Composites Based on Maleated Polypropylene and Methyl Cellulosic Fiber: Mechanical and Thermal Properties

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ABSTRACT: Composites based on maleated polypropylene and methyl cellulosic fiber were prepared by extrusion followed by injection molding. The methyl cellulosic fiber was pretreated with tetrabutyl orthotitanate prior to compounding. The mechanical and thermal properties, as well as morphology of composites, were investigated by means of tensile, impact, dynamic mechanical analysis, thermogravimetric measurements, and scanning electron microscopy. Static tensile tests showed that the stiffness and tensile strength of composites tend to increase with increasing fiber content. However, the elongation at break appeared to decrease with increasing fiber content. In contrast, the impact strength of composites increased slightly with increasing fiber content. The improvements in tensile and impact properties were attributed to the interaction between the functional group of maleic anhydride and tetrabutyl orthotitanate. Such interaction tended to improve the interfacial bonding between the methyl cellulosic fiber and polypropylene matrix. Thermogravimetric measurements revealed that the incorporation of methyl cellulosic fiber into maleated polypropylene results in a marked reduction of thermo-oxidative stability. The effects of coupling agent additions on the mechanical properties of composites are discussed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1647-1653, 1999

Key words: maleated polypropylene; composites; methyl cellulose; coupling agent; tetrabutyl orthotitanate; mechanical property

INTRODUCTION

Polymer composites reinforced with short fibers are used increasingly in a variety of industrial applications owing to their high stiffness, high strength-to-weight ratios, and ease of processing. Their properties can be tailored according to the types of reinforced fibers and matrix materials used.¹⁻⁵ The use of natural fibers such as wood, jute, pineapple, sisal and cotton in polymeric composites have received considerable attention recently. This is because they are inexpensive, biodegradable, renewable, and environmentally

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friendly.⁶⁻¹⁰ In addition, wood and cellulosic fibers exhibit several attractive mechanical properties for use as reinforcements in thermoplasrics. These include high specific strength and stiffness, high aspect ratio of about 100, less fiber breakage during compounding, and low hardness, which minimizes abrasion of the equipment during processing.^{11–14} In this regard, wood fiberreinforced thermoplastics show promise to be used as materials for automotive components, frames, shipping crates and pallets, storage bins, and seasonal furniture.¹⁵ However, cellulosic fibers also has disadvantages, such as low processing temperature, poor moisture resistance, and poor bonding with polymers.^{16,17} The poor interfacial bonding between the hydrophilic wood fiber and the hydrophobic polymer matrix generally

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leads to a lower tensile strength. The interfacial bonding can be improved by chemical modification of the surface of cellulose fibers with various coupling agents and compatibilizers.¹⁸⁻²⁴ These agents can modify the surface by interacting with both the fiber and matrix, thereby forming a link between the components. For example, Kokta and coworkers reported that coupling agents such as silanes and isocynates improve the mechanical properties and dimensional stability of cellulosic fiber/polyethylene (PE) composites.^{18,21} In some studies, cellulose fibers were surface treated with maleic anhydride-grafted polypropylene (maleated PP).^{25–28} The beneficial effects of maleated PP on increasing the tensile strength of wood fiber/PP composites is attributed to the esterification reaction between wood fiber hydroxyl group and anhydride functional group of maleated PP.^{27,28} More recently, Liao et al. indicated that titanate coupling agents are very effective to improve the compatibility between the wood fiber and PE matrix, thereby improving the mechanical properties accordingly.

Generally, cellulosic fiber-reinforced thermoplastics exhibit higher strength and stiffness, but lower impact toughness when compared with unfilled polymers. The impact strength of wood fiber/PP composites can be increased by the incorporation of elastomer particles (EPDM) in the PP matrix. However, the addition of EPDM leads to a decrease in both stiffness and tensile strength of composites.⁹ PP is a versatile commodity polymer that is used in many applications, for example, car, architectural material, furniture, insulation, and electronic piece. Various inorganic particulates, short glass fibers, as well as natural fibers have been incorporated into PP to increase its mechanical performance performance. In this article, we attempt to use methyl cellulose fiber as a reinforcement material for PP composites, and to investigate the thermal, static, and dynamic mechanical properties of such composites. Methyl cellulose is widely used as an additive during the synthesis of polymer resin. It can also serves as a thickener, binder, and emulsion stabilizer in the plastics industries.²⁹ The surface of methyl cellulose fiber was treated with tetrabutyl orthotinanate for this study. Moreover, maleated PP was also added in the PP composites to facilitate stronger interaction between the cellulose fiber and PP matrix.

EXPERIMENTAL

Materials

Methyl cellulose (MC) fiber used in this work was purchased from Shanghai Chemical Co. (China). The PP polymer (Profax 6331, USA) with a melt flow index of 12 g/10 min was supplied by Himont Company. Maleated PP (Hercoprime HG 201, USA) used was a commercial product of the Himont Company.

Preparation of Composites

Tetrabutyl orthotitanate solution (5 wt %) was prepared by dispersing it in acetone. The solution was then sprayed on the fiber surface, and the weight ratio of fiber to tetrabutyl orthotitanate was fixed at 99 : 1. The surface-treated fiber was then heated in an oven at 60°C for 72 h.

PP pellets were initially dried at 90°C for 24 h. The blend consisting of PP (90 wt %) and maleated PP (10 wt %) was prepared in Brabender extruder at 220°C, and was subsequently pelletized. This blend was designated as MPP throughout this article.

Composites with MPP/MC weight ratios of 95/5, 90/10, 80/20, and 75/25 were initially prepared by blending MPP pellets with the pretreated fiber in a Brabender single-screw extruder at 195°C and 35 rpm. The resulting blends were pelletized. As MPP and MC fiber were not mixed properly during the initial blending in a single-screw extruder, they were subjected to additional extrusion treatment. The MPP/MC pellets were fed into Brabender twin-screw extruder again at 200°C and 20 rpm, and the products were granulized. Using these granules, tensile bars according to ASTM D638 standard were injection molded. For the purpose of comparison, composites reinforced with MC fiber without surface modification were also prepared under similar processing conditions. Untreated MC fiber was designated as MC' in this article.

Mechanical Measurements

The static tensile behavior of composites was investigated at room temperature using an Instron model 4206 at a crosshead speed of 1 mm/min. Five specimens of each composition were tested and the average values reported.

Notched Izod impact specimens with dimensions of $65 \times 12.8 \times 3.2$ mm were cut from the injection-molded tensile bars. The length direc-

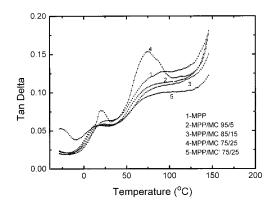


Figure 1 Tan δ vs. temperature for MPP and MPP/MC composites.

tion of impact specimens is parallel to mold-filling direction. An average of six specimens were tested in each case.

Dynamic mechanical behavior of composites was determined with a DuPont dynamic mechanical analyzer (model 983) at a fixed frequency of 1 Hz, an oscillation amplitude of 0.2 mm. The size of specimens for dynamic mechanical analysis (DMA) was $55 \times 12.8 \times 3.2$ mm. The temperature of the specimens was increased from -30 to 150° C at a heating rate of 2° C/min.

Thermal Analyses

The thermal behavior of composites was determined using a Seiko thermogravimetric analyzer (TGA; model SSc-5200) under a helium protective atmosphere. This facility was also equipped with a differential thermal analyzer (DTA). The temperature was scanned from 30 to 600°C at a heating rate of 10°C/min.

Morphological Observations

The composite specimens were fractured in liquid nitrogen prior to the examination in a scanning electron microscope (SEM; JEOL SM 820). The fractured surfaces were coated with a thin layer a gold.

RESULTS AND DISCUSSION

Effects of Coupling Agent

Figure 1 shows the tan δ vs. temperature curves for MPP and MPP/MC composites. The results of DMA measurements are summarized in Table I. The glass transition temperatures (T_g) for MPP and MC are designated as T_g^1 and T_g^2 , respectively. The difference in T_g^1 and T_g^2 value (D) is also listed in Table I. It is apparent from Table I that the D value tends to decrease with increasing MC fiber content. This implies that the compatibility between the MPP and MC fiber is improved as the MC content increases. This is due to the amount of tetrabutyl titanate in composites increases with increasing fiber content. Moreover, Table I also reveals that the *D* value of MPP/MC 85/15 is much smaller than that of MPP/MC'85/ 15. Apparently, the coupling agent, i.e., tetrabutyl titanate, has a significant effect in improving the interfacial bonding between MC fiber and MPP matrix. It should be noted that the incorporation of maleic anhydride grafted PP (MPP) in the composites investigated also exhibit beneficial effects in enhancing such an interfacial bonding. In general, there are two approaches commonly used to enhance the chemical or physical interactions between the reinforcements and polymer matrix. The first method involves the modification of the matrix structure via chemical reactions, while the second route utilizes the coupling agents to modify the chemical nature of the fiber surface. In this study, tetrabutyl orthotitanate is used as the surface modifier for cellulosic fiber. leading to an improvement in the compatibility between MC and MPP. The possible chemical reaction is depicted in Figure 2(a). Because of its chemical structure, cellulosic fiber is hydrophylic; hence, many hydroxyl groups are available for interaction with water molecules by hydrogen bonding. In contrast to glass fibers where water adsorbs at the surface, cellulosic fiber interacts with water not only at the surface, but also in the bulk.^{30,31} Gauthier et al. pointed out that the compatibilizers used in the cellulosic fiber/poly-

Table IThe Glass Transition Temperatures ofMPP, MC and MPP/MC Composites

Specimen	T_g^1 , °C	T_g^2 , °C	$D = T_g^2 - T_g^1$
MC	_	83.76^{a}	_
MPP	23.05	_	_
MPP/MC 95/5	15.56	80.90	65.34
MPP/MC 90/10	15.65	80.38	64.73
MPP/MC 85/15	21.17	84.73	63.56
MPP/MC 80/20	20.09	82.30	62.21
MPP/MC 75/25	19.96	75.27	55.31
MPP/MC' 85/15	14.74	87.09	72.35

^a Determined by differential scanning calorimetry.

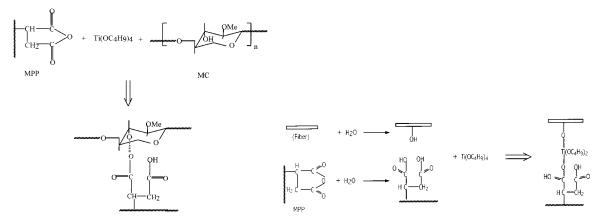


Figure 2 (a) Possible reaction between the functional group of MPP, tetrabutyl orthotitanate, and cellulosic fiber leading to the formation of ternary polymer product; (b) Schematic diagram showing the possible reaction between tetrabutyl orthotitanate and OH-groups of cellulosic fiber and MPP.

olefin composites must possess a function highly reactive with the OH-groups of the cellulose.³¹ In this context, it is considered that tetrabutyl orthotitanate can effectively react with the OHgroups of the cellulosic fiber and with the OHgroups developed in MPP via hydrolytic reactions [Fig. 2(b)]. Consequently, the surface tension between the cellulosic fiber and MPP is reduced accordingly. A previous study³² has investigated the performance of potassium titanate whiskerreinforced PP composites. The whisker was surface treated with tetrabutyl orthotitanate, while the PP was modified with maleated PP. The results showed that there exists a strong interaction between the functional group of MPP and tetrabutyl titanate, thereby effectively reducing the surface tension between the whisker and matrix.32

Mechanical Properties

Figures 3 shows the variations of tensile strength and Young's modulus with fiber content for MPP/MC composites, respectively. The storage modulus vs. temperature of the composites determined from DMA measurements is shown in Figure 4. It can be seen from Figure 3 that both the tensile strength and stiffness of composites appear to increase significantly with increasing fiber content. The tensile strength increases almost linearly with increasing fiber content up to 15 wt %; thereafter it tends to increase steadily. The increase in tensile strength of the composites is related the improvement of the compatibility between the fiber and matrix, as discussed above.

The storage modulus of composites also appears to increase with increasing fiber content (Fig. 4). Therefore, MPP/MC composites have much potential for applications of environmentally degradable plastics owing to their strength and stiffness increases with increasing fiber content. It is well known that natural starch fillers are commonly added to the polyolefins to increase their degradation rate. However, the starch/polyolefins blends exhibit low mechanical strength, thereby restricting their uses in many applications. In previous studies, Tjong et al. have investigated the mechanical properties and degradation behavior of the blends of polyolefins with polycaprolactone (PCL). The results showed that the tensile strength of MPP/PCL and maleated PE/PCL de-

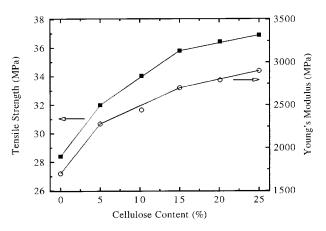


Figure 3 Variations of tensile strength and Young's modulus of composites with fiber content for MPP/MC composites.

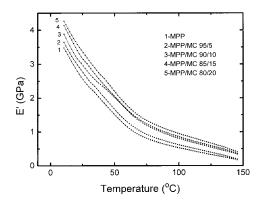


Figure 4 Storage modulus vs. temperature for MPP and MPP/MC composites.

crease dramatically with increasing PCL content.^{33,34} In terms of the high cost of PCL and poor mechanical performance of the PCL/polyolefins blends, thus low cost MPP/MC composites with favorable mechanical properties appear to be another promising class of biodegradable structural materials.

Figures 5 and show the variation of tensile strain at break with whisker content for MPP/MC composites. The tensile ductility appears to decrease with increasing fiber content. In general, the strain at break and impact strength of filled thermoplastics show a decreasing trend as a function of filler concentration. In contrast, the impact strength of MPP/MC composites increases considerably with the addition of fiber content ≥ 5 wt % (Fig. 6). Improvement in impact strength can be explained by interactions between the functional group of MPP and titanate coupling agent.

Morphology

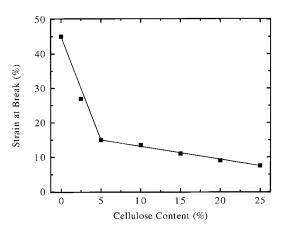


Figure 7(a)–(d) shows the SEM micrographs of MPP/MC 95/5, 90/10, 85/15, and 75/25 composites

Figure 5 Variation of strain at break with fiber content for MPP/MC composites.

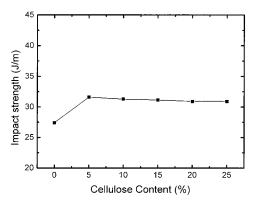


Figure 6 Variation of impact strength with fiber content for MPP/MC composites.

cryo-fractured in liquid nitrogen. The fracture surfaces are perpendicular to MFD. At low fiber loading, the fibers are dispersed more uniformly in the matrix, and they oriented parallel to MFD. In this case, the tensile strength increases dramatically with the addition of MC fibers up to 15 wt %. At higher fiber loading, some agglomeration of MC fibers can be observed [Fig. 7(c)]. Moreover, the fibers appear to be oriented more randomly. Therefore, the increasing trend in tensile strength is slow down considerably [Fig. 3(a)].

Thermal Behavior

Figure 8 shows the TG curves for MC, MPP and MPP/MC composites. The 5% weight loss temperature $(T_{-5\%})$ for these specimens are listed in Table II. The maximum weight loss temperature for MPP (T_{max}^1) and MC (T_{max}^2) determined from the derivative weight-loss (DTG) curves are also tabulated. Furthermore, the melting temperatures of all specimens determined by DTA measurements are also given in Table II. From this table, the melting temperature of MPP is 167.9°C, and all the composites studied only exhibit one melting temperature associated with that of MPP phase. The incorporation of MC to MPP has no effect in shifting the melting temperature of MPP. In contrast, the addition of MC fiber to MPP leads to a dramatic decrease in $T_{-5\%}$, i.e., from 395°C for MPP copolymer to 339.9°C for MPP/MC 75/25 composite. It is evident from Figure 8 that the MPP/MC composites with higher MC content exhibit higher weight loss than those with lower MC content and MPP copolymer at $T_{-5\%}$. This is attributed to MC has lower $T_{-5\%}$ (269.9°C) than that of MPP copolymer. In this context, MC has poorer thermo-oxidative stability than MPP.

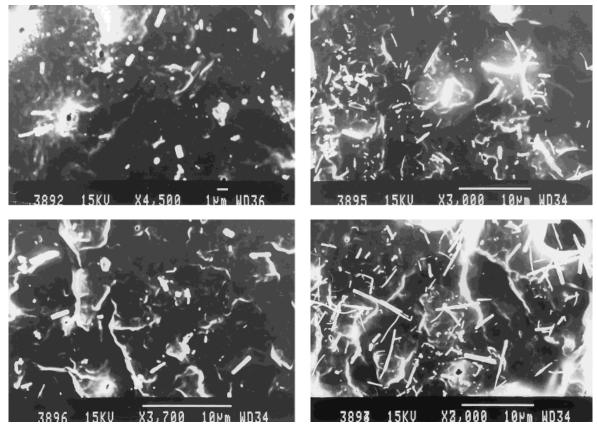


Figure 7 SEM micrographs showing the fracture surfaces of (a) MPP/MC 95/5, (b) MPP/MC 90/10, (c) MPP/MC 85/15, and (d) MPP/MC 75/25 composites.

Hence, the incorporation of MC into MPP matrix facilitates the oxidative degradation of MPP.

CONCLUSION

Maleated PP composites reinforced with tetrabutyl orthotitanate-treated methyl cellulosic fiber

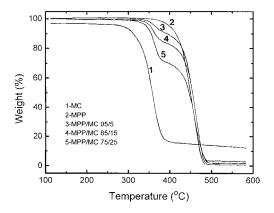


Figure 8 Thermogravimetric curves for MPP, MC, and MPP/MC composites.

were prepared by intrusion followed by injection molding. Mechanical measurements showed that the tensile strength, stiffness, and impact strength of the composites tend to increase with increasing fiber content. This was attributed to the interaction between the functional group of maleic anhydride and the tetrabutyl orthotitanate coupling agent. DMA measurements revealed that such interaction results in the improvement

Table II	Thermal Properties of MPP, MC, and
MPP/MC	Composites

Specimen	$T_m, ^{\circ}C$	$T^{1}_{\max}, ^{\circ}C$	$T^2_{\max}, ^{\circ}C$	$T_{-5\%}, ^{\circ}C$
MC	_	354.2	_	269.9
MPP	167.9		453.7	395.0
MPP/MC 95/5	167.8	358.5	459.8	360.4
MPP/MC 90/10	167.8	358.0	457.3	352.8
MPP/MC 85/15	168.0	359.6	458.8	348.9
MPP/MC 80/20	168.0	360.4	453.4	343.9
MPP/MC 75/25	166.7	363.1	454.8	339.9
MPP/MC' 85/15	168.0	360.5	457.4	351.5

Y. Xu is on sabbatical leave from University of Dalian, and Y. Z. Meng is on leave from Dalian University of Technology.

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