Maleated Polypropylene as a Coupling Agent for Polypropylene–Waste Newspaper Flour Composites

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Received 22 July 1997; accepted 22 July 1998

ABSTRACT: This paper reports on the influence of maleated polypropylene (MAPP) on the properties of polypropylene (PP)/newspaper flour (PF) composite, and the compatibilization mechanism was also studied. The results of mechanical tests and scanning electron microscope (SEM) showed that MAPP was a true coupling agent for PP/PF blends. The existence of chemical bonds between paper flour and MAPP was proved by gravimetric analysis, while the cocrystallization between bulk PP and PP segments of MAPP was evidenced by differential scanning calorimeter (DSC) and wide angle X-ray diffraction (WAXD) analysis. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 333–337, 1999

Key words: coupling agent; maleated polypropylene; paper flour; polypropylene

INTRODUCTION

In recent years, the use of wastepaper as filler in thermoplastics is attracting more and more attention in research laboratories.[1–3] Contaminants (inks, coatings, etc.), which have very adverse effects on paper recycled from wastepaper, have little effect on these composites. Thermoplastics composites based on wastepaper offer a number of benefits, such as high specific stiffness and strength, desirable fiber aspect ratio, flexibility during processing with less abrasive to the equipment, low density, biodegradability, and low cost per volume basis. Polypropylene composites containing 50% reclaimed newspaper pulp have been successfully introduced by the Mitsubishi Corp. in Japan under the Papia tradename for injection molding and thermoforming of automotive components.[4]

The main problem of preparation of wastepaper–thermoplastics composites is the incompatibility of hydrophilic paper filler and hydrophobic thermoplastics matrix, which yields composites of poor properties. Brown and Soto observed that the addition of conventional silane coupling agent had little effect on the ultimate properties of wastepaper–thermoplastics composites,[2] while some other studies showed that functionalized thermoplastics such as maleated polypropylene can be used to improve the compatibility of wastepaper and thermoplastics.[5,6] In this article maleated polypropylene was selected as a coupling agent for polypropylene–waste newspaper flour composites, and its effect on properties and compatibilization mechanism were investigated.

EXPERIMENTAL

Materials

Waste newspaper flour (PF) was grounded in a ball mill to the size of 40 mesh; polypropylene (PP) was supplied from Jinshan Petroleum Co. (Shanghai, China), melt flow index 2 g/10 min; Maleated polypropylene (MAPP) was obtained from Jieshijie Chemical Industrial Co. (Shanghai, China), melt flow index 12 g/10 min.

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Journal of Applied Polymer Science, Vol. 71, 333–337 (1999)
 CCC 0021-8995/99/020333-05

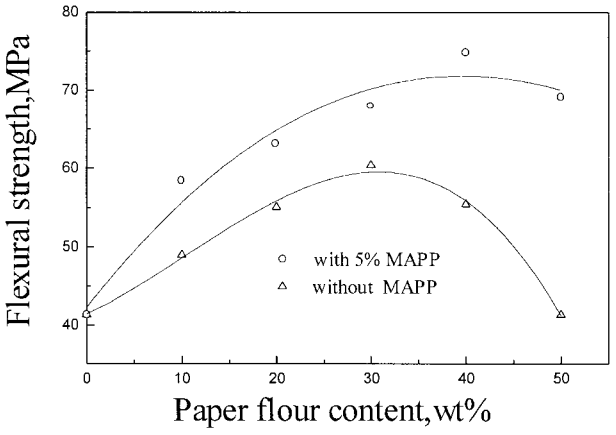


Figure 1 Flexural strength versus paper flour content.

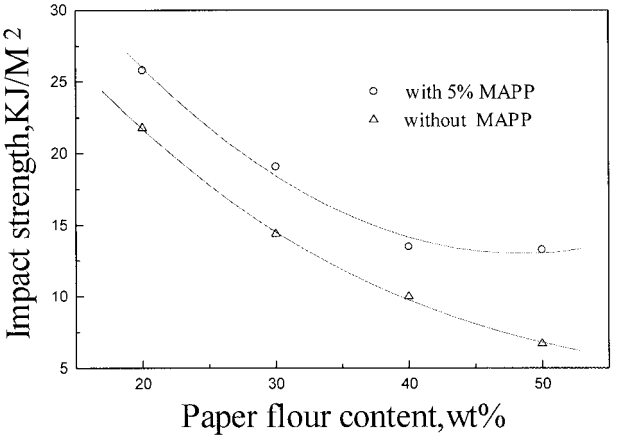


Figure 2 Impact strength versus paper flour content.

Preparation of Samples

The blending of materials was done at 185–190°C in a two-roll mill, paper flour was added after PP had melted, and the mixing was carried out for 10 min. After mixing, the blends were removed for compression molding at 185°C for 10 min. Finally, the composites were cooled to room temperature by cool pressing.

Tests

The flexural strength, modulus, and unnotched Charpy impact strength were measured following the Chinese national standards 1446–83, 1449–83, and 1043–79, respectively.

The morphology of the impact fracture surfaces of samples was observed with a Phillips-515 scanning electron microscope (SEM) after coating with gold.

A Perkin–Elmer DSC-7 differential scanning calorimeter (DSC) was used to study the thermal transition behavior of PP, MAPP, and their blends, PP/MAPP (wt ratio 50 : 50), heating rate 10°C/min.

The crystal structures of PP, MAPP, and PP/MAPP were studied through wide angle X-ray diffraction (WAXD), CuKα line, nickel filter.

Melt flow properties of composites were measured on a capillary rheometer at 190°C, using a capillary die of L/D = 40; Robinowitsch correction was applied.

RESULTS AND DISCUSSION

Effect of MAPP on Mechanical Properties of the Composites

Because of the poor compatibility of PP and PF, it is nearly impossible to prepare the PP/PF blends

Table I Effect of MAPP Content on Mechanical Properties

Content of MAPP (wt %)	Flexural Strength (MPa)	Impact Strength (kJ/M^2)	Flexural Modulus (MPa)
0	41.29	6.68	2842
0.5	56.78	7.47	3114
1	57.57	9.69	3004
2	58.30	10.42	3024
3	57.69	10.69	2945
5	69.85	13.01	3119
10	78.41	17.17	2916
20	73.30	22.52	2975
30	77.35	23.10	2927

Composition: (PP + MAPP)/PF = 50 : 50.

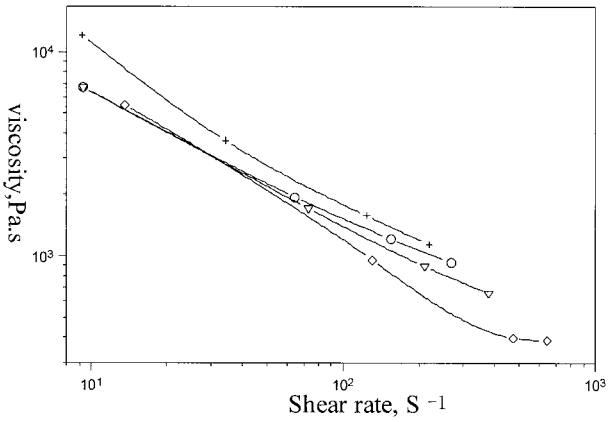


Figure 3 The rheological behavior of PP/PF composites (190°C). (◇) w(PF) = 40%, w(MAPP) = 0%; (△) w(PF) = 50%, w(MAPP) = 10%; (○) w(PF) = 50%, w(MAPP) = 0%; (+) w(PF) = 50%, w(MAPP) = 5%. Composition: PF + PP + MAPP = 100%.

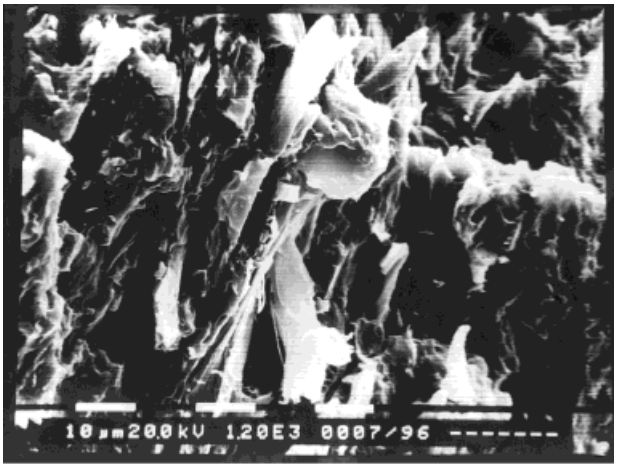
with good mechanical properties. As seen in Figures 1 and 2, for uncompatibilized composites the flexural strength reached maximum at 30 wt % PF content, and then decreased with the further increase of the amount of PF; while the impact strength decreased drastically with the PF content, the samples containing 0 and 10 wt % PF can't even be fractured. In order to improve the compatibility, MAPP was added into the composites. As seen in Figures 1 and 2, the addition of 5 wt % MAPP produced a significant improvement of the mechanical properties, both flexural strength and impact strength increased to a great extent; especially when PF content was 50 wt %, a 68% increase of flexural strength and a 98% increase of impact strength were observed. Furthermore, the maximum value of flexural strength appeared when PF content was 40 wt %.

The influence of MAPP content on mechanical properties of the composites (PP/PF = 50 : 50) is shown in Table I. Generally, the strength values increased with the increase of MAPP content. As can be seen, 0.5 wt % MAPP was enough to remarkably increase the values of both flexural and impact strengths, but when MAPP content varied from 1 to 3 wt % the strength values almost remained unchanged; when MAPP content was up to 5 wt %, strength values began to increase again; flexural strength stopped increasing when MAPP content was up to 10 wt %, but impact strength continued to increase. The flexural modulus had a certain increase due to the addition of MAPP.

In a word, the mechanical properties of PP/PF composites can be significantly improved by the addition of MAPP.

Effect of MAPP on Rheological Behavior of Composites

Figure 3 shows the influence of the addition of PF and coupling agent on the flow properties of PP melts. The increase of PF content results in an increase of the apparent viscosity of composites. It is worth noting that adding 5 wt % MAPP gave the system a further increase in viscosity, though the viscosity of MAPP was lower than that of PP.



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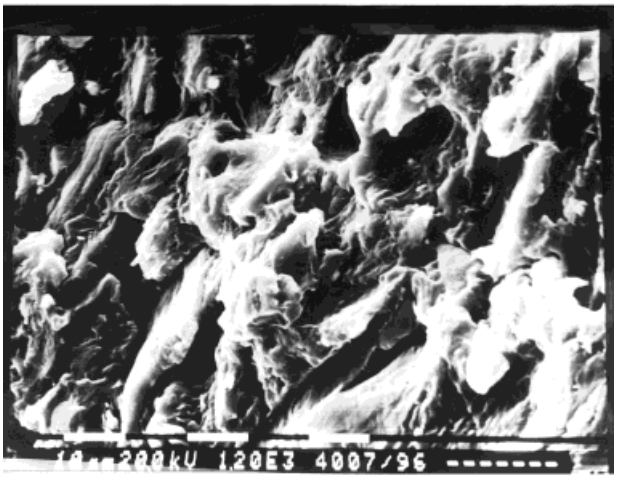

B

Figure 4 SEM micrograph of fracture surface of PF/PP composite. (A) w(PF) = 50 wt %, w(MAPP) = 0 wt %. (B) w(PF) = 50 wt %, w(MAPP) = 5 wt %.

Table II Lattice Parameters of PP, MAPP, and PP/MAPP

Parameter (Å)	PP[a]	PP	MAPP	PP/MAPP
a	6.65	6.63	6.66	6.62
b	20.96	21.14	21.14	21.16
c	6.50	6.43	6.52	6.53

[a] Data from ref. 7.

This phenomenon implies that MAPP might have improved the interfacial adhesion of PP and PF. When MAPP content was 10 wt %, the viscosity of the whole system decreased, which indicates that only part of MAPP played the role of improving the adhesion of PP and PF.

SEM Analysis

Scanning electron microscope (SEM) was used to study the impact fracture surfaces of composite samples containing 50 wt % paper flour. SEM micrographs of the fracture surfaces are shown in Figure 4.

The micrograph of the sample without MAPP [Fig. 4(A)] shows poor wetting of paper flour by the PP matrix; the fracture occurred in the interface of paper flour and PP, and paper fibers were pulled out because of the insufficient adhesion between paper flour and PP. While Figure 4(B) shows that when 5 wt % MAPP was added, the fracture occurred in the matrix material; the paper fibers were covered by layers of PP matrix.

All the above illustrate that the presence of MAPP enhanced the adhesion of paper flour and PP, improved the compatibility of the two phases, and therefore led to better mechanical properties.

Compatibilization Mechanism of MAPP

As we all know, a coupling agent effects compatibilization by interacting with both the filler and the matrix, thus forming a link between the components. We have shown that MAPP had an excellent compatibilizing effect on PP/PF composites; as to the essence of the compatibilization of this type, we think that the PP segments of MAPP formed miscible blends with the bulk PP through cocrystallization, and the polar part of MAPP (maleic anhydride) formed a chemical bond with the paper flour. The following is our study of the compatibilization mechanism of MAPP.

The Interaction Between MAPP and PP

Cocrystallization is the driving force of compatibilization between crystalline/crystalline components of the same kind. We measured the crystal structures of PP, MAPP, and MAPP/PP (50 : 50)

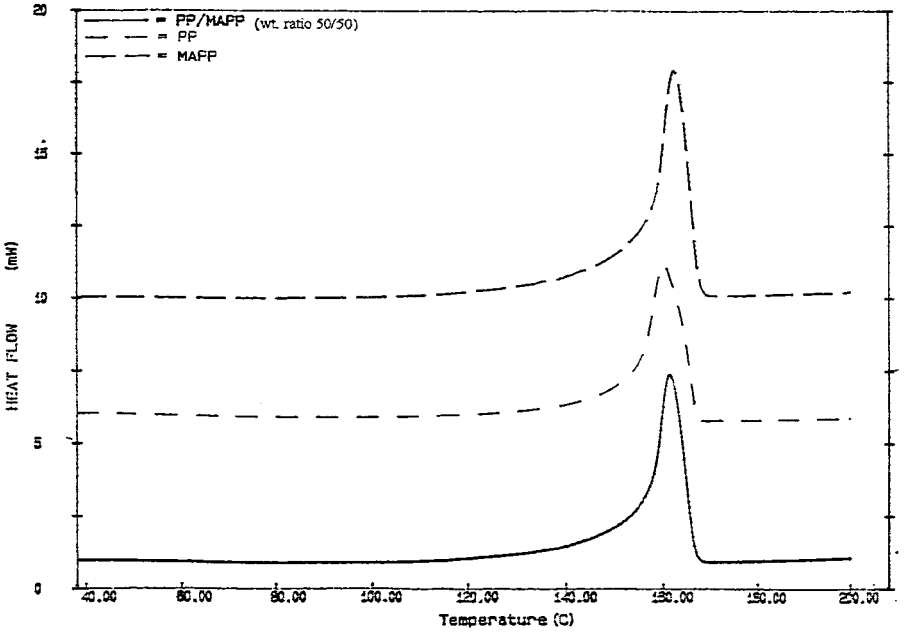

Figure 5 DSC curves of PP, MAPP, and MAPP/PP.

Table III Weight Percent of the Composite Retained After Extraction

PF (%)	PP (%)	MAPP (%)	Weight Retention (%)
50	50	—	52.35
50	45	5	54.92
40	60	—	40.35
40	55	5	42.83

with a wide angle X-ray diffractometer. The results demonstrate that all the crystalline of PP, MAPP, and MAPP/PP existed in α crystal form, and had the same lattice parameters (Table II).

The DSC curves of PP, MAPP, and MAPP/PP are shown in Figure 5. The MAPP/PP blends had only one melting peak, which situated between the peaks of PP and MAPP. This proves that MAPP cocrystallized completely with PP.

Specific Interaction Between MAPP and Paper Flour

The composite samples were Sohxleet-extracted with hot xylene for 24 h to remove all components not covalently bonded to paper flour. The extraction residual weights are shown in Table III. Compared with samples without MAPP, all the residuals of samples with 5 wt % MAPP had more weight. This result suggests that part of MAPP was chemically attached to the surfaces of paper flour, so it remained within the residual after extraction. Taking account of the abundant hydroxyl groups on the surfaces of paper flour and the maleic anhydride groups on PP segments of MAPP, it is reasonable for us to propose that MAPP can react with paper flour through esterification. In a previous study, with infrared spectroscopy (IR), Felix and Gatenholm had proved that in the pure cellulose–PP composites, MAPP was covalently bonded to cellulose fibers through esterification.[8]

CONCLUSION

MAPP is a very good coupling agent for polypropylene–waste newspaper flour composites, can improve the compatibility of polypropylene and paper flour, and hence increase the mechanical properties of the composites. The compatibilization mechanism is that MAPP forms chemical bonds with paper flour and the PP segments of MAPP cocrystallize with the bulk PP.

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