

Thermal and Thermomechanical Properties of Biocomposites Made from Modified Recycled Cellulose and Recycled Polypropylene

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ABSTRACT: Residual cellulose fibers from the paper industry have been used as reinforcements in recycled polypropylene (PP) composites. The main obstacle to obtaining good properties with this biocomposite is deficiencies in the compatibility between the nonpolar matrices and the polar cellulose fibers used as reinforcements. The aim of this work was to improve the compatibilization between these cellulose fibers and the PP matrix with four different methods: modification by the addition of polypropylene–maleic anhydride copolymer (PPgMA) during the process of blending, preblending modification of the cellulose with a solution of PPgMA, modification of cellulose by silanes (vinyltrimethoxysilane), and acetylation of cellulose. Blends with all of the differently modified celluloses were prepared with the cellulose content varied up to 40%, and then all of the blends were subjected to thermal (differential scanning cal-

orimetry and thermogravimetric analysis) and thermomechanical (dynamic mechanical thermal analysis) analyses. The results showed that the addition of cellulose fibers improved the thermomechanical behavior of the PP, increasing the value of the log of the dynamic modulus, and affected the thermal and thermooxidative behavior. Moreover, an advantage of the use of a recycled PP containing a small quantity of ethyl vinyl acetate (EVA) as a prime material in the composition was the enhancement of mechanical properties. The use of these methods for the modification of cellulose led to more desirable thermal and thermooxidative stabilities. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2353–2360, 2003

Key words: composites; fillers; poly(propylene) (PP); thermal properties

INTRODUCTION

Composites, consisting of an association of a polymeric matrix and a synthetic filler (e.g., glass fiber, silicon carbide, carbon, or aramid) as reinforcement have been used increasingly in all materials fields (automotive, packaging, construction, etc.) because of the combination of their high performance and great versatility. However, current environmental problems caused by a concentration of these products in waste areas, their partial combustibility, and the increasing demand for techniques for the recycling of postconsumer materials have resulted in the replacement of synthetic fillers by natural organic ones such as cellulose, wood fibers, starch, and so on.^{1–8} These kind of fibers, compared to inorganic fillers, may afford many advantages, including low cost, lower density, no abrasion of the processing equipment, similar moduli, good thermal properties, and the subsequent possibility of treatment at normal processing temperatures of polyolefines, and biodegradability.^{9,10} Moreover, com-

posites made of cellulosic fibers and polypropylene (PP) are completely combustible, without the production of harmful gases or solid residues.¹¹ In addition, the possibility of blending postconsumers plastics material from municipal solid waste and industrial waste with residual cellulosic fibers from the paper industry and finding a useful application has become very attractive and promising in the last years, and a lot of work has been developed in this field.^{2,12–14}

Natural fibers present a series of advantages such as low density, high specific strength and modulus, renewable and biodegradable characteristics, and reasonable processibility at low cost. However, the main problem in the combination of natural fibers with polyolefines is the deficient compatibility between the nonpolar matrices and the polar fibers.

To enhance the filler–matrix interactions, different treatment methods based on the modification of the hydrophilic character have been developed. Basically, all the methods that enhance adhesion between polymer matrix and cellulose reinforcement are based on the same principle, the introduction of a material that possesses a function highly reactive with the hydroxyl groups of the cellulose and a nonpolar chain, preferably with a polymeric structure.^{15,16}

Graft copolymerization with polypropylene–maleic anhydride (PPgMA) copolymer is one of the most used procedures for improving interfacial adhesion.

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The PP chain is the responsible for the reaction with the polymer, whereas the carboxylic group of the maleic anhydride (MA) esterifies with the hydroxyl group of the cellulose substrate. Several authors have found that pretreating cellulose fibers with PPgMA improves compatibility due to the covalent and nitrogen bonds formed across the interface and enhances the mechanical properties of the final composite.^{17,18} Other authors have used PPgMA directly in extrusion processes and have obtained good quality products with this easy processing method.¹⁹

Treatment with silanes is another of the techniques because organosilanes are good coupling agents.^{8,20,21} The basic formula of silane coupling agents includes an organofunctional group on one side of the chain and an alkoxy group on the other. The organofunctional group is the one that causes the reaction with the polymer; meanwhile, the alkoxy group undergoes hydrolysis, condensation, and later esterification with the hydroxyl groups of the cellulose.²²

Another treatment method widely used nowadays is acetylation.^{4,23,24} Treating the cellulose fibers with an acetic acid solution leads to a reaction within the hydroxyl groups of the cellulose and the acid and subsequent esterification.

In this article, a study of the properties of composites made of residual cellulose fibers and recycled PP is evaluated. In particular, the different modification treatments of cellulose are also compared with respect to changes in the thermal and thermomechanical properties. Differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) were used to determine the best method to enhance the compatibility filler–matrix. Biocomposites prepared with differently modified celluloses, all of them with the same content (40 wt %) were studied to show the differences between the composites obtained by blending with unmodified cellulose and the ones obtained with the differently modified celluloses.

EXPERIMENTAL

Residual cellulose from the Kraft process and used in the paper industry was supplied by Komotini Paper Mill S.A. (Komotini, Greece) and was used for the further modification and preparation of the composites. As a polymer matrix, PP modified with ethyl vinyl acetate (EVA) (PPEVAmoD) and supplied by Polykemi (Ystad, Sweden) was used. This PP was obtained from recycled plastic bottle tops, and the presence of EVA was due to the fact that the inner surface covering of the PP bottle tops was usually made of EVA. The EVA content in the supplied PPEVAmoD was estimated by thermogravimetric analysis (TGA) and was around 2.5 wt %.

Vinyltrimethoxysilane (97%, Aldrich), acetic acid glacial (100%) and acetic anhydride (97%, both supplied by Merck), and PPgMA Epolen (Eastman-

Kodak) were used for the different cellulose modifications.

Cellulose modification

The cellulose was modified by three different methods to enhance adhesion to the matrix in further processing:

Treatment with PPgMA

PPgMA was dissolved in toluene at about 100°C. When it was completely dissolved, the cellulose fibers were immersed in solution and kept there for 5 min at 100°C. The cellulose was filtered and then kept in the oven at 70°C for 24 h to evaporate the solvent completely.²⁵ The quantities of PPgMA and cellulose were calculated as 5wt % PPgMA in the cellulose fibers.

Treatment with silanes

Vinyltrimethoxysilane was dissolved in a hot solution (~60°C) of acetone/water (95/5 v/v) with a 3% (based on the cellulose weight) of benzoyl peroxide as an initiator.²⁶ The cellulose fibers were immersed in the solution and kept there for 2 h at that temperature. The cellulose was filtered and then kept in the oven at 70°C for 24 h. The quantity of the silane used was calculated as 5 wt % silane in the cellulose fibers.

Acetylation

The cellulose fibers were soaked in glacial acetic acid with 3–4 drops of sulfuric acid at room temperature for 1 h and were then decanted. The fibers were then soaked in acetic anhydride with two drops of sulfuric acid for 5 min. The fibers were washed with water several times, filtered, and then dried in the oven at 70°C for 24 h.²³ The degree of acetylation was estimated by TGA, and it was around 1.9 wt %.

Blending

Table I gives the composition and characteristics of the prepared blends. To study the influence of the cellulose content, we prepared three different blends with unmodified cellulose, varying the cellulose content from 20 to 60 wt %. To study the influence of the modifiers, we prepared blends with 40 wt % of the differently modified celluloses. Also, we prepared another blend by mechanical modification, with the cellulose unmodified at a percentage of 40% and the addition of PPgMA as a compatibilizer during blending with the PP. Blending was performed in a Brabender roll–mixer at 190°C and a rotor speed of 70 rpm for 18 min. The PP was added first, and the cellulose fibers were not added until the PP was completely melted in the mixer.

TABLE I
Compositions of the Blends

Sample	Composition
20nomod	20% Unmodified cellulose + 80% PP
40nomod	40% Unmodified cellulose + 60% PP
60nomod	60% Unmodified cellulose + 40% PP
40modMAmec	40% Cellulose + 5% PPgMA (with respect to the cellulose weight) + 60% PP
40modMASol	40% Cellulose-modified PPgMA + 60% PP
40modsilanes	40% Cellulose-modified silanes + 60% PP
40acetylated	40% Cellulose modified by acetylation + 60% PP

Characterizations

All the blends were characterized by thermal and thermomechanical analysis. TGA and DSC experiments were performed in N₂ and in O₂ atmospheres.

TGA was performed on a Mettler Toledo TGA/SDTA 851^e, and the samples were heated from 25 to 700°C at 10°C/min (N₂ and O₂). DSC was performed in a Mettler Toledo DSC 820. In a N₂ atmosphere, the samples were heated from 25 to 210°C at 10°C/min, then cooled from 210 to 25°C at -10°C/min, kept at 25°C for 2 min, and then heated again from 25 to 210°C at 10°C/min, with the gas flow kept at 80 mL/min. In an O₂ atmosphere, the samples were heated from 25 to 400°C at 10°C/min at a gas flow of 80 mL/min.

DMTA experiments were performed in a Polymer Laboratories dynamic mechanical thermal analyzer (PL-DMTA Mk II). The samples were tested from -120 to 140°C at a heating rate of 2°C/min.

From the DSC curves in N₂, the crystallinity (X_c) values were obtained from the integral of the peak

obtained in the second heating for each sample through the following formula:

$$X_c = (\Delta H / \Delta H_0) / (100 / w)$$

where ΔH₀ = 191,3 J/g is the heat of fusion for the 100% crystalline isotactic PP and w is the mass fraction of PP in the composite.

RESULTS AND DISCUSSIONS

Figure 1 shows the TGA curves in N₂ of the biocomposites prepared with different contents of unmodified cellulose (20nomod, 40nomod, and 60 nomod), together with the curves for the PPEVAmo and the composites with cellulose used as a raw material. When the influence of the cellulose content was studied, we concluded that the composites presented a thermal response in between the PP and the cellulose behavior. In all the curves, a first degradation could be observed that corresponded to the cellulose part of the

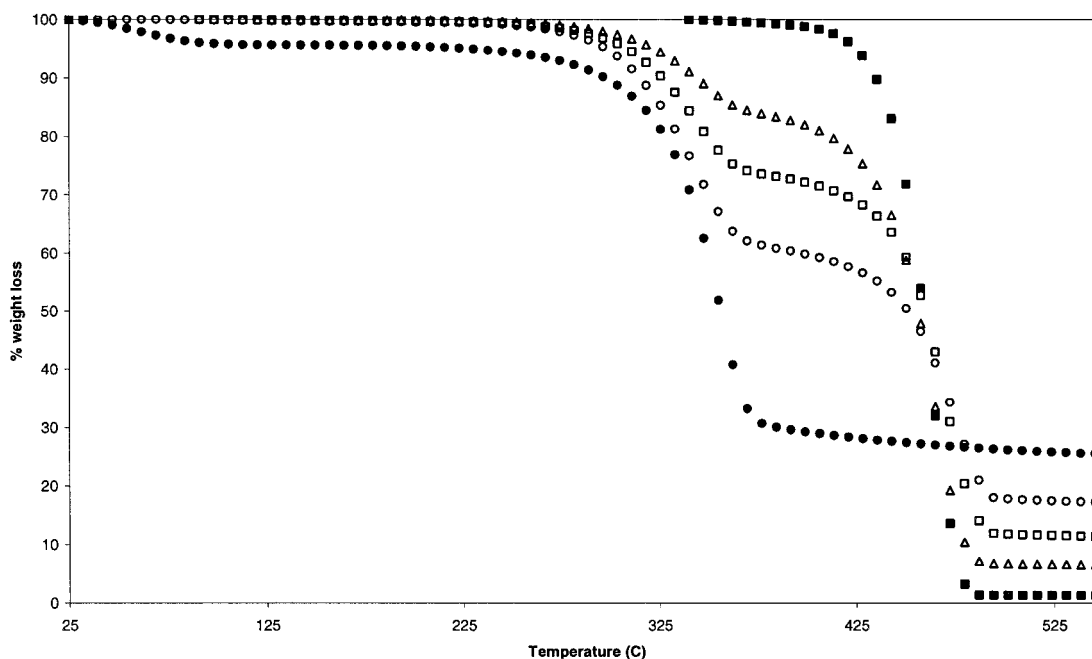


Figure 1 Thermal stability of composites with different cellulose contents: (■) PPEVAmo, (●) cellulose, (△) 20nomod, (□) 40nomod, and (○) 60nomod.

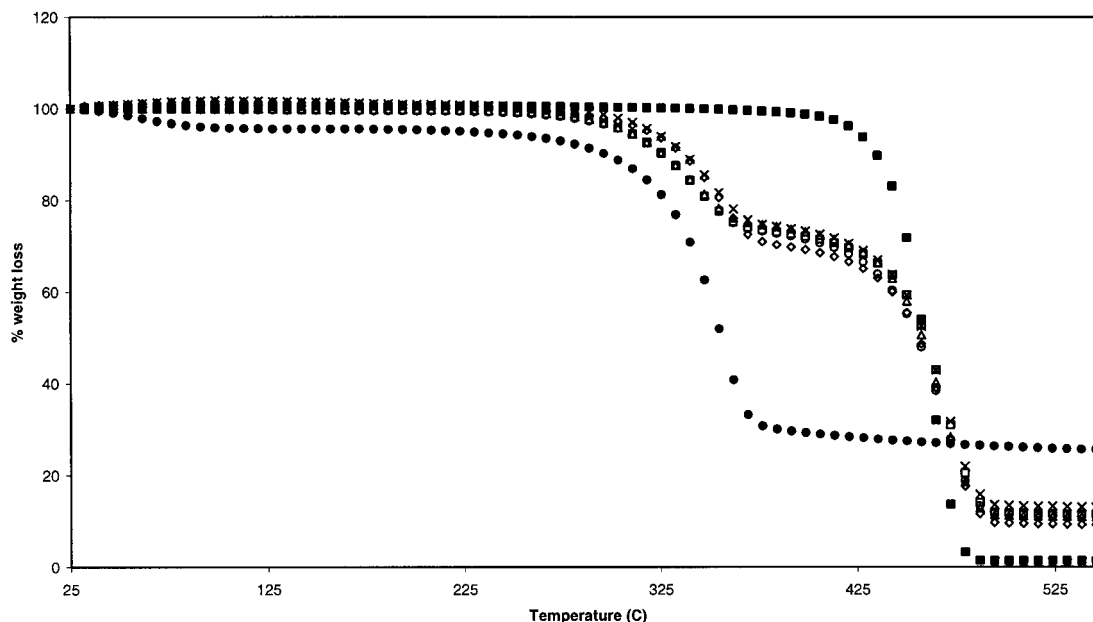


Figure 2 Thermal stability of different composites with 40 wt % cellulose: (■) PPEVAmod, (●) cellulose, (□) 40nomod, (△) 40modMAmec, (○) 40modMASol, (×) 40modsilanes, and (◇) 40acetylated.

biocomposite, and then a later second degradation step of the PP content was observed. The displacement of the curves could also be appreciated with the increase in cellulose content. As the cellulose content increased, the first step in the curve got closer to the pure cellulose degradation step, whereas the second step moved away from that of the pure PP. Also, the weight loss that occurred in the cellulose at 40–100°C due to the water content disappeared in the biocomposites. This showed us that the water present in the

prime cellulose evaporated during the blending and that the obtained composites did not present any later water absorption.

Figure 2 shows the TGA curves in N_2 of the biocomposites prepared with differently modified celluloses, all of them with the same content (40 wt %). The biocomposites prepared from cellulose modified with silanes and acetylated began to degrade at a slightly higher temperature than the others. Also, the curves for PPEVAmod and cellulose were added to the

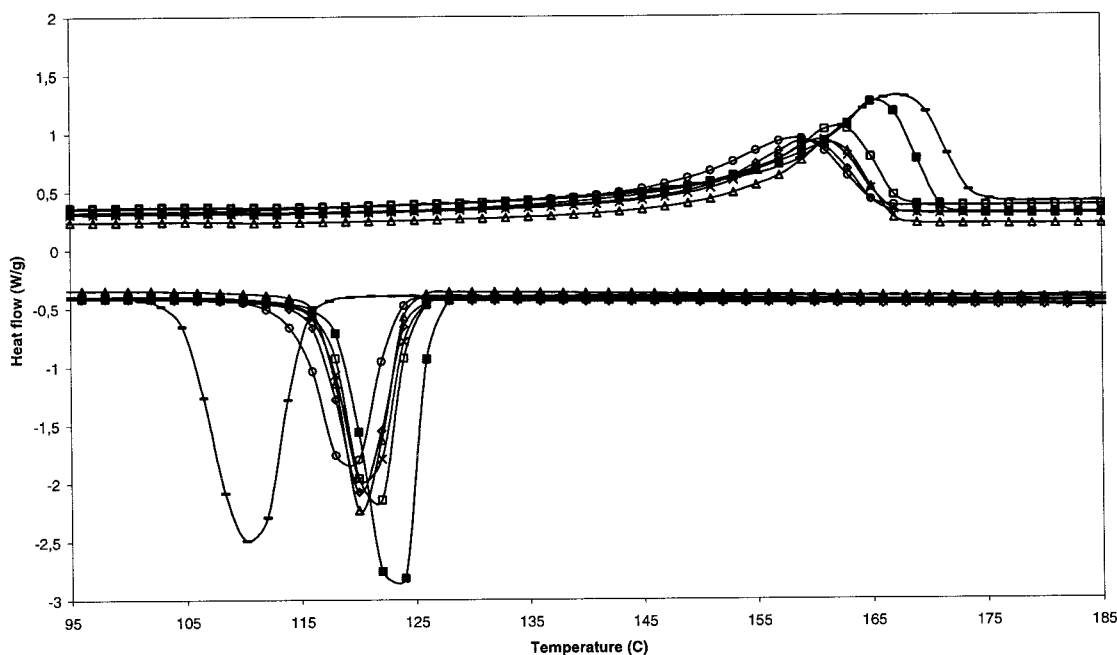


Figure 3 Crystallization characteristics of the different composites with 40 wt % cellulose: (□) PPEVAmod, (□) 40nomod, (△) 40modMAmec, (○) 40modMASol, (×) 40modsilanes, (◇) 40acetylated, and (—) pure PP.

TABLE II
Crystalline Fraction and T_c of the Composites
with 40% wt Cellulose

Sample	X_c (%)	T_c (°C)
PPEVAmod	40.79	123.17
40nomod	42.73	121.33
40modMAmec	41.51	120.33
40modMASol	40.32	119.00
40modsilanes	40.32	120.83
40acetylated	39.46	120.33
Pure PP	43.86	110.67

graph, and we observed, as we noticed before, that the degradation of the composites could be divided into two steps, one due to the cellulose and one later due to the PP and that the water contained in the cellulose completely evaporated during the blending.

Figure 3 presents the DSC curves in N_2 of the bio-composites prepared with the differently modified celluloses at 40 wt %. When we observed the crystallinity values of the different composites with 40 wt % cellulose (Table II), no tendency was observed. Other authors have found that the crystallinity of the composites was higher than the pure PP.¹⁷ In our study, the composites did not follow this tendency because they were prepared from a modified PP. In Figure 3, in addition to PPEVAmod and the composites, an additional curve for a pure commercial PP was added. PPEVAmod had approximately the same crystallinity value but a higher crystallization temperature (T_c) than the commercial pure PP. This led us to conclude that the crystallization process occurred more rapidly, and the crystals formed were smaller in PPEVAmod,

which gave a higher nucleation, probably due to the EVA itself that acted as a coupling agent for the PP. The addition of other compatibilizers or coupling agents can, in some cases, as occurred with the cellulose modified with PPgMA, lead to even more desirable results because the additional PP chains present in the compatibilizer itself. However, in some other cases (e.g., the cellulose modified with silanes and acetylated cellulose), the modification led to lower crystallinity and T_c values, probably because the compatibilization bore the addition of new molecules with radical groups that interfered in the crystallization process, complicating the packaging of the chains, and therefore, the crystalline fraction decreased. The values of crystallinity and T_c did not decrease more than 2% and 4°C, respectively, from the values that other authors¹⁷ have found for pure commercial PP composites, which is a very small difference. The unmodified composite and the one mechanically modified with MA had higher crystallinity values.

Figure 4 presents the thermooxidative stability of the different composites with 40 wt % of cellulose. The oxidation temperature (T_{ox}) was calculated for every sample. As shown in Figure 4 and Table III, the addition of the cellulose, modified or unmodified, affected the thermooxidative stability. The addition of new reactive chemical groups and the processing of the material contributed to the loss of oxidative stability, appreciable by the decrease in T_{ox} (Table III). However, the use of PPgMA as a modifier during the mixing process seemed to inhibit in some way these disadvantages, producing major thermooxidative sta-

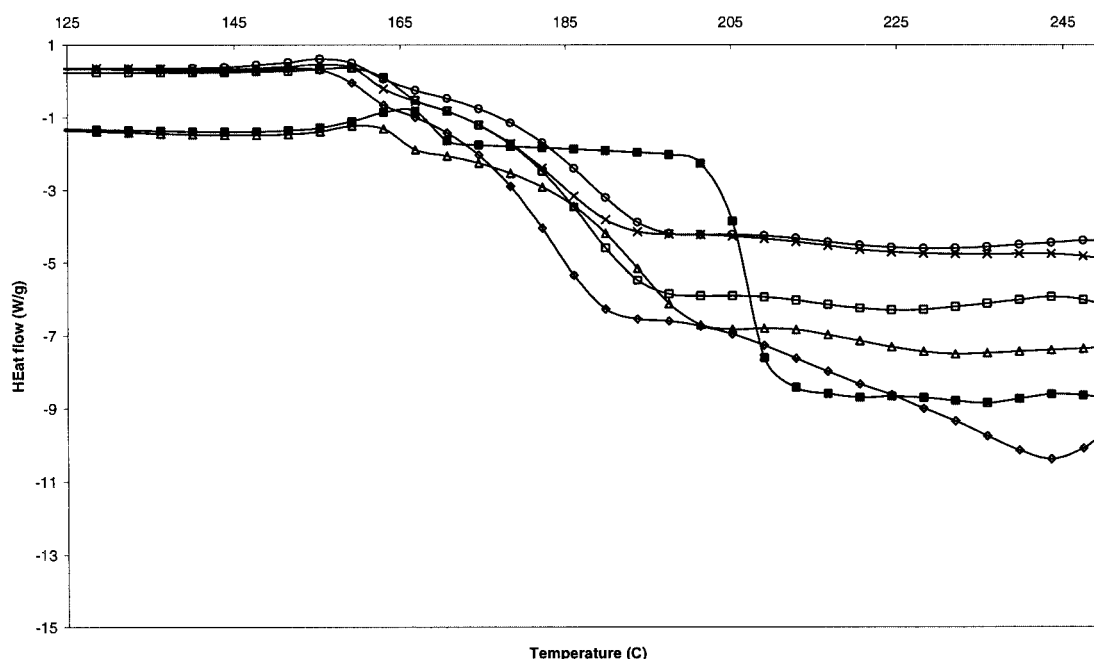


Figure 4 Thermooxidative stability of the different composites with 40 wt % cellulose: (□) PPEVAmod, (□) 40nomod, (△) 40modMAmec, (○) 40modMASol, (×) 40modsilanes, and (◇) 40acetylated.

TABLE III
 T_{ox} Values of the Composites with 40 wt % Cellulose

Sample	T_{ox} (°C)
PPEVAmo	204
40nomod	180
40modMAmec	185
40modMAsol	180
40modsilanes	179
40acetylated	172

bility and increasing the T_{ox} by 5°C when compared to the composite prepared with unmodified cellulose.

DMTA results

Figures 5 and 6 present the log of the dynamic modulus (E') and $\tan \delta$, respectively, of PPEVAmo and the composites with 20, 40, and 60% unmodified cellulose. Two different transitions were observed, the β -transition between -20 and 20°C and the α -transition between 30 and 100°C. The latter transition could be subdivided in two subtransitions, α_a , between 30 and 80°C, and α_b , between 80 and 100°C. From this last temperature, the points did not follow a clear trend because of the deformation of the material due to high temperatures next to the melting point. Every transition implied a change in the decreasing slope of the log E' curve and the increase in the $\tan \delta$, which indicated that the blends became more viscous in nature with rising temperature.

In Figure 5, the enhancing effect of the content of cellulose in the mechanical properties is clearly

shown. The values of E' increased with the cellulose content up to 40wt % cellulose, which represented the best mechanical properties because the composite prepared with 60 wt % cellulose presented lower values of E' .

Figure 6 shows the chain flexibility, related to the sharpening of the β -transition peak. Sharper peaks are characteristics of lower crystallinity and, therefore, with lower moduli, polymers. With increasing crystallinity, the transition became broader, and the peaks were smoothed. This gave us an idea about the chain flexibility of the material; sharper peaks are related to higher chain flexibility; that is, every transition showed the increase in the value of $\tan \delta$ and the subsequent increase in the loss modulus (E''), but after the transition, part of this increase could be recovered, lowering again the E'' value. Therefore, the results in Figure 6 are consistent with the ones presented in Figure 5.

Figures 7 and 8 show the log E' and $\tan \delta$, respectively, for the composites with 40% cellulose modified by different methods. The composite with unmodified cellulose had the highest modulus, and the composites made from cellulose treated with silanes and acetylated cellulose also had good behavior, whereas the composites prepared with cellulose modified with MA, both mechanically and in solution, did not show any enhanced mechanical behavior. This could, at first instance, seem to be a contradictory result because the modifications of the cellulose were considered a method to enhance the compatibilization filler-matrix and, therefore, improve the mechanical properties. As discussed before, the use of PPEVAmo as a prime

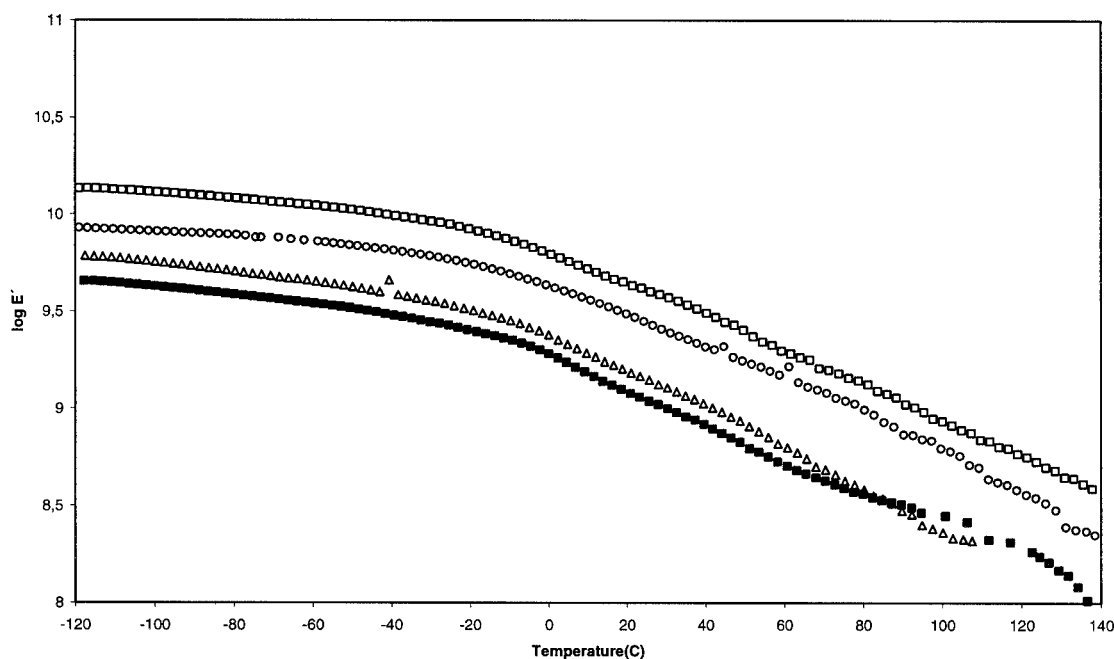


Figure 5 Log E' of the unmodified composites with different cellulose contents: (■) PPEVAmo, (△) 20nomod, (□) 40nomod, and (○) 60nomod.

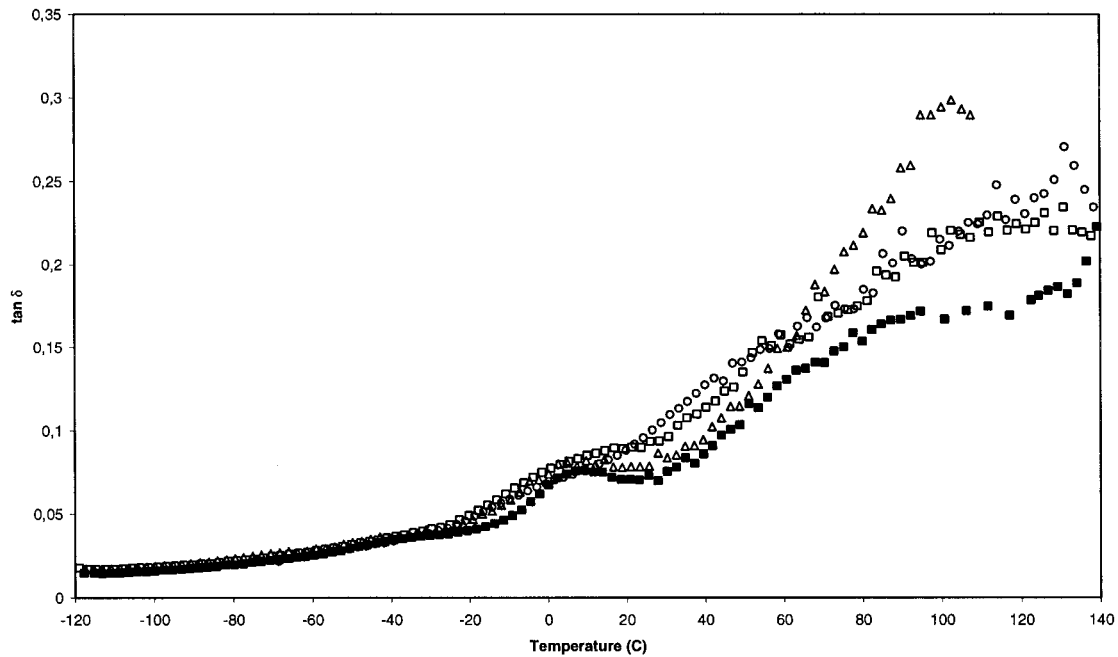


Figure 6 Tan δ of the unmodified composites with different cellulose contents: (■) PPEVAmod, (Δ) 20nomod, (\square) 40nomod, and (\circ) 60nomod.

product in the preparation of the composites gave enhanced mechanical properties with respect to the use of unmodified PP. To prove this, an additional composite prepared with a recycled PP from plastic bottles tops was tested and added to the graphs (Comp40 PPrecycled). The results showed that this later composite also presented very good mechanical properties, approximately in the same range as the composites.

CONCLUSIONS

The use of PP already modified with EVA as prime polymer for the composites enhanced from the beginning the thermomechanical characteristics of the composites without any compatibilization method. Therefore, with respect to the mechanical properties, the modification or lack thereof of the cellulose did not seem to play a very important role in the enhancement

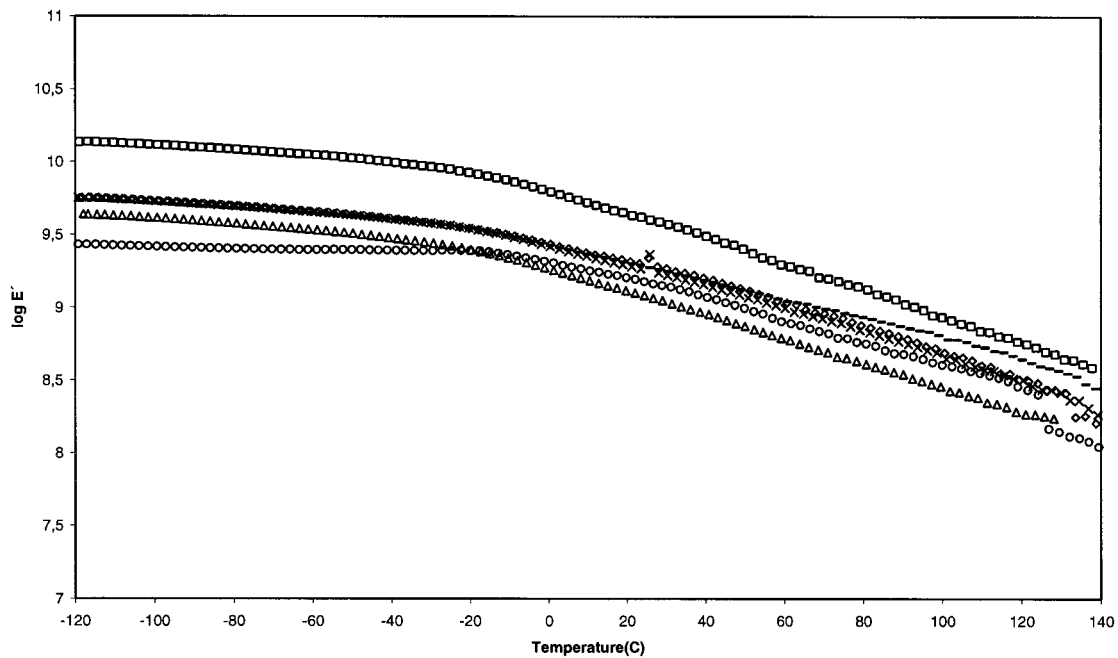


Figure 7 Log E' of the modified composites with 40% cellulose contents: (\square) 40nomod, (—) 40PPrecycled, (Δ) 40modMA-mec, (\circ) 40modMASol, (\times) 40modsilanes, and (\diamond) 40acetylated.

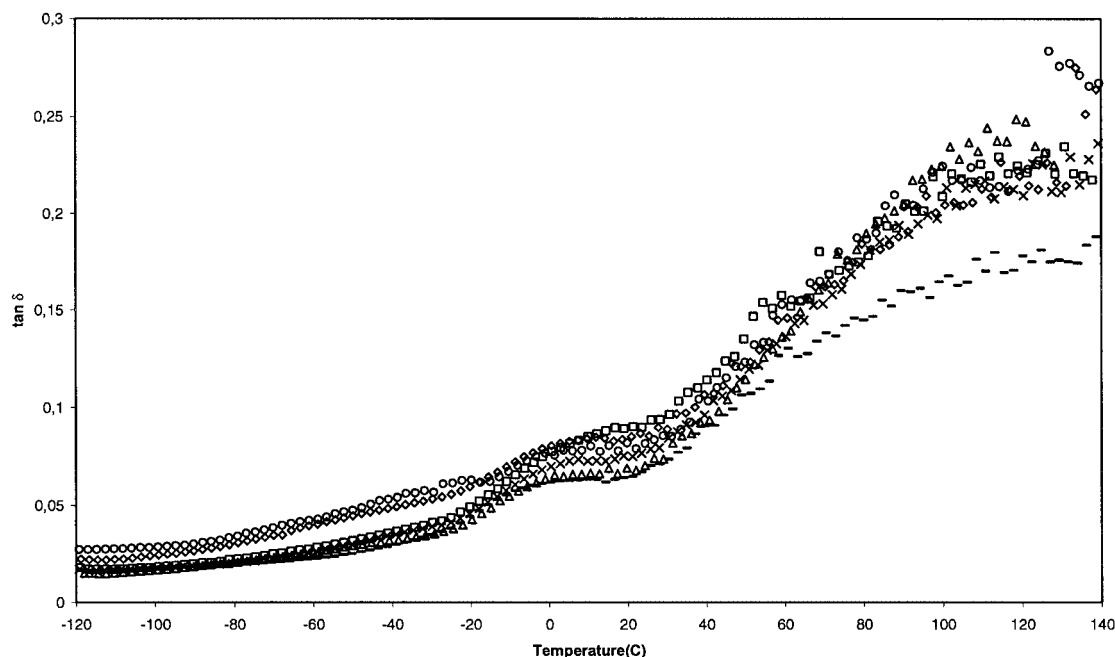


Figure 8 Tan δ of the modified composites with 40% cellulose contents: (\square) 40nomod, (—) 40PPrecycled, (Δ) 40modMAmec, (\circ) 40modMAsoL, (\times) 40modsilanes, and (\diamond) 40acetylated.

of E' and $\tan \delta$. However, the modification methods did, instead, enhance the thermal and thermooxidative stabilities. We concluded that 40 wt % cellulose in PP gave the best mechanical properties. All the compatibilizers tested presented similar results, and none of them gave better properties than the rest; even the composite prepared with cellulose mechanically modified with MA were better than the rest with respect to thermooxidative stability.

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References

- Bledzki, A. K.; Reihmane, S.; Gassan, J. *Polym Plast Technol Eng* 1998, 37, 451.
- Dintcheva, N. T.; La Mantia, F. P. *Polym Adv Technol* 1999, 10, 607.
- George, J.; Bhagawan, S. S.; Thomas, S. J. *Therm Anal* 1996, 47, 1121.
- Glasser, W. G.; Taib, R.; Jain, R. K.; Kander, R. *J Appl Polym Sci* 1999, 73, 1329.
- Hamdan, S.; Hashim, D. M. A.; Ahmad, M.; Embong, S. *J Polym Res* 2000, 7, 237.
- Park, B.-D.; Balatinecz, J. *J Polym Compos* 1997, 18, 79.
- Wielage, B.; Lampke, T.; Marx, G.; Nestler, K.; Starke, D. *Thermochim Acta* 1999, 337, 169.
- Wu, J.; Yu, D.; Chan, C.-M.; Kim, J.; Mai, Y.-W. *J Appl Polym Sci* 2000, 76, 1000.
- Karnani, R.; Krishnan, M.; Narayan, R. *Polym Eng Sci* 1997, 37, 476.
- Ratajska, M.; Boryniec, S. *Polym Adv Technol* 1999, 10, 625.
- Joly, C.; Kofman, M.; Gauthier, R. *J Macromol Sci Pure Appl Chem* 1996, 33, 1981.
- Ha, C.-S.; Park, H.-D.; Cho, W.-J. *J Appl Polym Sci* 1999, 74, 1531.
- Mamunya, E. P.; Mishak, V. D.; Semenovich, G. M.; Lebedev, E. V. *Vysokomol Soedin Ser A Ser B* 1994, 36, 1358.
- Ren, S.; Hon, D. N. S. *J Reinf Plast Compos* 1993, 12, 1311.
- Gauthier, R.; Joly, C.; Coupas, A. C.; Gauthier, H.; Escoubes, M. *Polym Compos* 1998, 19, 287.
- Bledzki, A. K.; Gassan, J. *Prog Polym Sci* 1999, 24, 221.
- Amash, A.; Zugenmaier, P. *Polym Bull (Berlin)* 1998, 40, 251.
- Amash, A.; Zugenmaier, P. *Polymer* 1999, 41, 1589.
- Collier, J. R.; Lu, M.; Fahrurrozi, M.; Collier, B. J. *J Appl Polym Sci* 1996, 61, 1423.
- Bataille, P.; Ricard, L.; Sapieha, S. *Polym Compos* 1989, 10, 103.
- Felix, J. M.; Gatenholm, P.; Schreiber, H. P. *Polym Compos* 1993, 14, 449.
- Ishida, H. *Polym Compos* 1984, 5, 101.
- Albano, C.; Gonzalez, J.; Ichazo, M.; Kaiser, D. *Polym Degrad Stab* 1999, 66, 179.
- Gomez-Bueso, J.; Westin, M.; Torgilsson, R.; Olesen, P. O.; Simonson, R. *Holz Roh- Werkst* 1999, 57, 433.
- Felix, J. M.; Gatenholm, P. *J Appl Polym Sci* 1991, 42, 609.
- Matias, M. C.; De La Orden, M. U.; Sanchez, C. G.; Urreaga, J. M. *J Appl Polym Sci* 2000, 75, 256.