0.5-1% moisture content to prevent steaming in the mixer and deactivation of the coupling agent. The titanate based coupling agent LICA38 was supplied by Kenrich Petrochemicals, Inc. (New York, NY). The ethylene-maleic anhydride copolymer Cel-span 334 was supplied by Phoenix Plastics Co., Inc. (TX, USA) and contained 8 mol % monomeric units of maleic anhydride and 92 mol % polyethylene.

Preparation of composites

The blending process of the composites without coupling agents took place in a Brabender Plasticorder. A W50H mixer head with roller type blades was used. This mixer had a capacity of approximately 55 cm^3, and the blades provided a high shear mixing. The rotor velocity of the mixer was 40 rpm, and the processing temperature ranged between 155 and 185°C. The prepared blends were ground in a Condux mill and molded by compression in a Dake laboratory press to obtain the ASTM test specimens.

For the preparation of the composites with titanate based compatibilizer, the cellulosic fiber material was first wetted with the coupling agent. LICA38 was added in a proportion between 0 and 0.8% by weight in an agitator rotating at 1500 rpm. The blending of the samples was performed at a rotor velocity of 80 rpm in order to increase the specific energy input.

Mechanical properties

Five samples of each composite for each test were used to determine tensile strength, Young's modulus, deformation at fracture and notched Izod impact resistance. Tests were performed according to ASTM standard methods D638 and D256, respectively.

Scanning electron microscopy

Images were obtained with an Environmental Scanning Electron Microscope from Phillips operating at 30 kV.

Water absorption

Water absorption measurements were performed according to ASTM standard method D570. For each composite, three $3 \times 12 \times 50$ mm^3 samples were cut from pieces of the compression molded sheets. In order to determine their susceptibility to moisture, the samples were submerged in distilled water for one week at room temperature. The samples were weighed before and after each treatment, and the percent weight gain (PWG) was calculated as

$$ \text{PWG} = (W_f - W_0)/W_0 \times 100\% $$

where W_0 is the initial weight of the sample and W_f its final weight.

RESULTS AND DISCUSSION

The new composites were prepared according to the procedure indicated in the experimental section. The specific preparation conditions for each sample are summarized in Table I.

Processing temperature

The influence of the process temperature (mixing and molding) on the mechanical properties of the materials is studied in samples 1(a–c) using polypropylene as the matrix and rose fibers as the filler and varying the process temperature between 155 and 180°C. The mechanical properties of the resulting composites are summarized in Table II. As can be seen in Table II, the Young's modulus, tensile strength and impact resistance decrease slightly with increasing processing temperature. This is due to the thermal degradation of the organic material, which began at about 160°C and was visualized by the coloration of the samples. On the other hand, although the best mechanical properties were found at the lowest temperature, it has to be pointed out that a processing temperature as low as 155°C for PP is not appropriate because of the high torque measured for the screw driver of the extruder. Moreover, a lower processing temperature implies considerably longer residence times of the composite in the mixer and in the mold, which contributes further to making the process inefficient and uneconomical.

Filler material

In this part of the study, ligno-cellulosic fibers from rose, carnation, coffee husks and pine wood were tested. As the basic compounds of these natural fibers are cellulose, hemi-cellulose, lignin and water, the advantage of the use of these fillers, apart from their low cost and unlimited availability, is the low abrasion

TABLE I
Experimental Conditions for Preparation of New Fiber Reinforced Thermoplastic

Sample no.	Polymer	Filler	% Polymer	% Fiber	% A.M.	% LICA38	T(°C)	Mesh size
1a	PP	rose	50	50	0	0	155	>30
1b	PP	rose	50	50	0	0	165	>30
1c	PP	rose	50	50	0	0	180	>30
2a	PP	rose	50	50	0	0	165	>30
2b	PP	carnation	50	50	0	0	165	>30
2c	PP	coffee	50	50	0	0	185	>30
2d	PP	pine	50	50	0	0	185	>30
3a	PE	pine	100	0	0	0	185	–
3b	PE	pine	60	40	0	0	185	>30
3c	PE	pine	50	50	0	0	185	>30
3d	PE	pine	40	60	0	0	185	>30
4a	PE	pine	50	50	0	0	185	m < 20
4b	PE	pine	50	50	0	0	185	20 < m < 30
4c	PE	pine	50	50	0	0	185	30 < m < 40
4d	PE	pine	50	50	0	0	185	m < 40
5a	PP	rose	50	50	0	0	165	>30
5b	PP	rose	50	50	0	0.5	165	>30
5c	PP	rose	47.5	47.5	5	0.5	165	>30
5d	PP	rose	45	45	10	0.5	165	>30
5e	PP	rose	42.5	42.5	15	0.5	165	>30
6a	PP	rose	47.5	47.5	5	0	165	>30
6b	PP	rose	47.5	47.5	5	0.3	165	>30
6c	PP	rose	47.5	47.5	5	0.5	165	>30
6d	PP	rose	47.5	47.5	5	0.8	165	>30

TABLE II
Properties of New Fiber Reinforced Thermoplastics

Sample no.	Young's modulus (MPa)	Tensile strength (MPa)	Deformation at fracture (%)	Impact resistence (J/m)	Melt index (g/10 min)	Density (g/cm^3)	Water absorption (%)
1a	2063	13.7	1.77	28.3	0.26	1.09	–
1b	1983	13.1	1.94	27.6	0.26	1.09	–
1c	1958	12.6	1.59	27.2	0.26	1.09	–
2a	1983	13.1	1.94	27.6	0.26	1.09	–
2b	1663	11.8	1.75	19.9	0.24	1.13	–
2c	1940	12.4	1.7	33.8	0.42	1.13	–
2d	2252	13.6	0.83	29.3	0.05	1.12	–
3a	1250	27.7	11.30	47.5	1.61	0.90	–
3b	2100	15.8	0.86	33.1	0.24	1.08	–
3c	2252	13.6	0.83	29.3	0.05	1.12	–
3d	2430	11.4	0.91	25.5	not melting	1.15	–
4a	2416	14.6	1.09	35.0	0.08	1.11	–
4b	2252	13.6	0.86	29.3	0.05	1.12	–
4c	2243	14.0	0.63	35.0	0.12	1.12	–
4d	2289	13.8	0.80	33.7	0.09	1.12	–
5a	1983	13.1	1.94	27.6	0.26	1.09	5.60
5b	1768	13.0	1.72	32.3	0.23	1.07	3.12
5c	1657	13.8	1.63	39.7	0.19	1.07	1.51
5d	1579	13.8	1.55	47.3	0.16	1.07	1.01
5e	1324	13.2	2.21	64.5	0.13	1.05	0.68
6a	1697	16.1	1.89	45.0	0.17	1.06	1.74
6b	1617	14.2	1.74	38.4	0.19	1.08	1.69
6c	1657	13.8	1.63	39.7	0.19	1.10	1.51
6d	1584	13.8	1.70	37.8	0.22	1.07	1.43

TABLE III
Chemical Composition of Ligno-Cellulosic Fibers

Type of fiber	Cellulose and Hemicellulose (%)	Lignin (%)	Water (%)	Others (%)
Rose	50	5	40	5
Carnation	50	5	40	5
Coffee husk	35	25	35	5
Pine wood	42	30	23	5

caused to the components of the extruder, especially in comparison with composites carrying inorganic fillers or rice husks. The results of the mechanical properties [2(a–d) in Table II] determined for the composites prepared from PP and the mentioned fillers show that in all cases, reinforced thermoplastics of high modulus and good impact resistance are obtained. However, it has to be pointed out that the composites containing rose and carnation fibers had to be processed at 165°C in order to avoid degradation and guarantee their mechanical properties, while coffee husk and pine wood containing thermoplastics could be prepared at 185°C with the advantages mentioned above. The different thermostability of the two types of filler materials is explained by their chemical compositions, which are compared in Table III. In rose and carnation, the ratio of cellulose to lignin content is approximately 10, while it is only about 1.5 in coffee husk and pine wood. The fact that lignin contains aromatic rings while cellulose is made up of heteroaliphatic glucose units explains the higher thermostability of the former compounds.

Composition of composites

A factor that strongly influences the mechanical properties of polymer–fiber composites is the composition of the material. This is shown in Figure 1, where the dependence of Young's modulus, tensile strength and impact resistance on the composition of PP-pine composites is depicted.

In these composites, which are prepared without a coupling agent, the three parameters depend linearly on the filler content. As could be expected, the organic material acts as an efficient reinforcing agent, increasing a Young's modulus value of 20 MPa/weight %. The slope of the decrease in tensile strength and impact resistance is −0.28 MPa/weight % and −0.37 J/(m wt %), respectively. A further consequence of the addition of a filler is a strong decrease in the melt index of the obtained composites.

The loss in impact resistance can be reduced by using a coupling agent, as will be shown below.

Particle size

In order to evaluate the influence of the filler particle size on the mechanical properties of the composites,

each milled organic fiber material was separated into different fractions according to particle dimensions using a column of sieves with different mesh sizes. We studied particles retained in a 20 mesh sieve, particles passing a 20 mesh sieve but retained in a 30 mesh sieve and particles passing a 30 mesh sieve but retained in a 40 mesh sieve. Furthermore, the original mixture of different sizes was tested.

As can be seen from the results in Table II [samples 4(a–d)], within the experimental error, the particle size

(a)

(b)

(c)
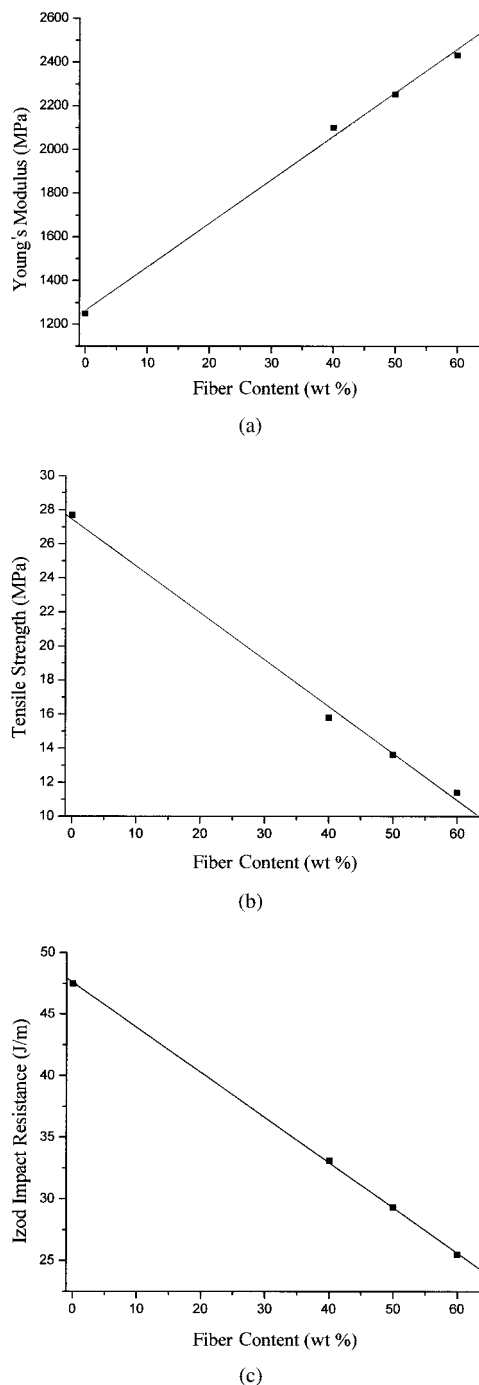
Figure 1 Dependence of (a) Young's modulus, (b) tensile strength and (c) impact resistance on the content.

in the studied range does not significantly influence the mechanical properties of the thermoplastic–fiber composites. This could be expected, as the present samples do not contain any coupling agent, and consequently the properties of the materials should be independent of the magnitude of the particle surface. When a coupling agent is used, it can be expected that smaller filler particles with larger specific surface will be able to form more links to the matrix, which would result in improved composite performance. This point is currently being studied.

Influence of coupling agent

It is well known that coupling agents can improve the adhesion between hydrophilic fiber material and hydrophobic matrix and that, in this way, useful composites with well balanced mechanical properties are obtained.

In this study, the influence of two different coupling agents and their combinations on the general characteristics of the composites is investigated. The first agent is a copolymer between PE and maleic anhydride, a compound that has proved to be efficient in compatibilizing phases of different polarity. The second one is LICA38,[10,11] a neopentyl(diallyl)oxy-tri(dioctyl)piro-phosphate titanate, which consists of long hydrophobic segments on the one hand and reactive ether groups on the other, which are capable of undergoing transetherification reactions with alcoholic hydroxyl groups like those in the glucose units of cellulose fibers.

As the maleic anhydride based compatibilizer is of polymeric origin, its addition to a 1:1 mixture of polymer and filler necessarily implies a relative reduction of the filler content in the composite, which has been shown in a previous paragraph to have an influence on the mechanical properties. In Figure 2, the dependence of Young's modulus and impact resistance on filler content for a composite with maleic anhydride compatibilizer is shown. The amount of the latter decreases when the filler content increases (see also Table I, sample 5). Also in this case, linear dependences are observed in the studied range. Although the addition of compatibilizer leads to a decrease in Young's modulus, the slope of the curves is significantly larger than that of the curves without compatibilizer. While Young's modulus increased at 20 MPa/weight % in a polymer–fiber composite without coupling agent, the increase with compatibilizer is 56 MPa/weight %.

Concerning impact resistance, a similar effect is observed. Furthermore, an increase of about 100% in the value of an analogue composite without maleic anhydride groups is found. This demonstrates the high efficiency of this compound in improving the adhesion between fiber material and matrix.
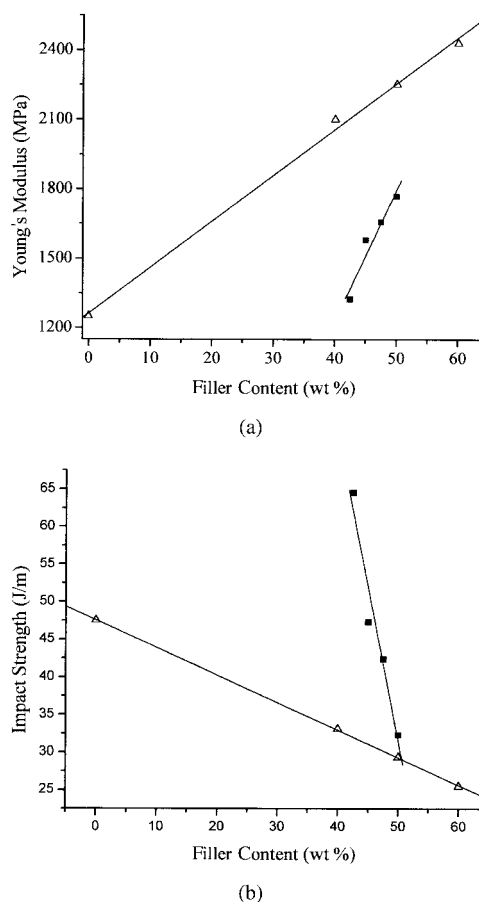
Figure 2 Dependence of (a) Young's modulus and (b) impact resistance on the filler content for a composite without coupling agent (△) and with maleic anhydride based compatibilizer (■).

The influence of varying the LICA38 content in the composites was studied for a PP–rose fiber blend, which also contained 5% of the maleic anhydride copolymer. As can be seen in Figure 3, the addition of this compatibilizer leads to a slight reduction of both Young's modulus and the impact resistance. This worsening of mechanical properties can be explained by the fact that both the maleic anhydride units and LICA38 react with the hydroxyl groups of the wood particles and can be considered competitors. Therefore, adding the less efficient LICA38 means reducing the number of anchoring sites available for the reaction of wood particles with the highly reactive maleic anhydride. On the other hand, when composites without maleic anhydride [Table II, samples 5(a) and 5(b)] are compared, with LICA38 as the only coupling agent, the addition of 0.5% of this compound causes a considerable increase (17%) in the impact resistance of the material.

The dependence of mechanical properties on the different coupling agents and their combinations used in the preparation of the composites can be understood when SEM images of the fractured samples are

(a)

(b)
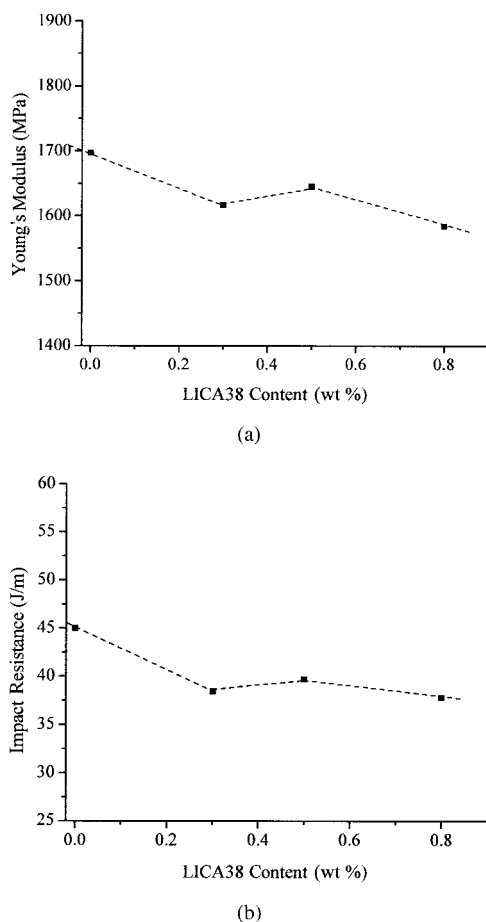
Figure 3 Dependence of (a) Young's modulus and (b) impact resistance on LICA38 content in PP-rose composite with 5% maleic anhydride based compatibilizer.

compared. Figure 4(a–d) depicts images of (a) a PP-pine fiber blend without coupling agent, (b) with 0.5% LICA38, (c) with 10% maleic anhydride based compatibilizer, and (d) with both coupling agents.

In the first case, the fiber surface is completely free of plastic particles, and a relatively strong fiber pull-out is observed. Both findings indicate that there is a poor adhesion between the two phases. The second image shows that little plastic strips are now bonded to the fiber particles, which explains the increased impact strength of this composite [Fig. 5(b)]. Finally, the images of Figure 4(c) and (d), are very similar, showing fiber surfaces which are covered with bigger plastic particles. This indicates on the one hand that a stronger adhesion exists between the organic material and the matrix, and on the other hand that a combination of both coupling agents does not contribute to an improvement in the material characteristics.
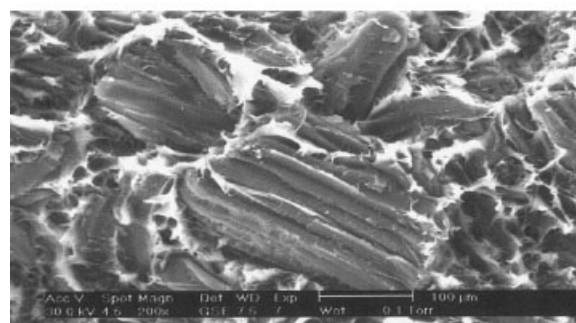
Water absorption

The absorption of water is an important problem when dealing with cellulose fiber reinforced thermo-
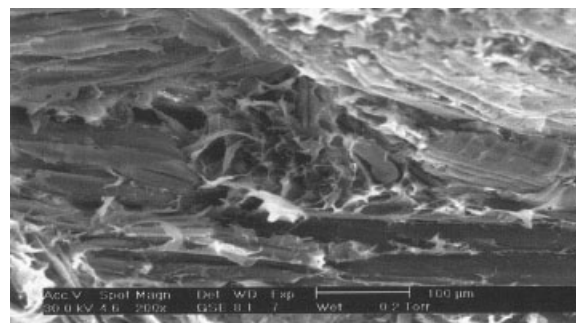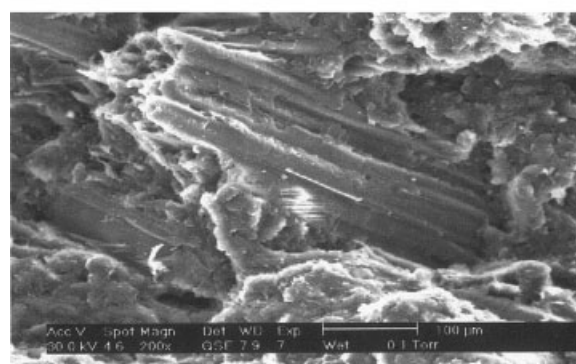

(a)
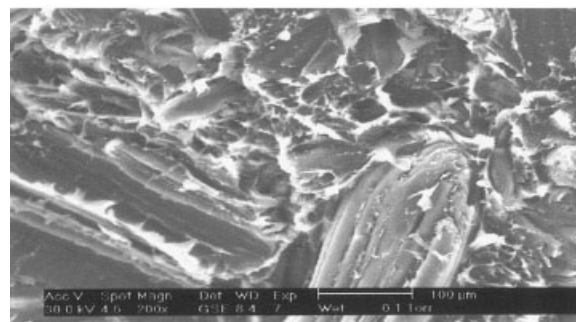
(b)

(c)

(d)

Figure 4 SEM photographs of fracture surface of PP-rose fiber composite: (a) without coupling agent, (b) with 0.5% LICA38, (c) with 10% maleic anhydride based compatibilizer, and (d) with both coupling agents.

plastics, because a high uptake of humidity worsens the mechanical properties of the material and changes the dimensions of the article by swelling. One of the objects of this work was to clarify the influence of compatibilizers on the absorption of water. In order to study this point, samples 5 and 6 were immersed for a week in water and the water uptake was determined gravimetrically. The results of this experiment are summarized in Table II.

A sample without any coupling agent [5(a)] absorbs 5.6 wt % water in a week. With the addition of 0.5% LICA38, the absorption of the corresponding composite [5(b)] was reduced significantly to only 3.12%. When, instead of LICA38, 5% of the maleic anhydride based compatibilizer was used, the reduction of the water uptake was even lower, at 1.74% [sample 6(a)]. The high efficiency of this coupling agent is further shown in samples 5(b–e), where an increase of its content to 15% in the blend reduces the water absorption to only 0.68%.

The application of a combination of both compounds is less efficient than using either compound by itself. When adding between 0.3 and 0.8% LICA to a composite with 5% maleic anhydride [samples 6(b–d)], the water absorption is further reduced with increasing LICA content but less significantly, reaching a value of 1.43 in the case of 0.8% LICA.

CONCLUSIONS

New cellulose fiber based reinforced thermoplastics with mechanical properties similar to those of commercial products can be prepared using material waste from coffee husks, rose and carnation fibers as an economic filler. The processing temperature has to be optimized according to the degradation temperature of the respective organic material used.

In composites without coupling agents, the mechanical properties of the material depend linearly on the filler-to-polymer ratio, in the sense that higher filler content produces a material with decreasing elastic modulus, while the impact resistance is improved.

The size of the filler particles used does not show a significant influence on the properties of composites that do not contain a coupling agent.

The performance of the reinforced thermoplastics can be significantly improved using compatibilizers such as maleic anhydride based copolyethylene or neoalkoxy titanates like LICA38. While the use of the individual compatibilizers leads to an improvement of the material performance, a combination of both did not have a positive effect.

Both titanate and maleic anhydride compatibilizer strongly diminish the water absorption of the prepared composites.

References

1. Schut, H. J. Plastics Technology; New York, 1999; pp 46–52.
2. Oksmann, K.; Clemons, C. J Appl Polym Sci 1998, 67, 1503.
3. Wang, Y.; Simonson, J.; Psascoal Neto, C.; Rocha, J.; Rials, T. G.; Hart, E. J Appl Polym Sci 1996, 62, 501.
4. Simonsen, J.; Jacobsen, R.; Rowell, R. J Appl Polym Sci 1998, 68, 1567.
5. Bletzki, A. K.; Gassan, J. Prog Polym Sci 1999, 24, 221.
6. Andersen Corporation. U.S. Pat. 6,015,612 (1999).
7. Advanced Environmental Recycling Technologies, Inc. U.S. Pat. 5,759,680 (1993).
8. Crane Plastics Company Limited Partnership. U.S. Pat. 5,866,264 (1996).
9. TREX Company L.L.C. U.S. Pat. 5,851,469 (1997).
10. Monte, S. J. In KEN-REACT® Reference Manual, 2nd ed.; Kenrich Petrochemicals: New York, 1993; pp 2–29.
11. Monte, S. J. J Elastomers and Plastics 1990, 22, 43.