Comparison of the Effects of Polyethylenimine and Maleated Polypropylene Coupling Agents on the Properties of Cellulose-Reinforced Polypropylene Composites

C. González-Sánchez,[1] M. González-Quesada,[1] M. U. de la Orden,[2] J. Martínez Urreaga[3]

[1]Departamento de Ingeniería Química y Tecnología del Medio Ambiente, Universidad de Oviedo, Julián Clavería, S/N 33071 Oviedo, Spain
[2]Departamento de Química Orgánica, Escuela Universitaria de Optica, Universidad Complutense de Madrid, Arcos de Jalón, S/N 28037 Madrid, Spain
[3]Departamento de Ingeniería Química Industrial, ETSI Industriales, Universidad Politécnica de Madrid, José Gutiérrez Abascal, 2. 28006 Madrid, Spain

ABSTRACT: The desire to improve the properties of cellulose-reinforced composites while producing them by methods as similar as possible to those used on an industrial scale is one of the driving forces in this field of research. In this work, extensive research for determining the mechanical, thermal, rheological, and physical properties of novel cellulose-reinforced polypropylene composites containing a polyethylenimine (PEI) coupling agent was conducted. A comparison of their properties with those of reference composites without any coupling agent or containing a maleated polypropylene (MAPP) coupling agent was also carried out. The presence of the PEI coupling agent mainly gave rise to a substantial increase in the tensile and flexural strengths and elongations as well as the impact strength, heat deflection temperature (HDT), melt volume flow index, and water absorption of PEI-containing composites in comparison with composites without any coupling agent added. However, the increases achieved in the tensile and flexural composite strengths and HDT were lower than those achieved with the MAPP coupling agent mainly for composites containing 50 wt % cellulose fibers. On the other hand, PEI-containing composites exhibited, in most cases, larger elongations and energies required to break in tensile tests as well as larger impact strengths, melt volume flow indices, and water absorption percentages than MAPP-containing composites. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 2555–2562, 2008

Key words: composites; poly(propylene) (PP); polyimines; cellulose; maleated polypropylenes

INTRODUCTION

Thermoplastic–matrix composites reinforced with cellulosic materials are objects of growing interest as alternative materials to glass-reinforced composites because of the inherent advantages of the former. Mainly, they are lighter and more economical than comparable glass-fiber-reinforced thermoplastics and are more sustainable materials. Cellulose fibers are renewable and CO_2-neutral, their manipulation has low health risks, and their thermoplastic composites are recyclable and can be disposed of more easily and safely than plastics containing glass fibers.[1–3]

Although the tensile strength of cellulose fibers is rather high (ca. 500 MPa for sisal and palm fibers and ca. 900 MPa for jute and flax fibers[4]) and the specific properties of cellulose-reinforced composite materials are good and even comparable to those of glass-fiber-reinforced composites in some cases, the values of their absolute properties are lower than expected. This is mainly due to the polar character of the cellulose fibers, which contrasts with the non-polar character of some of the most important thermoplastics used as matrices in composites (e.g., polyolefins) and leads to a poor dispersion of the fibers in the matrix and low interfacial adhesion. On the other hand, the thermal stability of cellulose fibers is limited in comparison with that of glass fibers.

Different methods have been used to improve the compatibility of the two phases (the polymeric ma-

trix and the cellulose fibers).[5,6] One of the most important chemical methods involves the use of coupling agents. They are compounds that can form covalent bonds with the hydroxyl groups of cellulose and react or entangle with the macromolecules of the polymeric matrix. Coupling agents based on silanes, triazines, and isocyanates have been employed and tested.[5] Among all the coupling agents available, maleated polyolefins are by far the most extensively studied and used. Several authors have demonstrated in the last 25 years the positive effect of adding maleated polyolefins to natural fiber/polyolefin composites.[7–14] In fact, maleated polyolefins are almost the only coupling agents used today for this kind of composite because of the simplicity of their use and the good average properties of the final materials. However, some properties of the final composites can be improved by the use of other coupling agents instead of the maleated polyolefins.

A literature review reveals that there are chemicals with suitable potential as coupling agents for cellulose/polymer composites that have scarcely been tried. That is the case of polyethylenimines (PEIs). PEIs are highly branched polymers with a large number of amine groups partially protonated under acidic or neutral pH conditions. Because of this cationic character, PEIs can be easily bonded to negatively charged surfaces, such as those of cellulose. PEIs can also be expected to form stable complexes with polypropylene (PP) because of the presence of acidic surface functions in the latter polymer, as shown by Aranberri-Askargorta et al.[15]

In a previous article,[16] we have shown that PEIs act as coupling agents in bleached cellulose/PP composites and that the use of small amounts of PEIs allow remarkable increases in the tensile properties of those composites.[16] PEIs have been covalently bonded to the cellulose surface in the composite interphase. It is therefore worthwhile to assess the improvements in the composite properties achieved by the addition of PEI to bleached cellulose/PP composites by comparison with the values of the composite properties achieved by the addition of maleated polypropylene (MAPP).

Therefore, this work was devoted to systematic and extensive research for determining the mechanical, thermal, and rheological properties of novel cellulose-reinforced PP composites containing a PEI coupling agent. A comparison of their properties with those of reference composites without any coupling agent or containing a MAPP coupling agent was also carried out. All the composites were obtained under the same conditions by the compounding of the raw materials through a continuous extrusion process scaled down from an industrial process.

EXPERIMENTAL

Materials and reagents

The bleached eucalyptus kraft pulp was supplied by ENCE-Navia, a kraft pulp mill located in Navia, Spain. It was made from *Eucalyptus globulus* wood by kraft pulping and subsequent bleaching with chlorine dioxide (elemental chlorine-free bleaching). Its chemical composition (by weight) was 91.88% cellulose, 7.71% hemicelluloses, 0.16% lignin, 0.07% extractives, and 0.18% ash. The average aspect ratio (length/diameter) of the fibers was 55. The PP used as a matrix consisted of a Moplen HP 648U homopolymer (Basell Polyolefins, Barcelona, Spain) with a density of 900 kg/m^3 (ISO 1183) and a melt flow index of 75 g/10 min (measured at 230°C and 2.16 kg) according to the ISO 1133 standard.

A commercially available maleic anhydride modified PP polymer (Epolene E-43) was used as a coupling agent for the reference composite materials (Eastman Chemical Products, Kingsport, TN). It had a density of 934 kg/m^3, an acid number of 45, a weight-average molecular weight of 9100, and a number-average molecular weight of 3900. The PEI used (Lupasol PR 8515; active matter > 98%, weight-average molecular weight = 2000; Chemical Abstracts Service no. 25987-06-8), kindly supplied by BASF Española S.A. (Barcelona, Spain), was used as received. The ratio of primary, secondary, and tertiary amines in this PEI was 1 : 0.92 : 0.70. Absolute ethanol and xylene (Fluka, Seelze, Germnay) were used without further purification.

Cellulose treatment and composite preparation

The bleached eucalyptus kraft pulp was sprayed with aqueous solutions of PEI and dried in a vacuum oven at 40°C for 24 h. Composites with 30, 40, and 50 wt % cellulose and 1.5 wt % PEI were prepared with the PEI-treated cellulose and PP. Reference composite materials with the same compositions were prepared with MAPP instead of PEI. Materials without coupling agents containing 30, 40, or 50 wt % untreated cellulose were also prepared. Composites were prepared by the compounding of the dried raw materials in a Berstorff ZE25 corotating, intermeshing twin-screw extruder (Berstorff, Hannover, Germany). Before the compounding, cellulose fibers were dried at 105°C in an air-circulating oven for 3 h to a moisture content lower than 1 wt %. Composite pellets obtained by compounding were also dried in the same way. Then, they were injection-molded into dog-bone-shaped test specimens according to the ISO 3167 standard in a 450-kN reciprocating injection-molding machine (Mateu & Solé, Barcelona, Spain).

TABLE I
Tensile Properties of the Bleached Eucalyptus Cellulose Fiber/PP Composites

Coupling agent	Cellulose content (wt %)	E_t (GPa)	σ_t (MPa)	e_t (%)	σ_{tb} (MPa)	e_{tb} (%)	W_t (J)	W_{tb} (J)
None	30	2.0 (0.1)	35.0 (0.4)	6.0 (0.3)	34.7 (0.3)	6.1 (0.4)	5.1 (0.4)	5.2 (0.4)
	40	2.1 (0.1)	30.6 (0.6)	3.5 (0.2)	30.5 (0.7)	3.6 (0.2)	2.5 (0.3)	2.5 (0.3)
	50	2.4 (0.1)	25.1 (0.8)	2.4 (0.1)	24.9 (0.8)	2.5 (0.2)	1.4 (0.1)	1.4 (0.1)
E-43 (1.5 wt %)	30	1.9 (0.1)	46.5 (1.0)	5.0 (0.4)	46.5 (1.0)	5.0 (0.4)	5.2 (0.6)	5.2 (0.6)
	40	2.2 (0.1)	46.3 (0.9)	3.9 (0.2)	46.2 (1.1)	3.9 (0.2)	4.0 (0.3)	4.0 (0.3)
	50	2.6 (0.1)	50.1 (1.0)	3.3 (0.1)	50.1 (1.0)	3.3 (0.1)	3.5 (0.3)	3.5 (0.3)
PEI (1.5 wt %)	30	2.0 (0.1)	39.0 (0.4)	6.7 (0.1)	38.8 (0.5)	6.8 (0.2)	6.4 (0.2)	6.5 (0.2)
	40	2.3 (0.1)	39.3 (0.9)	4.8 (0.3)	39.2 (0.9)	4.8 (0.3)	4.5 (0.4)	4.5 (0.4)
	50	2.5 (0.1)	33.1 (0.3)	2.8 (0.1)	32.9 (0.3)	2.8 (0.1)	2.1 (0.1)	2.2 (0.1)
Pure PP matrix		1.1 (0.1)	30.8 (0.2)	12.3 (0.2)	25.8 (1.5)	24.3 (3.2)	7.4 (0.2)	20.5 (3.3)

Testing

Tensile testing was performed according to the ISO R527 standard with an Instron model 1011 universal testing machine (Instron, High Wycombe, UK). The modulus of elasticity was determined at a nominal crosshead rate of 1 mm/min, whereas the rest of the tensile properties were determined at a crosshead rate of 5 mm/min. The ISO 178 standard was followed for flexural tests. The crosshead rate in the flexural tests was 2 mm/min with a support span-to-depth ratio of 16:1 and a support span of 64 mm. The values reported here for both tensile and flexural properties are the averages of six specimens. Standard deviations were calculated and are shown between parentheses in Tables I–III.

The unnotched Charpy impact strength was determined for $80 \times 10 \times 4$ mm^3 specimens with an Instruments JBA Charpy impact tester with 2.5- and 10-J pendulums (Instruments JBA, Vilassar de Dalt, Spain). Six unnotched specimens were also tested, and testing was performed in agreement with the ISO 179 standard.

Thermal properties were determined in a Deflex apparatus (JBA). The heat deflection temperature (HDT) was measured according to the ISO 75 standard by the immersion of two specimens in the oil bath of that apparatus and by heating at a rate of 120°C/min while a load of 1.80 MPa was applied. The Vicat softening temperature was measured according to the ISO 303 standard with a heating rate of 50°C/h and a load of 49 N.

The crystallinity percentage (X_c) values of the composites were determined with a Mettler–Toledo DSC822 differential scanning calorimeter (Mettler–Toledo, Schwerzerbach, Switzerland). Samples of about 5–6 mg of the composite materials were heated from 10 to 220°C at a heating rate of 10°C/min. Measurements were carried out under a nitrogen atmosphere. X_c of the samples was calculated in accordance with the following formula:

$$X_c = \frac{\Delta H_f}{\Delta H_f^o} \times \frac{100}{w}$$

where ΔH_f is the melting endotherm of the sample, ΔH_f^o is the enthalpy of fusion of a single crystal or a 100% crystalline sample of PP, and w is the weight percentage of PP in the sample. The ΔH_f^o value employed in the calculations was 209 J/g.[17]

TABLE II
Flexural and Unnotched Charpy Impact Properties of the Bleached Eucalyptus Cellulose Fiber/PP Composites

Coupling agent	Cellulose content (wt %)	E_f (GPa)	σ_f (MPa)	e_f (mm)	σ_{fb} (MPa)	e_{fb} (mm)	W_f (J)	W_{fb} (J)	Unnotched Charpy impact strength (kJ/m^2)
Without coupling agent	30	3.6 (0.1)	55.5 (0.4)[a]						22.6 (2.7)
	40	4.4 (0.1)	58.0 (1.1)	5.2 (0.3)	55.9 (1.5)	5.5 (0.3)	0.4 (0.03)	0.4 (0.03)	13.5 (2.7)
	50	5.1 (0.1)	55.7 (0.8)	4.0 (0.1)	53.2 (0.9)	4.3 (0.1)	0.3 (0.01)	0.3 (0.01)	9.6 (1.4)
E-43 (1.5 wt %)	30	3.6 (0.1)	66.1 (0.6)[a]						28.2 (2.5)
	40	4.1 (0.1)	76.8 (1.3)	6.0 (0.2)	75.8 (2.3)	6.0 (0.0)	0.5 (0.02)	0.5 (0.02)	18.6 (2.6)
	50	5.4 (0.03)	84.4 (2.4)	4.5 (0.2)	82.0 (4.0)	4.7 (0.1)	0.4 (0.03)	0.5 (0.02)	14.9 (2.3)
PEI (1.5 wt %)	30	3.6 (0.04)	57.5 (0.6)[a]						31.9 (3.4)
	40	4.5 (0.1)	67.3 (1.4)[a]						27.3 (2.6)
	50	5.3 (0.2)	67.6 (2.0)	4.5 (0.2)	65.6 (2.2)	4.8 (0.2)	0.4 (0.03)	0.4 (0.02)	19.0 (2.6)
Pure PP matrix		1.7 (0.1)	38.3 (0.5)[a]						66 (6.0)

[a] Flexural strength at 6-mm deformation.
Values in parentheses indicate standard deviations.

TABLE III
Thermal, Rheological, and Physical Properties of the Composites

Coupling agent	Cellulose content (wt %)	HDT (°C)	VICAT (°C)	MVFI (cm^3/10 min)	Water absorption (%)
Without coupling agent	30	89.5 (0.1)	119.0 (0.7)	64.8 (2.9)	0.5 (0.02)
	40	101.6 (2.3)	117.6 (1.8)	60.0 (1.5)	0.7 (0.05)
	50	100.9 (0.1)	120.0 (4.2)	43.3 (2.1)	1.02 (0.03)
E-43 (1.5 wt %)	30	118.4 (0.2)	128.5 (3.5)	69.3 (3.6)	0.4 (0.04)
	40	113.3 (3.3)	131.2 (1.1)	69.5 (1.6)	0.5 (0.07)
	50	129.1 (3.5)	136.4 (2.5)	58.6 (4.9)	0.8 (0.08)
PEI (1.5 wt %)	30	92.6 (4.7)	120.7 (4.0)	72.2 (2.9)	0.7 (0.01)
	40	102.1 (0.6)	126.9 (0.0)	61.9 (5.0)	1.0 (0.05)
	50	111.2 (1.6)	134.4 (0.8)	60.7 (12.0)	1.51 (0.16)
Pure PP matrix		63.4 (0.7)	106.5 (0.1)	106.27 (3.2)	0 (0)

Values in parentheses indicate standard deviations.

Melt volume flow index (MVFI) tests were done according to the ISO 1133 standard with a melt indexer Ceast model 6942.000 (Ceast, Lainate, Italy). Tests were done at 190°C according to that standard. However, because of the rather high viscosity of the composites in comparison with the polymeric matrix, a 3-mm-diameter nozzle had to be used instead of the 2.095-mm-diameter nozzle set by the ISO 1133 standard. Also, because of the wide variation of the composite viscosities with the fiber content, composites reinforced with a 30 wt % concentration of fibers were tested with a 10 kg weight, composites reinforced with a 40 wt % concentration of fibers were tested with a 15-kg weight, and composites reinforced with a 50 wt % concentration of fibers were tested with a 21.6-kg weight to allow the flowing of the composite melt through the nozzle and to meet the test duration times set by ISO 1133 as well. The melt volume flow rate values are the averages of 20 measurements.

Water absorption by the composites was determined according to the ISO 62 standard. Three speci-mens were dried in an air circulating oven at 50°C for 24 h and then immersed in distilled water at 23°C for 24 h.

RESULTS AND DISCUSSION

Tensile properties

The tensile properties of the composites studied in this work that were prepared without any coupling agent or with the E-43 or PEI coupling agents are shown in Figures 1–3 and Table I. Table I gives the mean values (with the corresponding standard deviations between parenthesis) of the tensile properties measured in pure PP and composites with different amounts of eucalyptus cellulose fibers and the coupling agents. As can be seen in Table I, the tensile modulus of elasticity (E_t) of the composites was not substantially affected by the use of either of the two aforementioned coupling agents, although slight increases could be observed when high reinforcement contents were used. Table I also shows that the
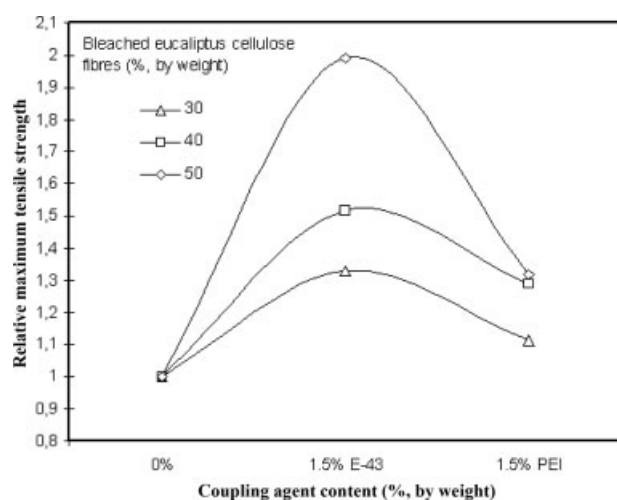

Figure 1 Relative maximum tensile strength variation with coupling agent type at different fiber contents in the bleached eucalyptus cellulose fiber/PP composites.
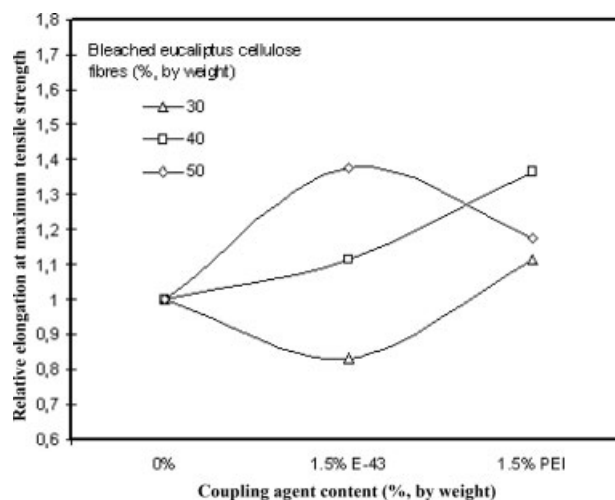

Figure 2 Relative variation of the elongation at maximum tensile strength in composites made with different coupling agents and fiber contents.
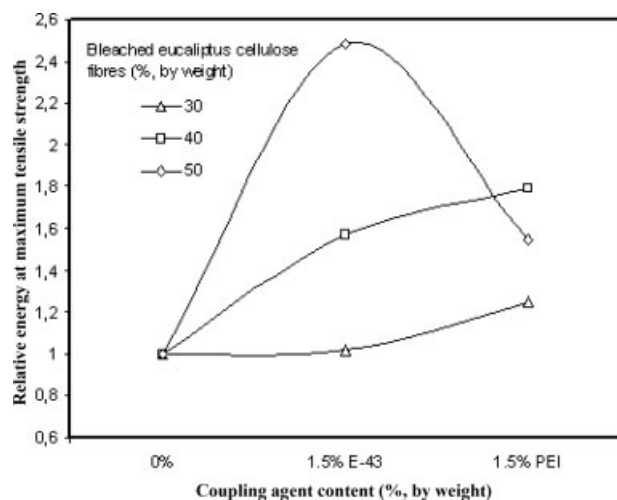
Figure 3 Relative variation of the energy at maximum tensile strength measured in the bleached eucalyptus cellulose fiber/PP composites.

tensile properties measured at the maximum strength and at break were very similar, revealing that the obtained composites were rather brittle.

Figure 1 shows the relative maximum tensile strength variations registered for the composites containing a 1.5 wt % concentration of the aforementioned coupling agents with respect to the composites with the same fiber content without any coupling agent added. The relative increases registered in the maximum tensile strength for the composites containing a 1.5 wt % concentration of the maleic anhydride modified PP coupling agent and a 30, 40, or 50 wt % concentration of the bleached cellulose fibers were 32.9, 51.4, and 99.3%, respectively. On the other hand, when the PEI coupling agent was used, the relative maximum tensile strength increases registered for composites with the same fiber contents were 11.5, 28.6, and 31.8%, respectively. Remarkable increases in the tensile strength, which becomes more relevant as the fiber content in the composite increases, have also been reported for other natural fiber composites.[11,18]

Figure 2 shows that the variations of the relative elongation at the maximum tensile strength (e_t) for the composites containing a 1.5 wt % concentration of the MAPP coupling agent and a 30, 40, or 50 wt % concentration of the cellulose fibers were −16.9, 11.3, and 37.5%, respectively. On the other hand, when the PEI coupling agent was used, those corresponding variations were 11.5, 36.4, and 17.5%, respectively.

Figure 3 shows that the increases in the relative energy at the maximum tensile strength (W_t) for the composites containing a 1.5 wt % concentration of the MAPP coupling agent and a 30, 40, or 50 wt % concentration of the cellulose fibers were 1.6, 57.1, and 148.2%, respectively. On the other hand, when the PEI coupling agent was used, those corresponding increases were 25.0, 79.0, and 54.4%, respectively.

The increases registered in the tensile strengths of the bleached cellulose fiber/PP composites containing the MAPP or PEI coupling agents reveal that stress transfer efficiency in the composites is better when they are present. The improved interfacial adhesion is a result, at least in part, of the formation of strong chemical bonds between the coupling agents and the cellulose fibers of the composites. In the case of MAPP, the formation of ester bonds between the maleic groups of the compatibilizer and cellulose hydroxyl groups has been repeatedly established. In the case of PEI-containing composites, the formation of covalent bonds between the coupling agent and the cellulose has also been demonstrated previously.[16] According to the superior values of the tensile strengths, stronger interfacial adhesion is achieved when MAPP is used; however, the higher elongations found in general when PEIs are used appear to indicate the existence in this case of a more flexible interphase.

Flexural properties

The flexural properties of the composites studied in this work that were prepared without any coupling agent or with E-43 or PEI-2 are shown in Figure 4 and Table II. As can be seen in Table II, the values of the flexural elastic modulus of the composites (E_f) were very similar for each material, and only slight increases were observed for the composites with a 50 wt % concentration of cellulose fibers and a 1.5 wt % concentration of the coupling agents. As shown in Table I for the tensile values, Table II shows that the elongations at the maximum and break flexural strength were very similar, thus also revealing the brittle character of the composites.

Figure 4 shows that the increases in the relative flexural strength (σ_f) for the composites containing a
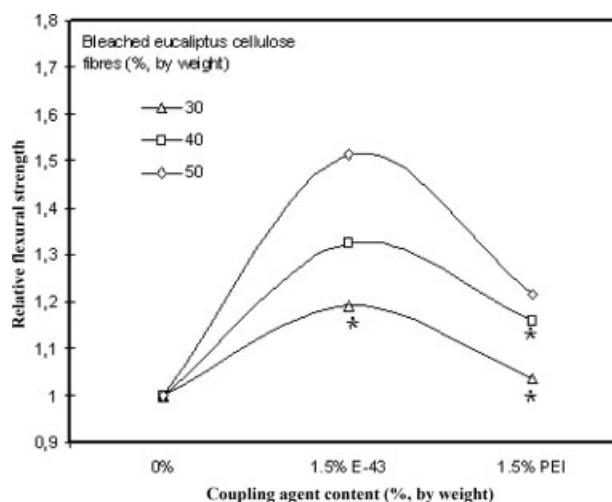

Figure 4 Effect of the coupling agent on the relative flexura strength of the cellulose/PP composites.

1.5 wt % concentration of the MAPP coupling agent and a 30, 40, and 50 wt % concentration of the cellulose fibers were 19.2, 32.4, and 51.5%, respectively. On the other hand, when the PEI coupling agent was used, those corresponding variations were 3.7, 15.9, and 21.4%, respectively. Points with an asterisk correspond to materials that did not break during the flexural test. In those cases, the flexural strength at deformation of 6 mm was determined according to the ISO 178 standard. Therefore, the flexural elongations at the maximum (e_f) and break strength (e_{fb}), the flexural strength at break (σ_{fb}), and the energies at the maximum (W_f) and break flexural strength (W_{fb}) could not be determined in those cases. The formation of strong chemical bonds between the coupling agents and the cellulose fibers produces a stronger polymer–fiber interface that results in better stress transfer efficiency. The higher values obtained with MAPP reveal again the existence of stronger interfacial adhesion in this case.

Table II shows that the elongations at the maximum and break flexural strength of the composites were very similar, thus also revealing their brittle character. This might be due to the balance between the reduction in the deformation of the modified matrix and the strength of the polymer–fiber interface provoked by the coupling agents' presence.

Energies at the maximum and break flexural strength were calculated from the area values under the corresponding flexural stress–strain curves up to the elongation at the maximum and break strengths, respectively. Their values are also shown in Table II. Only materials containing a 50 wt % concentration of cellulose fibers could be compared to study the effect of both coupling agents on the determined energies for the aforementioned reasons. The energy at the maximum flexural strength increased with the presence of MAPP and PEI coupling agents. The strong polymer–fiber adhesion promoted by the MAPP coupling agent was mainly responsible for the increases registered for W_f and W_{fb}.

Impact strength

The unnotched Charpy impact strength mean values (with the corresponding standard deviations) of the composites studied in this work are shown in Table II. The impact strength of the composites decreased with the increase in their fiber content because the mobility of the macromolecular chains of the polymer decreased and therefore their ability to absorb impact energy was reduced. In addition, the increase in the fiber content gave rise to weak points in the composite as well as areas of stress concentration where the fracture could easily be initiated.

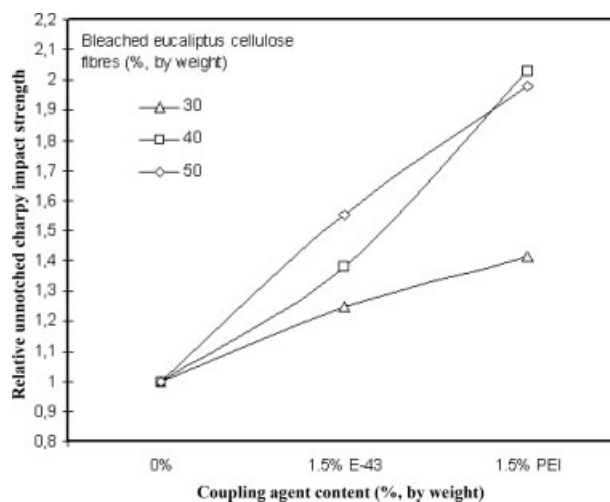Figure 5 shows that the increases in the unnotched Charpy impact strength for the composites contain-

Figure 5 Relative variation of the unnotched Charpy impact strength with coupling agent type in the cellulose/PP composites.

ing a 1.5 wt % concentration of the MAPP coupling agent and a 30, 40, or 50 wt % concentration of the cellulose fibers were 24.9, 37.8, and 55.5%, respectively. On the other hand, when the PEI coupling agent was used, those corresponding increases were 41.2, 102.0, and 98.1%, respectively. As can be seen, both coupling agents improved fiber dispersion, thus reducing the presence of fiber agglomerates in the composite, and this resulted in a reduction of the weak points in the composite material where the fracture could be initiated. The improvements achieved with PEI were remarkably greater than those achieved with MAPP, and this can be related to the lower crystallinity percentages observed in the DSC analysis of the composites made with PEI (43.5, 44.7, and 33% for composites containing 30, 40, and 50 wt % concentrations of the cellulose fibers and a 1.5 wt % concentration of the PEI coupling agent, respectively, whereas for composites containing the MAPP, those corresponding values were 54.9, 58.5, and 52.8%). The high impact strengths also appear to indicate the existence of a less rigid interphase in the PEI-containing composites in good agreement with the previously reported values of the tensile and flexural properties. This less rigid interphase in PEI-containing composites has also been shown with scanning electron microscopy. The scanning electron micrographs corresponding to composites made with PEIs, shown in a previous article,[16] revealed that the interfacial adhesion in these composites is stronger than in composites made with no coupling agent. However, the interfacial adhesion is clearly stronger in MAPP-containing composites than in those containing PEI, which can produce excessively rigid interphases with low impact strengths.
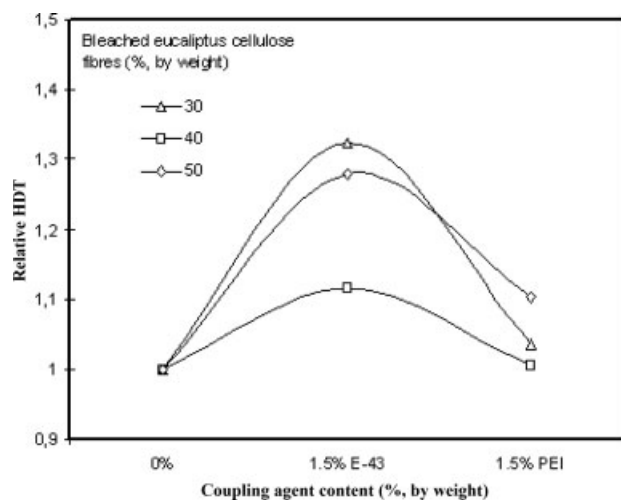
Figure 6 Relative HDT variation with coupling agent type at different fiber contents in the bleached eucalyptus cellulose fiber/PP composites.

Thermal properties

The thermal properties of the composites studied in this work are shown in Table III and Figures 6 and 7. As can be seen in Table III, composites with higher fiber contents showed higher HDT values. Similar results have been observed in a study of composites reinforced with different types of natural fibers[19] and can be explained if we take into account that the mobility of the polymeric macromolecular chains becomes more hindered as the amount of fibers in the composite increases and so the temperature necessary for achieving a defined composite deformation has to be higher as well. On the other hand, the Vicat temperature values of the composites did not change remarkably with the fiber content when no coupling agent was present.
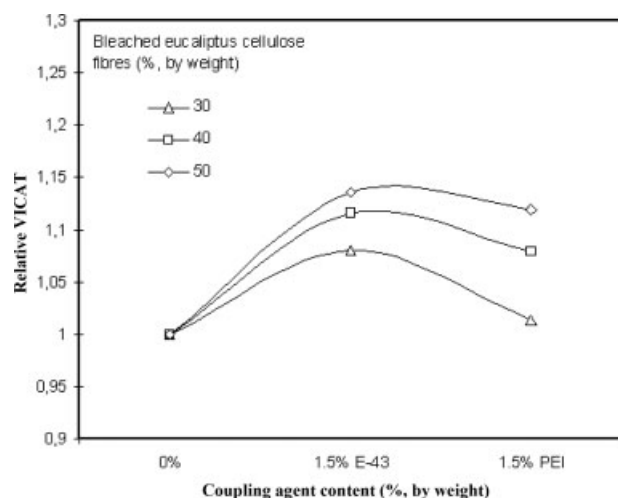

Figure 7 Relative Vicat variation with coupling agent type at different fiber contents in the cellulose/PP composites.

Figure 6 shows that composites containing MAPP presented higher HDT values than those containing PEI. This result can be explained as another result of the stronger interfacial adhesion achieved with MAPP, which has also been revealed in the analysis of the tensile and flexural properties. Figure 7 shows that the increases in the relative Vicat temperature for the composites containing a 1.5 wt % concentration of the MAPP coupling agent and a 30, 40, or 50 wt % concentration of the cellulose fibers were 8.0, 11.6, and 13.7%, respectively. On the other hand, when the PEI coupling agent was used, those corresponding variations were 1.4, 7.9, and 12.0%, respectively. The strong polymer–fiber interface and the improvement of fiber dispersion provided by the coupling agents hindered the penetration of the needle used for Vicat testing, thus leading again to an increase in the determined Vicat temperatures.

Melt volume flow index

The melt volume flow indices of the composites studied in this work that were prepared without any coupling agent or with the E-43 or PEI-2 coupling agent are shown in Table III (with the corresponding standard deviations) and Figure 8. The increases in the relative melt volume flow index for the composites containing a 1.5 wt % concentration of the MAPP coupling agent and a 30, 40, or 50 wt % concentration of the cellulose fibers were 6.9, 16.0, and 35.3%, respectively. On the other hand, when the PEI coupling agent was used, those corresponding variations were 11.3, 3.1, and 40.2%, respectively.

The melt volume flow index increase provided by both coupling agents is connected to the improvement in the fiber dispersion provided by them. The presence of MAPP and PEI in the composites led to a similar fiber dispersion in most cases. Therefore,
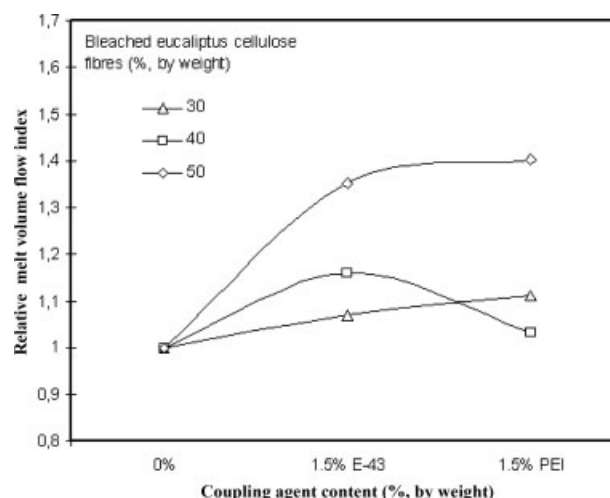

Figure 8 Relative variation of the melt volume flow index in the bleached eucalyptus cellulose fiber/PP composites made with different coupling agents and fiber contents.
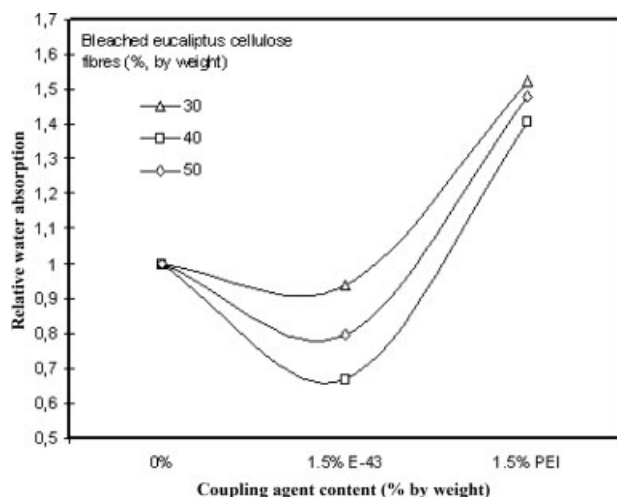
Figure 9 Relative water absorption in composites made with different coupling agents and fiber contents.

the melt volume flow indices of PP/bleached cellulose fibers containing MAPP or PEI were rather similar, regardless of which coupling agent was used.

Composite water absorption

The water absorption values of the composites studied in this work are shown in Table III and Figure 9. As can be expected, water absorption becomes more important as the fiber content increases. Figure 9 shows that the relative water absorption decreases when MAPP is used. This result can be explained if we consider that the reaction with MAPP reduces the number of free cellulose hydroxyl groups, which are responsible for the water uptake, and generates a less hydrophilic interphase. However, composites containing PEI as a coupling agent show increased water absorption. To explain this result, it must be taken into account that PEIs have a very large number of polar hydrophilic amine groups (primary, secondary, and tertiary amines) in their structure, as can be seen in Figure 10. Hence, although some of the amine groups react with the cellulose surface at the composite interface, there are still a large number of hydrophilic groups in the composite interface to favor the water uptake.
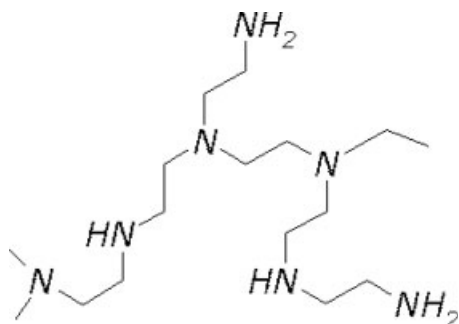

Figure 10 Chemical structure of PEI used.

CONCLUSIONS

1. Tensile and flexural strengths, as well as HDTs and Vicat temperatures, of cellulose–PP composites containing PEI as the coupling agent were greater than those of composites made without any coupling agent, showing the coupling action of PEIs in these composite materials.
2. Composites made with MAPP as the coupling agent showed higher mechanical strengths, as well as HDTs and Vicat temperatures, than those made with PEI.
3. However, composites containing the PEI coupling agent showed higher impact strengths than those prepared with MAPP. This result indicates that new types of modified PEIs could perhaps help in solving the problem of the inherently low impact properties of cellulose-reinforced composites.

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