Preparation and Mechanical Properties of Polypropylene–Clay Hybrids Based on Modified Polypropylene and Organophilic Clay

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ABSTRACT: Polypropylene–clay hybrids (PPCHs) were prepared by melt blending maleic anhydride modified PP and organophilic clay. In these PPCHs the silicate layers of the clay were exfoliated and dispersed to the monolayers. The hybridization of the clay in PP was achieved with modified PP with a small amount of maleic anhydride groups. The tensile modulus of the PPCH with 5 wt % clay was 1.9 times higher than that of the matrix resin at 25°C. The dynamic storage moduli (E') of the PPCHs were also higher than those of the modified PP. The E' was 2.5 times higher than that of the matrix resin at 60°C. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 1918–1922, 2000

Key words: polypropylene; organophilic clay; melt blending

INTRODUCTION

In recent years, organic–inorganic nanocomposites have attracted great interest to researchers because they frequently exhibit unexpected hybrid properties that are synergistically derived from the two components.[1–11] One of the most promising composite systems are hybrids based on organic polymers and inorganic clay minerals consisting of silicate layers.[4–11] In our previous works, we synthesized a nylon 6–clay hybrid (NCH) in which 10 Å thick silicate layers of clay minerals are dispersed homogeneously in the nylon 6 matrix.[4] The NCH exhibits various superior properties such as high strength, high modulus, and high heat resistance compared to nylon 6.[5] Since then, other polymer–clay hybrids such as polyimide,[6] epoxy resin,[7] polystyrene,[8] polycaprolactone,[9] acrylic polymer,[10] and polypropylene (PP)[11] were reported.

One of the most widely used polymers is PP, so PP–clay hybrids have attracted great research interest. We reported a novel approach to prepare a PP–clay hybrid (PPCH) by using a functional oligomer as a compatibilizer, in which the silicate layers of the clay were dispersed uniformly to the nanometer level.[11] In this case the PPCHs consisted of PP, the functional oligomer, and organophilic clay. Recently, we found that PP with functional groups was intercalated into the interlayers of the organophilic clay, as well as the functional oligomer.

We report a facile approach to prepare PPCHs using a modified PP and organophilic clay and study the mechanical properties.

EXPERIMENTAL

Materials

The materials used for the preparation of the samples were purified montmorillonite (Kunipia-F) from Kunimine Ind. Co., octadecylamine

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Table I Clay Contents of PPCHs and PPCC

	Clay Contents (wt %)
PPCH-2	2.1
PPCH-3	2.8
PPCH-4	3.8
PPCH-5	5.3
PPCC	4.4

from Wako Pure Chemical Co., maleic anhydride modified PP (PP-MA) from Exxon Chemical, and homo PP (MA2) from Mitsubishi Chemical. The acid value of the PP-MA was 2.1 mg KOH/g. (The amount of the modified MA was 0.2 wt %.) GPC was used to measure the weight-average molecular weight (M_w), which was 209,000.

Preparation of Organophilic Clay

Sodium montmorillonite (80 g, cation exchange capacity of 119 meq/100 g) was dispersed into 5000 mL of hot water (about 80°C) by using a homogenizer. Octadecylamine (31.1 g, 115 mmol) and concentrated HCl (11.5 mL) were dissolved into hot water. It was poured into the montmorillonite–water solution under vigorous stirring by using the homogenizer for 5 min and yielded white precipitates. The precipitates were collected, washed with hot water 3 times, and freeze-dried to yield an organophilic montmorillonite intercalated with octadecylammonium (C18-Mt). The interlayer spacing of the C18-Mt was about 22 Å, which was measured by X-ray diffraction (XRD). The XRD measurements were taken using a Rigaku RAD-B diffractometer with Cu-Kα radiation at 30 kV and 30 mA. The inorganic content of 69.2 wt % was found by measuring the weights before and after burning its organic parts.

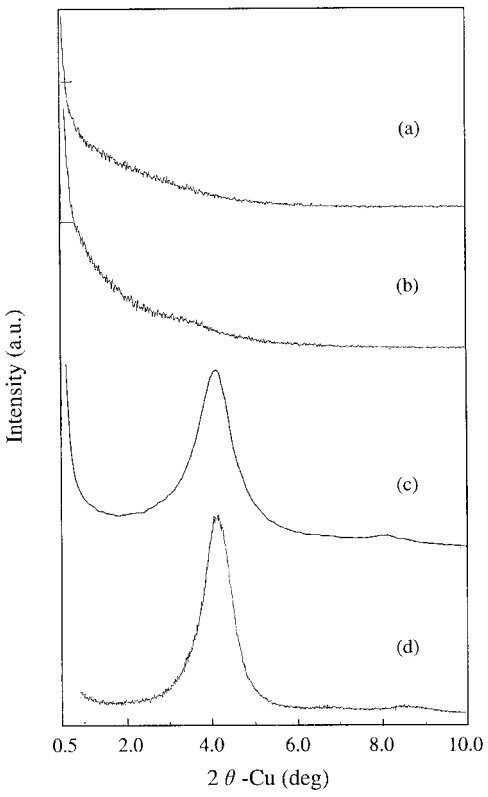

Figure 1 X-ray diffraction patterns for (a) PPCH-2, (b) PPCH-5, (c) PPCC, and (d) C18-Mt.

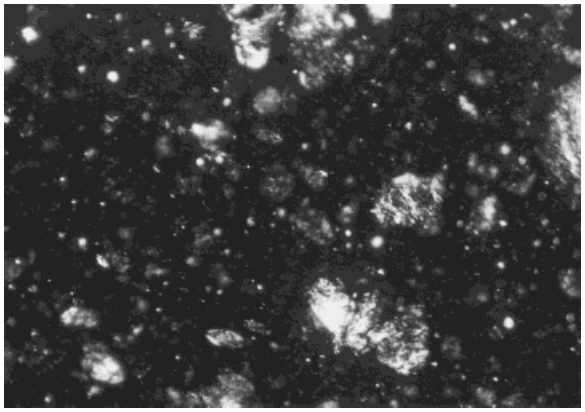

Figure 2 The optical microscope photograph of PPCC.

Preparation of PPCHs

The pellets of PP-MA and the powder of C18-Mt were melt blended at 200°C by using a twin-screw

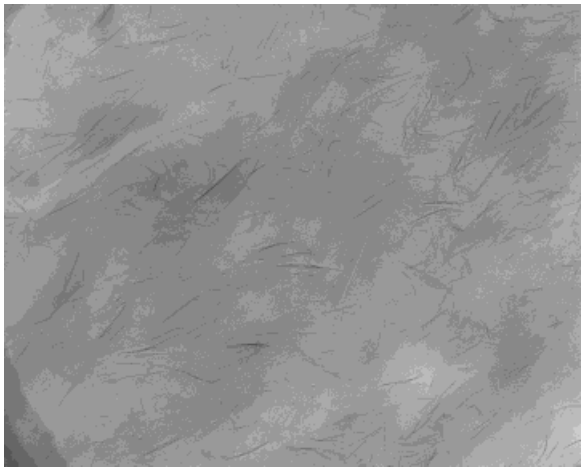

Figure 3 A TEM photograph of PPCH-2.

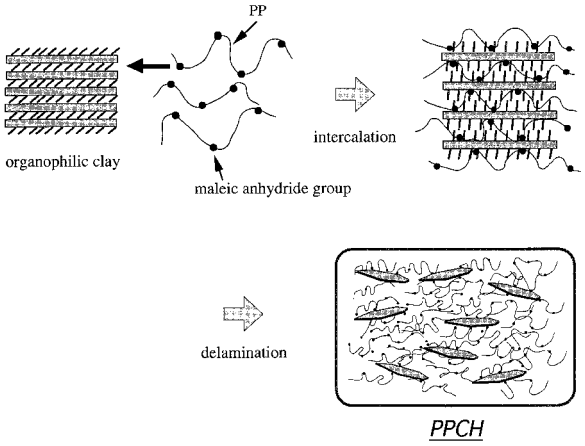

Figure 4 The schematic figure of the clay dispersing process.

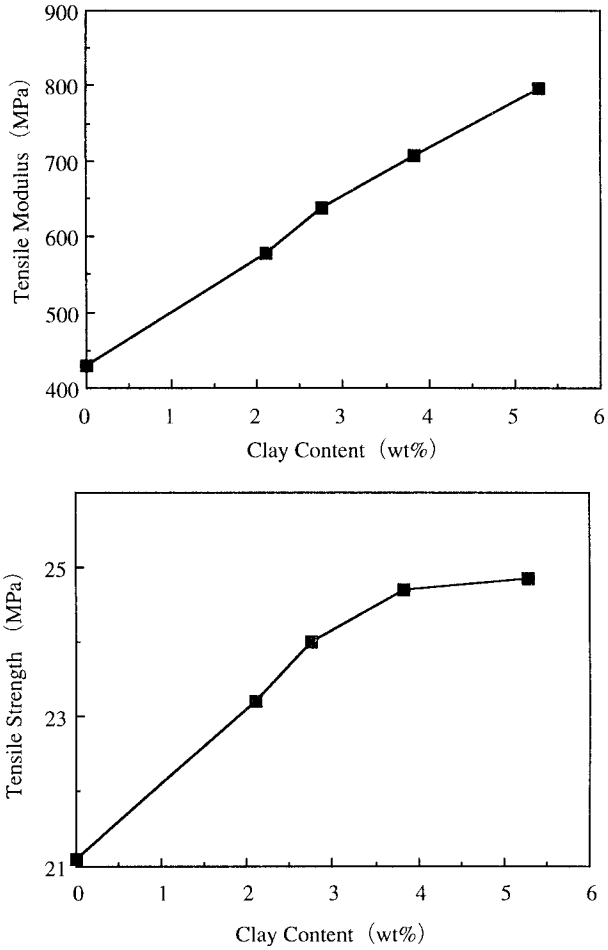

Figure 5 The tensile modulus and strength of PPCHs versus the clay contents.

extruder (SIKRC, Nissei Plastic Industrial Co.) to yield the PPCHs. The obtained strands were pelletized and dried under a vacuum at 80°C. In order to consider the effect of MA modification of PP, the composites of PP and C18-Mt (PPCC) were prepared. The contents of the inorganic clay of the PPCHs and PPCC were measured by burning the samples. The results are listed in Table I.

The dried pellets of the hybrids were injection molded into test pieces for tensile tests and measurements of the dynamic moduli by using an injection molder (PS40E2ASE, Nissei Plastic Industrial Co.). The temperatures of the cylinders were 180–190°C and that of the mold was 30°C.

Evaluation of Dispersibility of Clay

The dispersibility of the silicates layers in the hybrids was evaluated by using an X-ray diffractometer and transmission electron microscopy (TEM). The XRD patterns of the thin films of the hybrids were obtained. The TEM observations were performed for the thin sections of thin films with a Jeol-2000EX using an acceleration voltage of 200 kV.

Table II Results of Tensile Test

Sample	Modulus (MPa)	Strength (MPa)	Elongation (%)
PP-MA	429^{+8}_{-12}	$21.1^{+0.0}_{-0.0}$	> 200
PPCH-2	578^{+30}_{-27} (1.35)	$23.2^{+0.2}_{-0.1}$ (1.10)	> 200
PPCH-3	639^{+14}_{-14} (1.49)	$24.0^{+0.1}_{-0.2}$ (1.14)	> 200
PPCH-4	707^{+47}_{-50} (1.65)	$24.7^{+0.2}_{-0.2}$ (1.17)	$23.1^{+1.5}_{-1.6}$
PPCH-5	797^{+34}_{-29} (1.86)	$24.9^{+0.3}_{-0.8}$ (1.18)	$10.5^{+0.5}_{-0.5}$
PP	780^{+16}_{-10}	$32.5^{+0.1}_{-0.2}$	> 200
PPCC	830^{+22}_{-40} (1.06)	$31.9^{+0.1}_{-0.2}$ (0.98)	105^{+35}_{-30}

The values in parentheses are the relative values of the PPCHs and PPCC to those of *m*-PP and PP, respectively.

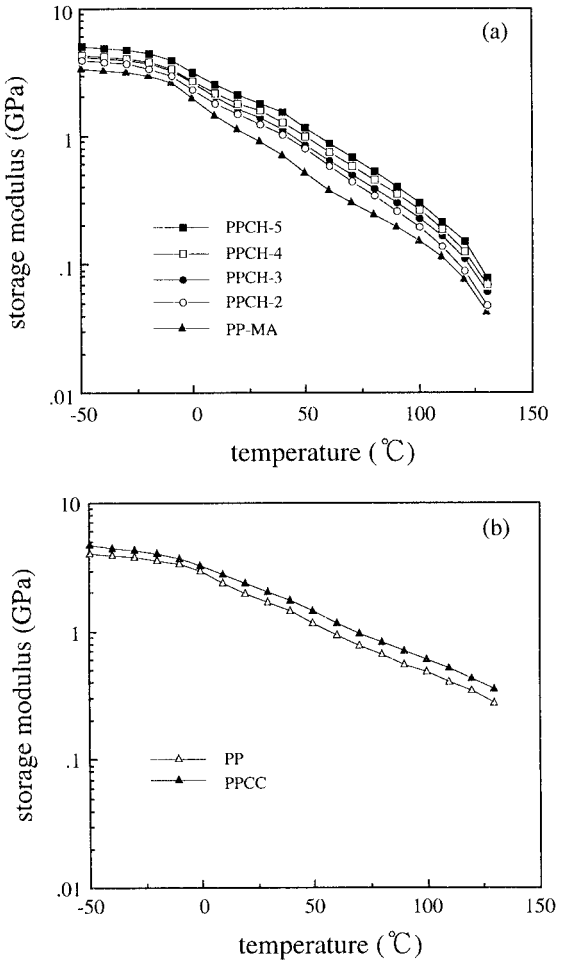

Figure 6 The dynamic storage moduli versus the temperature for (a) PP-MA and PPCHs and (b) PP and PPCC.

RESULTS AND DISCUSSION

Dispersibility of Clay in PPCHs

Figure 1 shows the XRD patterns of the samples and C18-Mt; the peaks correspond to the (001) plane reflections of the clays. There were no peaks in the XRD patterns of the PPCHs. Thus, this suggested that there were no stacked clays in the PPCHs. On the other hand, there was an apparent peak in the PPCC and the interlayer spacing was not different from that of C18-Mt. This indicated that PP was not intercalated into the interlayers of the clay at all. Therefore, it is apparent that the polymer chains of the PP-MA could be intercalated into the clay interlayers by the interactions between the MA groups and the clay surface.

Figure 2 shows the polarized microscopy photograph of the PPCC. In the PPCC there were many aggregates of the clays at the micron level. Figure 3 shows the TEM photograph of PPCH-2, in which the dark lines are the cross sections of silicate layers of 10-Å thickness. The silicate layers were exfoliated and dispersed to the monolayers in the PP-MA. Figure 4 shows a schematic of the process in which the organophilic clay was dispersed in the PP-MA. The hybridization of the clay in PP was achieved with modified PP with a small amount of MA groups.

Study of Mechanical Properties of PPCHs

Table II shows the results of the tensile test and Figure 5 shows the tensile modulus and strength versus the clay contents. The tensile moduli of the

Table III Dynamic Storage Moduli of Hybrids and Related Samples at Various Temperatures and Glass-Transition Temperatures (T_g), Obtained from tan δ

	Storage Modulus (GPa)				
Sample	−50°C	30°C	60°C	100°C	T_g (°C)
PP-MA	3.39	0.899	0.376	0.151	6
PPCH-2	3.96 (1.17)	1.25 (1.39)	0.586 (1.56)	0.192 (1.27)	6
PPCH-3	4.15 (1.22)	1.38 (1.53)	0.641 (1.70)	0.229 (1.52)	8
PPCH-4	4.31 (1.27)	1.56 (1.73)	0.759 (2.00)	0.263 (1.74)	6
PPCH-5	5.02 (1.48)	1.82 (2.02)	0.869 (2.31)	0.302 (2.00)	8
PP	4.08	1.69	0.649	0.475	13
PPCC	4.71 (1.15)	2.05 (1.21)	1.15 (1.24)	0.597 (1.26)	9

The values in parentheses are the relative values of the PPCHs and PPCC to those of PP-MA and PP, respectively.

[a] These temperatures were measured at the peak tops of the tan δ.

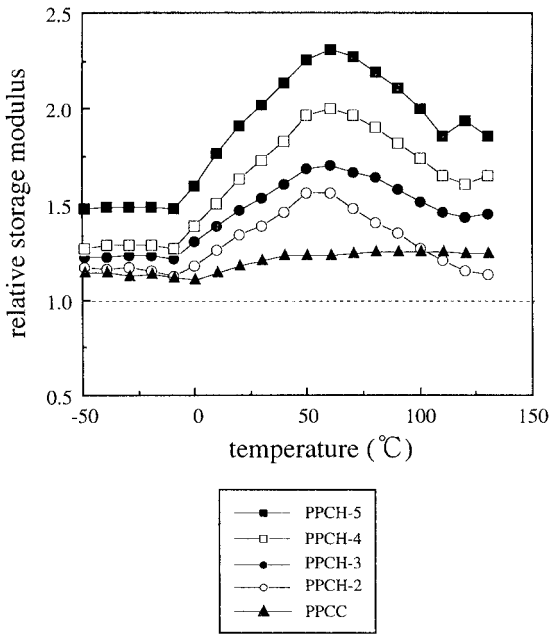

Figure 7 The relative dynamic storage moduli of the PPCHs to PP-MA and PPCC to PP.

PPCHs rose as the clay contents increased. The modulus of PPCH-5 was 1.9 times higher than that of PP-MA. The tensile strengths of the PPCHs were also increased compared to that of PP-MA. The strength of PPCH-5 was 20% higher than that of PP-MA. On the other hand, the modulus of PPCC was 1.06 times higher and the strength decreased compared to that of PP. The elongations of the PPCHs with $<$ 3 wt % clay contents were over 200%. The PPCHs with $<$ 4 wt % clay contents showed yielding points, but PPCH-5 did not have a yielding point.

The dynamic storage moduli of the PPCHs and PPCC are plotted versus the temperature in Figure 6. The representative values of the storage moduli at −50, 30, 60, and 100°C and the glass-transition temperatures (T_g) are listed in Table III. The dynamic storage moduli of the PPCHs were higher than those of PP-MA. In order to clarify the effect of the hybridization with the clays, the relative storage moduli of the PPCHs to those of PP-MA are plotted in Figure 7. The relative storage moduli of the PPCHs below the T_g (around 10°C obtained from tan δ) were relatively small. However, above the T_g they drastically increased up to the peak tops at about 60–70°C and then decreased. The storage modulus of PPCH-5 was 2.5 times higher than that of PP-MA at 60°C. On the other hand, the relative storage moduli of PPCC-5 were relatively small and almost constant versus the temperature.

CONCLUSION

We prepared PPCHs by melt blending MA modified PP and organophilic clay. In these PPCHs the silicate layers were exfoliated and dispersed to monolayers. The modulus and strength of the PPCHs increased as the clay contents increased. For example, the modulus and strength of PPCH-5 were about 90 and 20% higher compared to those of modified PP. The dynamic storage moduli of the PPCHs were higher than that of modified PP. The storage modulus of PPCH-5 was 2.5 times higher than that of modified PP at 60°C.

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