Preparation and Mechanical Properties of Polystyrene–Clay Hybrids

NAOKI HASEGAWA, HIROTAKA OKAMOTO, MASAYA KAWASUMI, ARIMISTU USUKI

Toyota Central Research and Development Laboratories, Inc., Nagakute-cho, Aichi, 480-1192, Japan

ABSTRACT: Polystyrene–clay hybrids (PSCHs) were prepared by melt blending a styrene vinyloxazoline copolymer with organophilic clay. In the PSCHs, the silicate layers of the clay were delaminated and dispersed homogeneously to the nanometer level. The moduli of the PSCHs were higher than that of the PS copolymer. For example, the tensile modulus of the PSCH with 5 wt % clay was 1.4 times higher compared to that of the PS copolymer. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 3359–3364, 1999

INTRODUCTION

In recent years, organic–inorganic nanometer composites have attracted great interest from researchers since they frequently exhibit unexpected hybrid properties synergistically derived from the two components.[1–13] One of the most promising composite systems would be hybrids based on organic polymers and inorganic clay minerals consisting of silicate layers.[4–13] In our previous works, we synthesized a nylon 6-clay hybrid (NCH) in which 10-Å-thick silicate layers of clay minerals are delaminated and dispersed homogeneously in the nylon 6 matrix.[5] The NCH exhibits various superior properties such as high strength, high modulus, and high heat resistance compared to nylon 6.[6] Since then, other polymer–clay hybrids such as polyimide,[7] epoxy resin,[8] polycaprolactone,[9] acrylic polymer,[10] and polypropylene[11] were reported.

Polystyrene (PS) is one of the most widely used polymers. Many researchers have been interested in PS–clay hybrids (PSCHs).[8a,12,13] Moet et al. reported PSCHs prepared by polymerization of styrene in the excitance of organophilic clay.[12] Giannllis et al. reported the intercalation of PS into organophilic clay interlayers by heating a mixture of PS and organophilic clay above the glass transition temperature of PS.[13] However, there was no report of delaminated-type PSCHs.

Recently, we reported that a polyolefin oligomer with polar groups, that is, hydroxy groups and maleic anhydride groups, intercalated into organophilic clay interlayers, and the silicate layers were dispersed at the nanometer level.[11] In this article, we used PS copolymerized with oxazoline groups as polar groups and prepared delaminated-type PSCHs by melt blending the PS copolymer with organophilic clay and studied the dispersibility of clays and the mechanical properties of PSCHs.

EXPERIMENTAL

Materials

The materials used for the preparation of the PSCHs are purified montmorillonite (Kunipia-F) from Kunimine Ind. Co., (Tokyo, Japan) octadecyl trimethylammonium chloride from Tokyo Chemical Co. (Tokyo, Japan), the styrene methylvinyloxazoline copolymer (RPS-1005) from Nippon Shokubai Co. (Osaka, Japan), and polystyrene (G590H) from Japan Polystyrene Inc. (Tokyo, Japan).
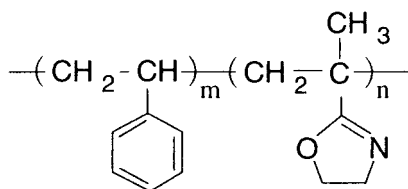
Figure 1   Structure of PSoz.

Figure 1 shows the chemical structure of the styrene methylvinyloxazolene copolymer. The methylvinyloxazoline content of the copolymer is 5 wt %. The MW measured by GPC is 200,000. This polymer is termed PSoz.

Preparation of Organophilic Clay

Sodium montmorillonite (80 g; cation-exchange capacity: 119 meq/100 g) was dispersed into 5000 mL of hot water (about 80°C) using a homogenizer. Octadecyl trimethylammonium chloride (37.8 g, 115 mmol) was dissolved into hot water. It was added into the montmorillonite–water solution under vigorous stirring using the homogenizer for 5 min to yield white precipitates. The precipitates were collected and washed with hot water three times and freeze-dried to yield an organophilic montmorillonite intercalated with octadecyl trimethylammonium. It is termed C18TM-Mt. The interlayer spacing of C18TM-Mt was about 22 Å measured by X-ray diffraction (XRD). The XRD measurements were taken using a Rigaku RAD-B diffractometer with CuKα radiation at 30 kV and 30 mA. The inorganic content was 71.0 wt % by measuring the weights before and after burning its organic parts.

Preparation of PS–Clay Hybrids

The compositions of prepared hybrids are shown in Table I. The powder of PSoz (or PSoz/PS) and C18TM-Mt were melt-blended at 180°C using a twin-screw extruder TEX30α-45.5BW (Japan

Table I   Compositions of PSCHs, PSCC, and PS-ox/PS

Sample	PSoz (wt %)	PS (wt %)	C18TM-Mt (wt %)
PSCH-1	93.0	0	7.0
PSCH-2	46.5	46.5	7.0
PPCC	0	93.0	7.0
PSoz/PS	50	50	0

Table II   Clay Contents of PSCH and PSCC

Sample	Clay Contents (wt %)
PSCH-1	4.8
PSCH-2	4.7
PSCC	4.4

Steal Industrial Co.) to yield the hybrids. The obtained strands were pelletized and dried at 60°C.

To consider the effect of oxazoline groups, the composites of PS and C18TM-Mt were prepared. The sample is abbreviated as PSCC (PS–clay composite).

The contents of the inorganic clay of the PSCHs and PSCC were measured by burning the samples. The results are listed in Table II.

The dried pellets of the hybrids were injection-molded into test pieces for tensile tests and measurement of the dynamic moduli using an injection molder PS40E2ASE (Nissei Plastic Industrial Co.). The temperatures of the cylinders were 190–200°C and that of the mold was 50°C.

Evaluation of Dispersibility of the Clay in the PS Matrix

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

Tensile Test

The tensile tests were carried with an Instron Model 4302 at 25°C. The head speed was 5 mm/min. All measurements were done in five replicates and the value averaged.

Measurement of Dynamic Moduli

The dynamic moduli of the PSCHs were measured using an Iwamoto viscoelastic meter VES-F. The storage moduli of the PSCHs versus temperature were obtained by sinusoidally vibrating the samples in the tensile mode at 10 Hz. The temperature range was between −30 and 120°C. The heat speed was 2°C/min.
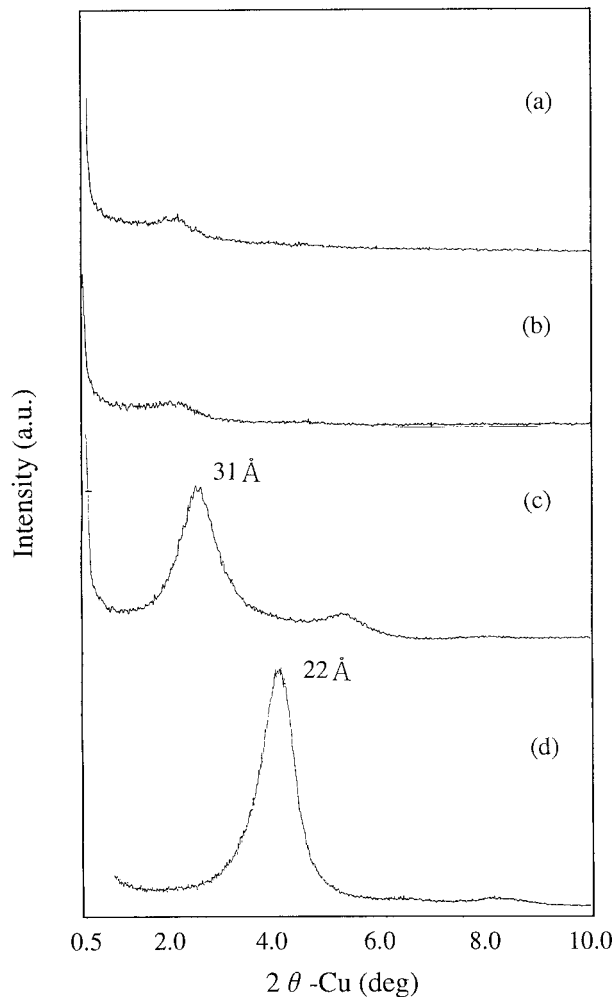
Figure 2 XRD patterns of the PSCHs, PSCC, and C18TM-Mt: (a) PSCH-1; (b) PSCH-2; (c) PSCC; (d) C18TM-Mt.

RESULTS AND DISCUSSION

### Dispersibility of the Clay in PSCHs

Figure 2 shows the XRD patterns of the PSCHs, PSCC, and C18MT-Mt, where the peaks correspond to the (001) plane reflections of the clays. In the XRD patterns of PSCC, an apparent peak was observed at 31 Å, which had a smaller angle by 9 Å than that of C18MT-Mt. It showed that PS intercalated into the C18TM-Mt interlayers during melt blending, but the layered structures of silicates remained in the PSCC.[13] On the other hand, there were no apparent peak observed in the XRD patterns of the PSCHs.

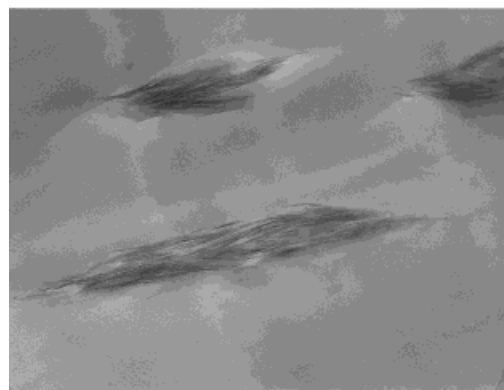Figure 3 shows TEM photographs of the PSCHs and PSCC, where the dark lines are the
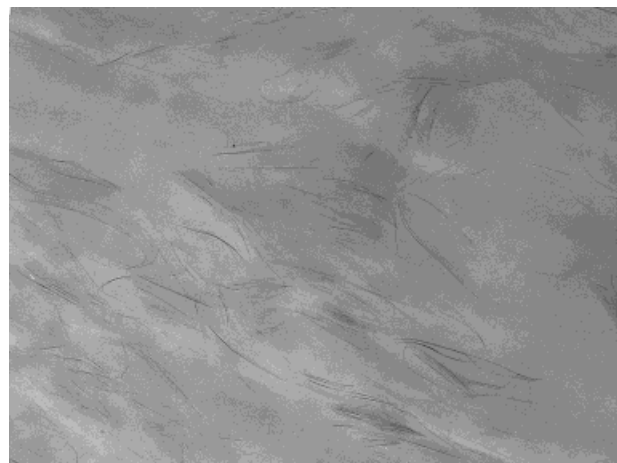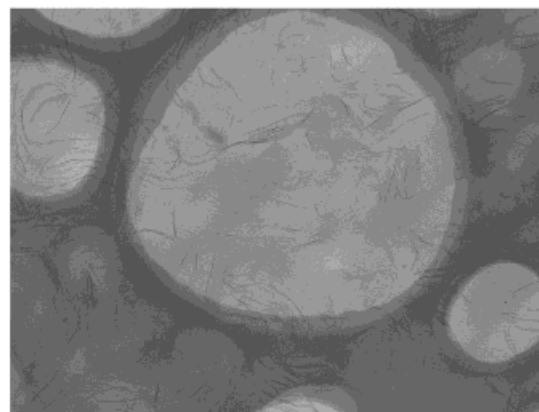
Figure 3 TEM photographs of the PSCHs and PSCC: (a) PSCH-1; (b) PSCH-2; (c) PSCC.
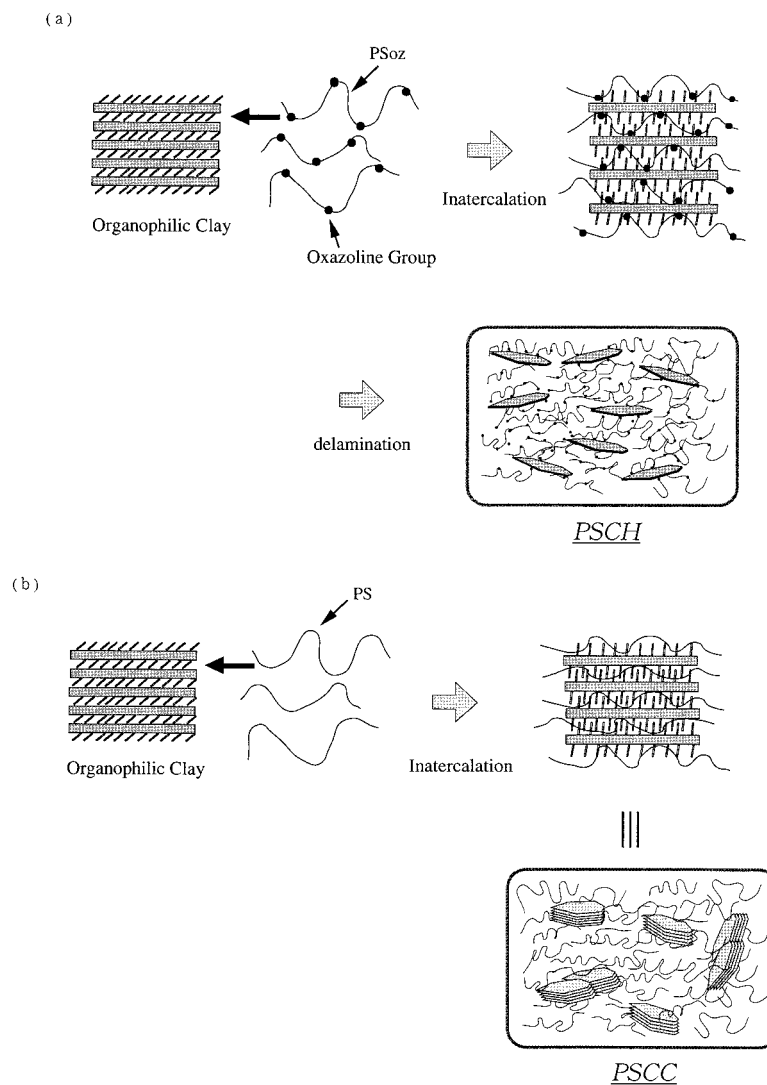
Figure 4 Schematic representation of the dispersion process into PSCH-1 and PSCC: (a) PSCH-1; (b) PSCC.

cross sections of silicate layers of 10 Å thickness. In PSCH-1, silicate layers were delaminated and dispersed to the monolayer. On the other hand, in the PSCC without PSoz, the layered structures of silicates were observed at about 500–1000 nm. So, it is apparent that, due to the existence of

Table III   Results of Tensile Test[a]

Sample	Modulus (MPa)	Strength (MPa)	Elongation (%)
PSCH-1	$1.78^{+0.05}_{-0.04}$ (1.38)	$38.3^{+2.8}_{-3.5}$ (0.82)	$2.3^{+0.2}_{-0.2}$
PSCH-2	$1.74^{+0.05}_{-0.05}$ (1.33)	$38.7^{+2.4}_{-2.5}$ (0.91)	$2.4^{+0.1}_{-0.3}$
PSCC	$1.40^{+0.02}_{-0.04}$ (1.09)	$44.0^{+0.1}_{-0.2}$ (0.90)	$4.1^{+0.2}_{-0.2}$
PSoz	$1.29^{+0.01}_{-0.01}$	$46.5^{+1.5}_{-2.0}$	$4.0^{+0.1}_{-0.2}$
PSoz/PS	$1.30^{+0.03}_{-0.02}$	$42.7^{+1.5}_{-1.0}$	$3.5^{+0.1}_{-0.1}$
PS	$1.30^{+0.02}_{-0.01}$	$48.9^{+0.1}_{-0.2}$	$5.6^{+0.1}_{-0.2}$

[a] The values in parentheses are the relative values of the hybrids to those of the matrix polymer.
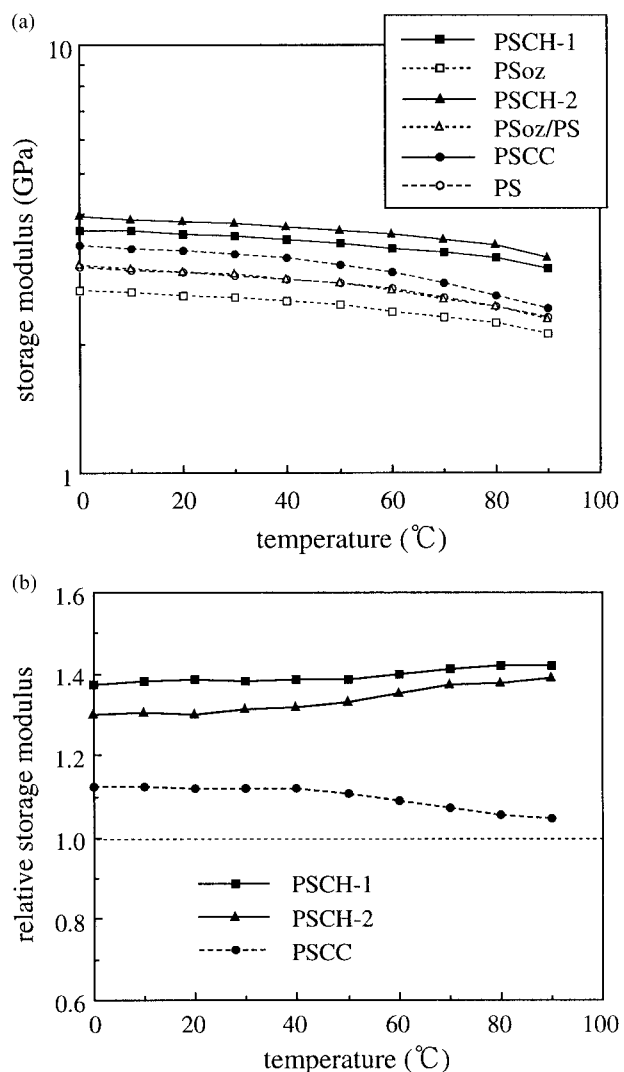
Figure 5 (a) Dynamic storage moduli of the PSCHs and PSCC. (b) Relative dynamic storage moduli of the PSCHs and PSCC.

oxazoline groups, silicate layers were delaminated in the PSCHs. Figure 4 presents a schematic representation of the mixing process of PSoz and organophilic clay into the PSCH-1. It is guessed that the driving force of the hybridization originates from strong hydrogen bonding between the oxazoline groups of PSoz and the oxygen groups of the silicates.

In PSCH-2 whose matrix consisted of PS and PSoz, silicate layers were dispersed to the monolayer as the PSCH-1. In this case, PSoz was a compatibilizer between PS and C18TM-Mt.

Study of Mechanical Properties of PSCHs

Table III shows the results of the tensile test of the PSCHs. The modulus of PSCH-1 was 1.4 times higher than that of PSoz. On the other hand, the tensile modulus of PSCC was only 1.1 times higher than that of PS. As the dispersibility of the clay in the matrix polymer was improved, the reinforcement of the clay also improved. The tensile strengths and the elongations of the PSCHs and PSCC were smaller than those of the matrix polymers.

The dynamic storage moduli (E') of the PSCHs and PSCC are plotted versus temperature in Figure 5(a). The values of E' at 0, 30, and 80°C and the glass transition temperatures (T_g's) are listed in Table IV. To clarify the effect of the hybridization with the clays, the relative storage moduli of the PSCHs and PSCC to those of the matrix polymers are plotted in Figure 5(b). The relative storage moduli of the PSCHs were higher than those of PSCC at all temperatures. The E' of PSCH-1 was 1.4 times higher than that of the matrix polymer at all temperatures. On the other hand,

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

Sample	Storage Modulus[a] (GPa)				Glass Transition Temperature[b] (°C)
	0	30	80	100	
PSCH-1	3.66 (1.37)	3.56 (1.38)	3.19 (1.42)	2.34 (1.53)	118
PSCH-2	3.96 (1.30)	3.80 (1.31)	3.39 (1.38)	2.53 (1.39)	118
PPCC	3.40 (1.12)	3.24 (1.12)	2.60 (1.06)	20.6 (1.01)	120
PSoz	2.67	2.58	2.25	1.53	118
PSoz/PS	3.05	2.90	2.46	1.82	118
PS	3.03	2.89	2.46	2.03	120

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

the E' of PSCC was only 1.1 times higher than that of PS. It is apparent that the hybridization with the clays in the matrix leads to high reinforcement. The T_g's of the PSCHs were equivalent to those of the matrix polymers.

CONCLUSIONS

We prepared PSCHs by melt blending PSoz and C18TM-Mt. In the PSCHs, silicate layers of clay were delaminated and uniformly dispersed to the nanometer level. The storage moduli of the PSCHs were higher than those of matrix polymers at all temperatures. The storage modulus of PSCH-1 with 5 wt % clay was 1.4 times higher than that of PSoz at 30°C.

REFERENCES

1. Schmidt, H. In Polymer Based Molecular Composites; Schaefer, D. W.; Mark, J. E., Eds.; Materials Research Society: Pittsburgh, 1990; p 3.
2. Novak, B. M. Adv Mater 1993, 6, 422.
3. Lu, S.; Melo, M. M.; Zhao, J.; Pearce, E. M.; Kwei, T. K. Macromolecules 1995, 28, 4908.
4. Richard, A. V.; Jandt, K. D.; Edward, J. K.; Giannelis, E. P. Macromolecules 1995, 28, 8080.
5. Usuki, A.; Kawasumi, M.; Kojima, Y.; Fukushima, Y.; Okada, A.; Kurauchi, T.; Kamigaito, O. J Mater Res 1993, 8, 1179.
6. Kojima, Y.; Usuki, A.; Kawasumi, M.; Fukushima, Y.; Okada, A.; Kurauchi, T.; Kamigaito, O. J Mater Res 1993, 8, 1185.
7. Yano, K.; Usuki, A.; Okada, A.; Kurauchi, T.; Kamigaito, O. J Polym Sci A Polym Chem 1993, 31, 2493.
8. (a) Usuki, A.; Hizutani, T.; Fukashima, Y.; Fujimoto, M; Fukumori, K.; Kojma, Y.; Sato, N.; Kurauchi, T.; Kamigaito, O. U.S. Patent 4 889 885, 1989. (b) Wang, M. S.; Pinnavaia, T. J. Chem Mater 1994, 6, 468. (c) Lan, T.; Pinnavaia, T. J. Chem Mater 1994, 6, 2216. (d) Kelly, P.; Akelah, A.; Qutubuddin, S.; Moet, A. J Mater Sci 1994, 29, 2274.
9. Messersmith, P. B.; Giannelis, E. P. J Polym Sci A Polym Chem 1995, 33, 1047.
10. Biasci, L.; Aglietto, M.; Ruggeri, G.; Ciardelli, F. Polymer 1994, 35, 3296.
11. (a) Usuki, A.; Kato, M.; Okada, A.; Kurauchi, T. J Appl Polym Sci 1997, 63, 137. (b) Kato, M.; Usuki, A.; Okada, A.; Kurauchi, T. J Appl Polym Sci 1997, 66, 1781. (c) Kawasumi, M.; Hasegawa, N.; Kato, M.; Usuki, A.; Okada, A. Macromolecules 1997, 30, 6333. (d) Hasegawa, N.; Kawasumi, M.; Kato, M.; Usuki, A.; Okada, A. J Appl Polym Sci 1998, 67, 87.
12. Moet, A. Mater Lett 1993, 18, 97. Moet, A.; Akelah, A.; Hiltner, A.; Baer, E. Mater Res Soc Symp Proc 1994, 351, 91.
13. Vaia, R. A.; Ishii, H.; Giannelis, E. P. Chem Mater 1993, 5, 1694. Vaia, R. A.; Jandt, K. D.; Kramer, E. J.; Giannelis, E. P. Macromolecule 1995, 28, 8080.