Preparation and Mechanical Properties of Polypropylene−Clay Hybrids

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ABSTRACT: Polypropylene (PP)−clay hybrids (PPCH) have been prepared by simple melt-mixing of three components, i.e., PP, maleic anhydride modified polypropylene oligomers (PP-MA), and clays intercalated with stearylammonium. The dispersibility of 10-Å-thick silicate layers of the clays in the hybrids was investigated by using a transmission electron microscope and X-ray diffractometer. It is found that there are two important factors to achieve the exfoliated and homogeneous dispersion of the layers in the hybrids: (1) the intercalation capability of the oligomers in the layers and (2) the miscibility of the oligomers with PP. Almost complete hybrids were obtained in the case where the PP-MA has both intercalation capability and miscibility. The hybrids exhibit higher storage moduli compared to those of PP especially in the temperature range from T_g to 90 °C. The highest relative storage modulus at 80 °C of the hybrid based on a mica and the miscible PP-MA is as high as 2.0 to that of PP and is 2.4 to that of the PP/PP-MA mixture, which is considered to be the matrix of the PPCH. Also, the effects of the kinds of clays and oligomers on the dynamic moduli are discussed.

1. Introduction

In recent years, organic−inorganic nanometer composites have attracted great interest from researchers since they frequently exhibit unexpected hybrid properties synergistically derived from two components.[1−11] One of the most promising composite systems would be hybrids based on organic polymers and inorganic clay minerals consisting of layered silicates.[4−11] In our previous works, we synthesized nylon 6−clay hybrids (NCHs) in which 10-Å-thick silicate layers of clay minerals are dispersed homogeneously in the nylon 6 matrix.[5] The NCH exhibits various superior properties such as high strength, high modulus, and high heat distortion temperature, compared to nylon 6.[6] The most characteristic feature of the NCH is that the drastic change in these properties could be derived with a few percents of the clays. The same concept has been applied for various polymer systems such as polyimide,[7] epoxy resin,[8] polystyrene,[8a,9] polycaprolactone,[10] and acrylic polymer[8a,11] to date. However, the exfoliated and homogeneous dispersion of the silicate layers could be achieved only in a few cases, such as polymers containing polar functional groups, i.e., amide[5] and imide groups.[7] This is mostly due to the fact that the silicate layers of the clay have polar hydroxy groups and are compatible only with polymers containing polar functional groups.

Polypropylene (PP) is one of the most widely used polyolefin polymers. Since it does not include any polar groups in its backbone, it was thought that the homogeneous dispersion of the silicate layers in PP would not be realized. Actually, the hybrid state in a PP matrix was not realized even by using a montmorillonite intercalated with distearyldimethylammonium ion (DSDM-Mt) in which the polar surfaces of the clay should be covered with nonpolar long alkyl groups.[12] Recently, we have reported a novel approach to prepare a PP−clay hybrid by using a functional oligomer.[12] PP was mixed with DSDM-Mt and a polyolefin oligomer with polar telechelic OH groups (PO-OH) as a compatibilizer. In this process, at the first stage, the PO-OH oligomer intercalates between the layers of the clay through the strong hydrogen bonding between the OH groups of the PO-OH and the oxygen groups of the silicates. The interlayer spacing of the clay increases, and as a result, the interaction of the layers should be weakened. By mixing the DSDM-Mt/PO-OH composite with PP, the hybrid with improved dispersion of the silicate layers was obtained. However, some aggregates of the clay minerals were still observed in it. In this novel approach, there seems to be two important factors in terms of the structures of the oligomers in order to obtain the complete homogeneous dispersion of the silicate layers. Firstly, the oligomers should include a certain amount of polar groups to be intercalated between silicate layers through hydrogen bonding. Secondly, the oligomers should be well miscible with PP. Since the content of polar functional groups in the oligomers should affect the miscibility of it with PP, there must be an optimum content of polar functional groups in order to obtain the hybrids.

In this paper, we have used two types of maleic anhydride modified PP oligomers containing different amounts of maleic anhydride groups (PP-MA-1001, acid value = 26 mmol of KOH/g; PP-MA-1010, acid value = 52 mmol of KOH/g) and two types of organized clay, i.e., a montmorillonite intercalated with stearylammonium ion (C18-Mt) and a synthetic fluorinated mica intercalated with stearylammonium ion (C18-Mc) instead of DSDM-Mt and PO-OH. There are two main goals in this paper. The first one is to demonstrate the above conditions to achieve the hybrid structures, especially the miscibility effect of the oligomers on the dispersibility of the clay in a PP matrix. The second goal is to prepare PP−clay hybrids and to study the effect of hybridization on their dynamic mechanical behaviors compared to PP and PP/clay composites without the oligomers. Also, the effects of the kinds of clays and oligomers on their dynamic behavior are discussed.

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Table 1. Characterization of Maleic Anhydride Modified PP Oligomers

	characterization[a]		
grade	acid value, mg KOH/g	softening temp, °C	$(M_W)_{GPC}$
PP-MA-1001	26	154	40 000
PP-MA-1010	52	145	30 000

[a] The data were obtained from Sanyo Chemical Industries.

2. Experimental Section

Materials. The materials used for the preparation of the hybrids are purified montmorillonite (Kunipia-F) from Kunimine Co., synthetic fluorinated mica (ME-110) from Co-op Chemical Co., stearylamine from Wako Pure Chemical Industries, PP-MA (Table 1) from Sanyo Chemical Industries, and homo polypropylene (MA2, melt flow rate 16 g/min, JISK6758) from Mitsubishi Chemical.

Intercalation. Sodium montmorillonite (80 g, cation-exchange capacity 119 mequiv/100 g) was dispersed into 5000 mL of hot water (about 80 °C) by using a homogenizer. Stearylamine (31.1 g, 115 mmol) and concentrated hydrochloric acid (11.5 mL) were dissolved in water (2000 mL). It was poured into the hot montmorillonite−water solution under vigorous stirring for 5 min by using the homogenizer to yield white precipitates. The precipitates were collected on a glass filter, washed 3 times with hot water (>80 °C), and freeze-dried to yield a montmorillonite intercalated with stearylammonium (C18-Mt). The interlayer spacing of C18-Mt was measured by X-ray diffraction. Its inorganic content was calculated by measuring the weights before and after burning its organic parts. The interlayer spacing of the sodium montmorillonite is 12 Å, while that of the C18-Mt is about 22 Å. The measured inorganic contents of the C18-Mts are 67.4−68.4 wt % and slightly different depending on the lots. These results clearly indicate the almost quantitative intercalation of stearylammonium in the clay. The same procedure was used to prepare a synthetic mica intercalated with stearylammonium (C18-Mc). The interlayer spacing of the C18-Mc is about 22 Å. The measured inorganic contents are 68.8−70.8 wt %.

Evaluation of the Intercalation Capability of the PP-MAs. The intercalation capability of the PP-MAs into C18-Mt was evaluated simply by monitoring the interlayer spacings of the mixtures by using a X-ray diffractometer as follows. PP-MA-1010 was melt-mixed with C18-Mt (weight ratio C18-Mt:PP-MA = 1:3) by using a SIKRC twin-screw extruder manufactured by Nissei Plastic Industrial Co. The thin film of the mixture (400 μm) was prepared by pressing at 190 °C. X-ray diffraction (XRD) patterns of the film of the mixture were obtained by using a Rigaku RAD-B diffractometer with Cu Kα radiation. The same experiment was performed for the mixture of PP-MA-1001 with C18-Mt (weight ratio C18-Mt:PP-MA = 1:3).

Evaluation of the Miscibility between the PP-MAs and PP. The miscibility of the PP-MAs with PP was evaluated preliminarily by observing their phase separation textures as follows. PP was melt-blended with PP-MAs (weight ratio PP/PP-MA = 77:23) by using the twin-screw extruder. The compositions of the samples are summarized in Table 2. The blends of PP with PP-MA-1001 are abbreviated as PP/1001, while that of PP with PP-MA-1010 is given as PP/1010. Their optical phase-separation textures were observed by using an optical microscope.

Preparation of PP−Clay Hybrids. Four types of hybrids with different combinations of the organized clays and the PP-MAs were prepared as follows. The compositions of the prepared hybrids are listed in Table 2. The powdery three components of C18-Mt (54.8 g), PP (531 g), and PP-MA-1001 (164.4 g) were dry-mixed by shaking them in a bag. The mixture was melt-blended at 210 °C by using the twin-screw extruder to yield pale-yellow strands of the hybrids (the sample is abbreviated as PPCH-C18-Mc/1001). The obtained strands were pelletized and dried under vacuum at 80 °C. In order to see the effect of the oligomers on the dispersibility and mechanical properties of the hybrids, two conventional composites based on PP and the organized clays without the PP-MAs were prepared as listed in Table 2. The samples are abbreviated as PP/C18-Mt and PP/C18-Mc.

Table 2. Compositions of the Prepared Hybrids Based on PP, PP-MAs, and Organized Clays and of the Related Samples

	comp, wt %		
sample	PP	MA oligomer	org clay
PPCH-C18-Mt/1010	70.7	PP-MA-1010 21.9	C18-Mt 7.4
PPCH-C18-Mt/1001	70.8	PP-MA-1001 21.9	C18-Mt 7.3
PPCH-C18-Mc/1010	71.0	PP-MA-1010 22.0	C18-Mc 7.0
PPCH-C18-Mc/1001	71.1	PP-MA-1001 21.6	C18-Mc 7.3
PP/C18-Mt	93.1		C18-Mt 6.9
PP/C18-Mc	93.5		C18-Mc 6.5
PP/1010	78.4	PP-MA-1010 21.6	
PP/1001	76.3	PP-MA-1001 23.7	

Table 3. Measured Contents of the Inorganic Clay in the Hybrids

samples	clay contents, wt %
PPCH-C18-Mt/1010	4.82
PPCH-C18-Mt/1001	4.77
PPCH-C18-Mc/1010	4.86
PPCH-C18-Mc/1001	5.14

The dried pellets of the hybrids were injection-molded into test pieces (40 × 4 × 2 mm) for the measurements of the dynamic moduli by using a Nissei Plastic Industrial Co. PS40E2ASE injection molder. The temperatures of the cylinder were 170−190 °C, and that of the mold was 30 °C. Also, the thin films (400 μm) were prepared by pressing at 190 °C for the X-ray diffraction measurements.

The contents of the inorganic clay were measured by burning the samples. The results are listed in Table 3. All the samples contained about 5 wt % clays as inorganic parts. These values are equal to those expected from the feed compositions listed in Table 2.

Evaluation of the Dispersibility of the Clay in the PP Matrix. The dispersibility of the silicates layers in the hybrids was evaluated by using the X-ray diffractometer and a transmission electron micrograph (TEM). TEM observations of the hybrids were performed for the injection-molded samples by a Jeol-2000CX TEM using an acceleration voltage of 200 kV.

Measurements of Dynamic Moduli. The dynamic moduli of the hybrids were measured using a Iwamoto viscoelastic meter, VES-F. The storage moduli of the hybrids vs temperature were obtained by sinusoidally vibrating the samples in the tensile mode at 10 Hz. The temperature range was between −50 and 160 °C. The heat speed was 2 °C/min.

3. Results and Discussion

Evaluation of the Intercalation Capability of the PP-MAs. The XRD patterns of the mixtures of C18-Mt with the PP-MAs are shown in Figure 1 with those of C18-Mt itself and PP/C18-Mt. The (001) plane peaks of C18-Mt around $2\Theta = 4°$ in the XRD curves are shifted to lower angles in the mixtures regardless of the kind of PP-MA. This clearly indicates the strong intercalation capabilities of both PP-MA-1010 and PP-MA-1001 in the silicate layers. The results are quite different from that of the PP/C18-Mt composite, where the peak did not shift at all. This fact indicates that the PP does not intercalate into C18-Mt. The more detailed intercalation behavior of PP-MAs with different concentrations of maleic anhydride groups will be published elsewhere.[13]

Evaluation of the Miscibility between the PP-MAs and PP. Parts a and b of Figure 2 present the optical microphotographs of PP/1001 and of PP/1010 at

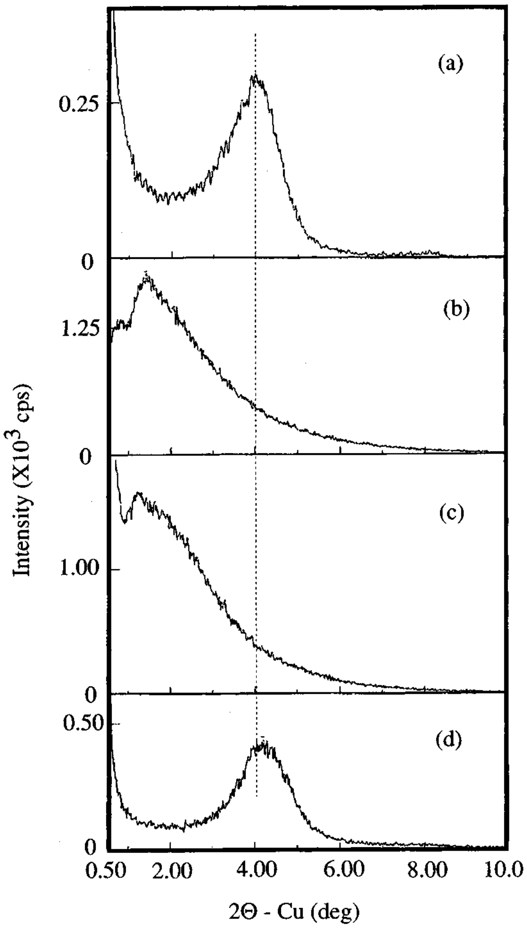

Figure 1. X-ray diffraction patterns of (a) C18-Mt, (b) the mixture of C18-Mt and PP-MA-1010 (C18-Mt:PP-MA = 1:3 by weight) obtained by melt blending, (c) the mixture of C18-Mt and PP-MA-1001 (C18-Mt:PP-MA = 1:3 by weight) obtained by melt blending, and (d) the mixture of C18-Mt and PP obtained by melt blending (C18-Mt:PP = 6.9:93.1 by weight).

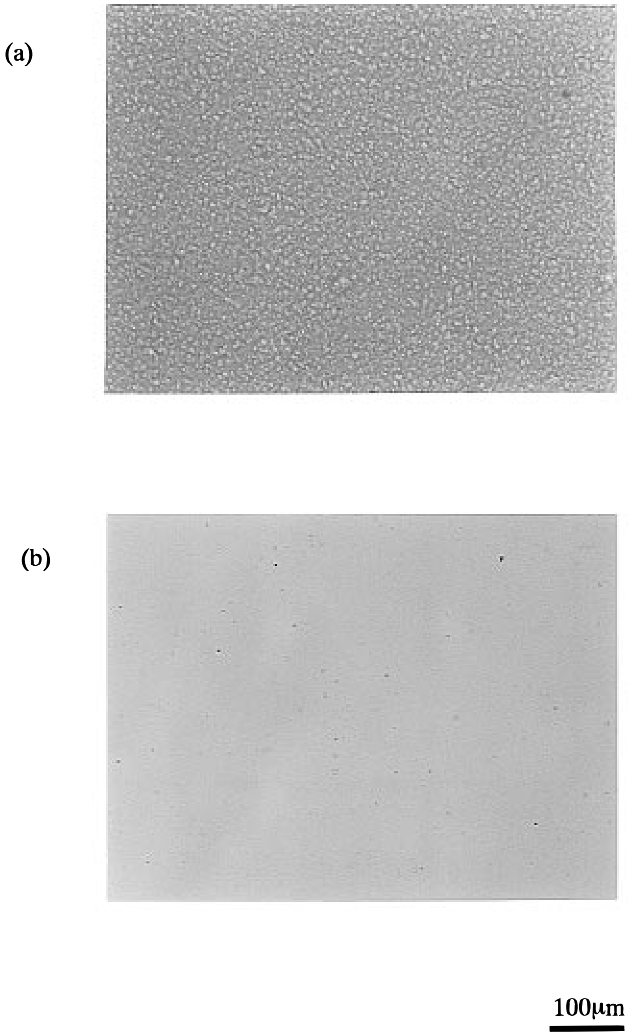

Figure 2. Optical polarized micrographs of the blends of PP with PP-MAs at their melt states (200 °C): (a) PP/1010, (b) PP/1001.

200 °C. Apparently, a macrophase separation texture was clearly observed for PP/1010, while no separation was observed for PP/1001. The miscibility between PP and PP-MA-1001 is much better than that between PP and PP-MA-1010. PP-MA-1010 contains 52 mmol of KOH/g of polar maleic anhydride group, while PP-MA-1001 contains 26 mmol of KOH/g. The results are quite reasonable since the maleic anhydride is a polar group and should decrease the miscibility with PP by increasing its content in the oligomers.

Dispersibility of the Clay Layers in the Hybrids. Direct evidence of the intercalation is provided by the XRD patterns of the obtained hybrids (Figure 3), where the peaks of C18-Mt and C18-Mc around 2Θ = 4° are shifted to lower angles in all the samples. This clearly indicates the intercalation of PP or/and PP-MAs between the silicate layers. The shapes of the XRD patterns are dependent on the kind of PP-MAs used. Relatively apparent and strong peaks of the clays were observed for the PPCHs with PP-MA-1010. These XRD patterns indicate that the clay layers still maintain a relatively strong ordering of the layered structures in the PPCHs with PP-MA-1010, although the interlayer spacings increased significantly compared to those of C18-Mt and C18-Mc. The interlayer spacing of the clay in PPCH-C18-Mt/1010 is about 59 Å, while that in PPCH-C18-Mc/1010 is about 64 Å. The interlayer spacing of PPCH-C18-Mt/1010 is quite close to that of the mixture of C18-Mt with PP-MA-1010 (1:3). From these results, only PP-MA may have intercalated between the layers in PPCH-C18-Mt/1010.

On the other hand, the XRD patterns of the PPCHs with PP-MA-1001 exhibit relatively small and unapparent peaks or shoulders with a gradual increase in the diffraction strength toward low angle. Completely dispersed hybrids such as NCH exhibit no peak but do exhibit a gradual increase in the diffraction strength.[5] Therefore, the clay layers in the PPCHs with PP-MA-1001 should be more exfoliated and dispersed compared to those in the PPCHs with PP-MA-1010.

In order to confirm the hybrid structures, the dispersibility of the silicate layers in PPCH-C18-Mt/1001 and PPCH-C18-Mc/1001 was observed by using TEM. TEM photographs of these samples are shown in Figure 4, where the dark lines are the intersections of the silicate layers of 10-Å thickness. Each layer of the clays is dispersed homogeneously in the PP matrix, although a slight amount of unexfoliated layers still exists. The existence of the small peaks in the XRD patterns of these samples should be attributed to these unexfoliated layers.

From these results, it was found that the miscibility of the oligomers with the matrix polymer apparently affects the dispersibility of the silicate layers in the PPCHs. By using the miscible oligomer with PP, i.e., PP-MA-1001, almost exfoliated and homogeneous dispersion of the hybrids could be achieved.

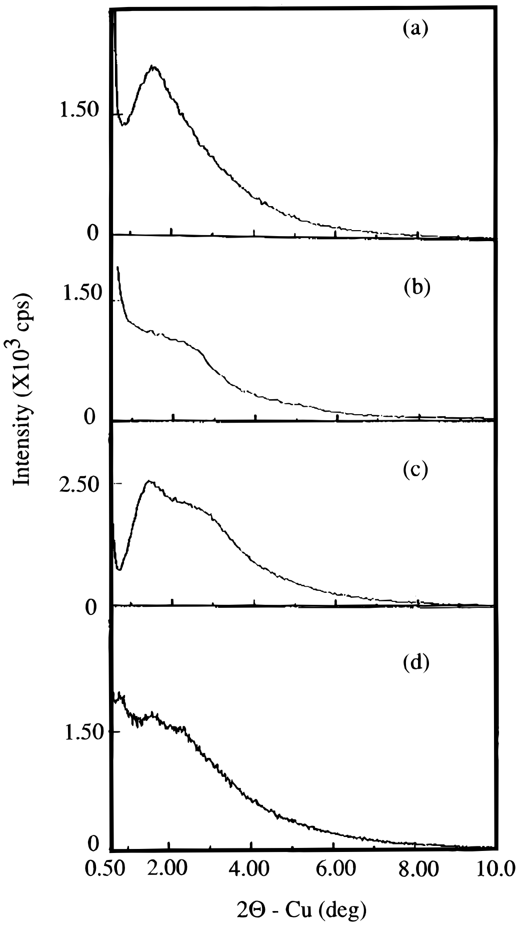

Figure 3. X-ray diffraction patterns of the PPCHs: (a) PPCH-C18-Mt/1010, (b) PPCH-C18-Mt/1001, (c) PPCH-C18-Mc/1010, (d) PPCH-C18-Mc/1001.

For the composites of PP and the organized clays without the PP-MAs, PP/C18-Mt and the PP/C18-Mc, the particles of the clays, whose sizes were several hundred micrometers, were clearly observed. Therefore, these materials are not considered to be hybrids but are considered to be conventional composites.

Possible Dispersion Mechanism. Now let us consider the dispersion mechanism of the clays in the PPCHs. When PP and C18-Mc or C18-Mt were blended, no increase of the interlayer spacing of the organized clays was observed, as shown in Figure 1. Therefore, only the PP-MAs can intercalate into the silicate layers at the first stage of the mixing process. Figure 5 presents a schematic representation of the mixing process of the three components, i.e., PP, PP-MA, and organized clay, into the PPCH. The driving force of the intercalation originates from the strong hydrogen bonding between the maleic anhydride group (or COOH group generated from the hydrolysis of the maleic anhydride group) and the oxygen groups of the silicates. The interlayer spacing of the clay increases, and the interaction of the layers should be weakened. The intercalated clays with the oligomers contact PP under a strong shear field. If the miscibility of PP-MA with PP is good enough to disperse at the molecular level, the exfoliation of the intercalated clay should take place smoothly (Figure 5). On the other hand, if the miscibility is not good enough, the phase separation occurs with no exfoliation. Therefore, it is quite reasonable to say not only the intercalation ability of the oligomers but also the miscibility should be a very important factor to achieve the exfoliated homogeneous dispersion of the clays in this novel approach using oligomers as a compatibilizer.

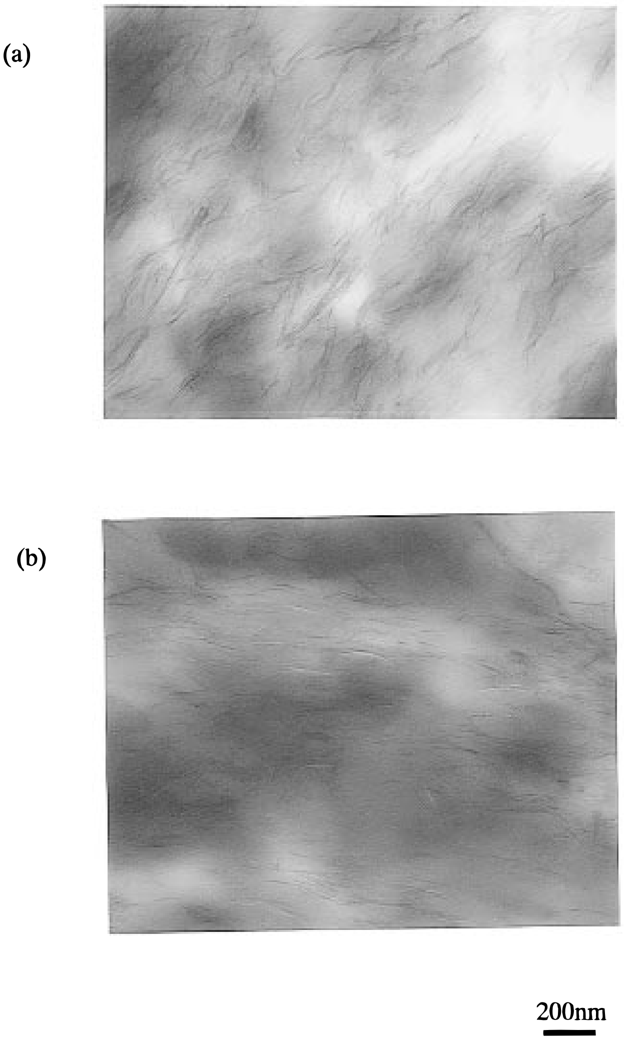

Figure 4. Transmission electron micrographs of the PPCHs: (a) PPCH-C18-Mt/1001, (b) PPCH-C18-Mc/1001.

Dynamic Moduli Study of the PPCHs. The dynamic storage moduli of the PPCHs were plotted vs temperature in Figure 6. The representative values of the storage moduli at −40, 20, 80, and 140 °C and the glass transition temperature (T_g) are listed in Table 4. The dynamic moduli of the PPCHs were higher than that of PP below 120 °C in the case of the PPCHs using PP-MA-1010 and below 140 °C in the case of the PPCHs using PP-MA-1001. The lower moduli of the hybrids above these temperatures should be attributed to the lower softening temperature of the PP-MAs as listed Table 1. In order to clarify the effect of hybridization with the clays, the relative storage moduli of the PPCHs to those of PP were calculated and plotted in Figure 7. Figure 7 presents the dependence of the kind of PP-MAs on the relative moduli of the PPCHs. All the PPCHs exhibit similar relative moduli curves vs temperature. Namely, below T_g (around 10 °C obtained from tan δ), the relative moduli are relatively small and are 1.3−1.4 to those of PP (Table 4). Above T_g, they increase drastically up to 1.7−2.0 around 50−80 °C and then decrease to melt. There are some differences in the relative moduli of the PPCHs depending on the kind of PP-MAs. As seen from Figure 7, the relative moduli of the PPCHs using PP-MA-1001 are higher than those of the PPCHs using PP-MA-1010 above 60 °C, regardless of the kind of clay. This is most probably due to

Table 4. Dynamic Storage Moduli of the Hybrids and of the Related Samples at Various Temperatures and Their Glass Transition Temperatures Obtained from tan δ

samples	storage modulus,[a] GPa				T_g,[b] °C
	−40 °C	20 °C	80 °C	140 °C	
PPCH-C18-Mt/1010	5.15 (1.31)	3.12 (1.58)	1.03 (1.59)	0.13 (0.60)	11
PPCH-C18-Mt/1001	5.26 (1.34)	3.09 (1.56)	1.10 (1.70)	0.21 (0.94)	8
PPCH-C18-Mc/1010	5.56 (1.42)	3.35 (1.69)	1.14 (1.76)	0.14 (0.63)	10
PPCH-C18-Mc/1001	5.35 (1.37)	3.24 (1.64)	1.31 (2.02)	0.23 (1.03)	13
PP/C18-Mt	4.50 (1.15)	2.36 (1.19)	0.82 (1.26)	0.28 (1.25)	9
PP/C18-Mc	5.04 (1.29)	2.72 (1.37)	0.90 (1.38)	0.28 (1.26)	9
PP/1010	3.92 (1.00)	1.99 (1.01)	0.60 (0.92)	0.15 (0.68)	13
PP/1001	4.04 (1.03)	2.02 (1.02)	0.55 (0.85)	0.14 (0.62)	10
PP	3.92	1.98	0.65	0.22	13

[a] The values in parentheses are the relative values of the hybrids to those of PP. [b] The glass transition temperatures were measured at the peak tops of tan δ.

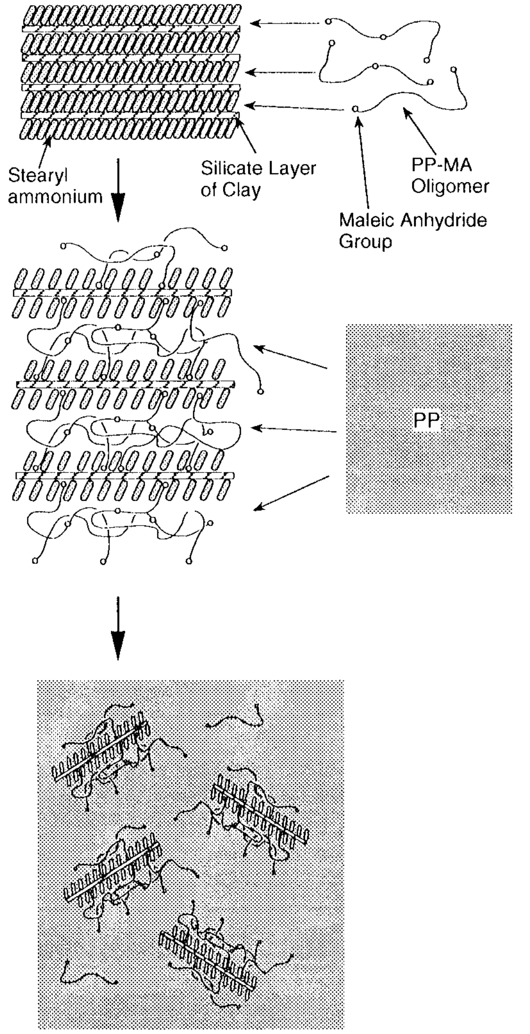

Figure 5. Schematic representation of the dispersion process of the organized clay in the PP matrix with the aid of PP-MAs.

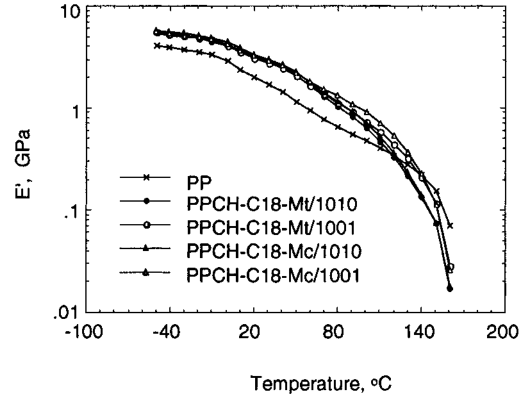

Figure 6. Dynamic storage moduli (E') of the PPCHs and PP as a function of temperature.

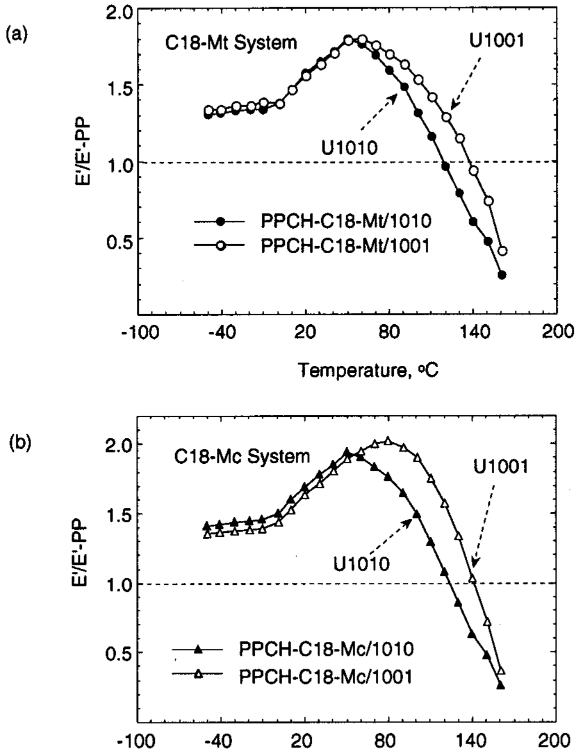

Figure 7. Dependence of PP-MAs on the relative dynamic storage moduli (E'/E'-PP) of the obtained PPCHs to that of PP as a function of temperature, (a) PPCHs based on C18-Mt, (b) PPCHs based on C18-Mc.

the fact that the softening point of PP-MA-1001 is higher than that of PP-MA-1010 by 9 °C. Also, the better dispersibility should be another reason. On the other hand, as seen from Table 4, the PPCHs using C18-Mc exhibited higher dynamic moduli compared to those of the PPCHs using C18-Mt. The reason is not clear at this stage.

In order to confirm the assumption that the reinforcement effect is attributed to the dispersed clays in the PPCHs, the dynamic moduli of PP/1001 and PP/1010, which are considered to be the matrixes of the PPCHs, and those of the blends of PP with the organized clays, the PP/C18-Mt and the PP/C18-Mc, were measured and plotted vs temperature as relative values to those of PP in Figures 8 and 9, respectively. The dynamic moduli

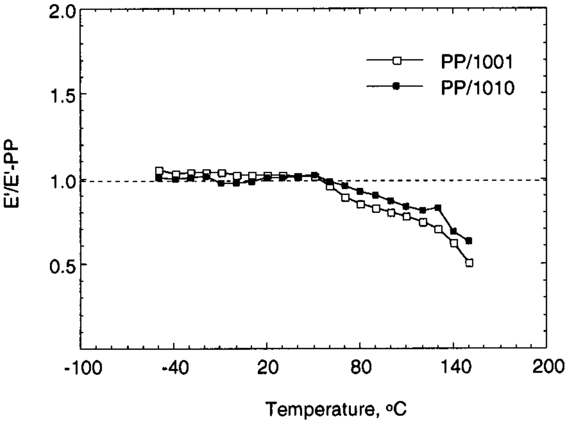

Figure 8. Relative dynamic storage moduli (E'/E'-PP) of the blends of PP with PP-MAs to that of PP as a function of temperature.

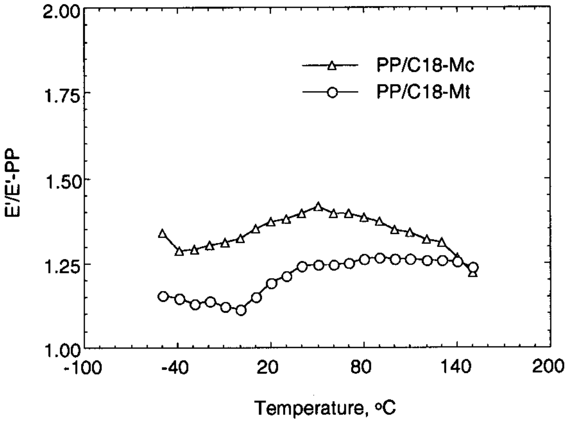

Figure 9. Relative dynamic storage moduli (E'/E'-PP) of the mixtures of PP with the organized clays to that of PP as a function of temperature.

of PP/1010 and PP/1001 exhibited lower values compared to those of PP above T_g, while those of the blends of PP with the clays exhibited slightly higher moduli. From these results, the enormous reinforcement effect observed in the PPCHs should be attributed to the hybrid structures of them in which the silicate layers are dispersed far better than those in the blends of PP and the clays.

Figure 10 presents the relative storage moduli of the PPCHs-PP-MA-1001 to those of the matrix, the PP/1001. Apparently, the relative moduli of the PPCHs are higher than unity over the whole temperature range, and these are considered to be the real reinforcement effect of the clays. PPCH-C18-Mc/1001 exhibited 2.4 times higher modulus at 90 °C by using only 5 wt % clay.

4. Conclusions

We have successfully prepared the polypropylene–clay hybrids by using the maleic anhydride modified polypropylene oligomers. In this novel approach, the miscibility of the oligomers with polypropylene affects the dispersibility of the clay in the hybrids. Almost complete hybrids were obtained in the case where the used PP-MA is miscible with PP. The PPCHs using miscible PP-MA-1001 exhibited higher storage moduli above T_g than those of the PPCHs using PP-MA-1010, regardless of the kind of the clays. The PPCHs using C18-Mc exhibited higher storage moduli than those of the PPCHs using C18-Mt. The best reinforcement effect was obtained in PPCH-C18-Mc/1001. In this case, the highest relative storage modulus to PP is 2.0 and that to the matrix PP/1001 is 2.4. Since we could not observe such a drastic reinforcement effect in either PP/C18-Mc or PP/C18-Mt, we concluded that the effect could be attributed to the hybrid structure in which the silicate layers are dispersed homogeneously. The concept used in this study would be used for a wide variety of combinations in polymer–clay hybrid systems.

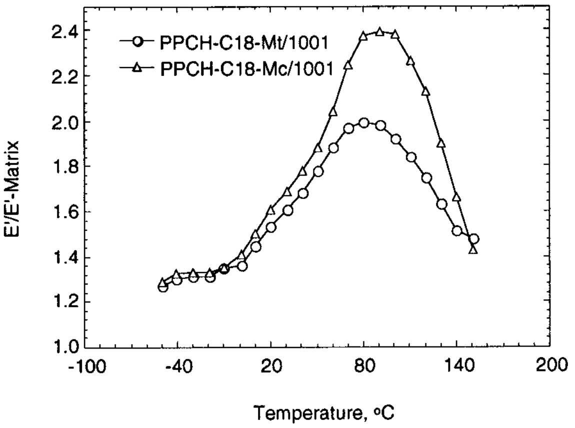

Figure 10. Relative dynamic storage moduli (E'/E'-matrix) of the PPCHs based on PP-MA-1001 to that of PP/1001 blends as the matrix of the PPCHs as a function of temperature.

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