JOURNAL OF MATERIALS SCIENCE 31 (1996) 4307–4310

Preparation and properties of polypropylene reinforced by smectite

N. FURUICHI, Y. KUROKAWA, K. FUJITA, A. OYA*
Faculty of Engineering, Gunma University, Kiryu, Gunma 376, Japan
H. YASUDA, M. KISO
Calp Corporation, Sodegaura, Chiba 299-02, Japan

Toluene solutions of hydrophobic smectite (SAN) and polypropylene (PP) were mixed thoroughly. Trimethylsilylated SAN was also used to examine the effects of the surface modification. In both the smectites, the resulting mixtures were transparent but the stacked layer structures were retained, with expansion of the interlayer distance from 2.26 nm to ~5 nm. The PP containing the fine SAN filler particles was prepared after removal of toluene, followed by mixing with the PP to produce a 3 wt% SAN content. The SAN particles were more finely dispersed in the resulting composites than was achieved by conventional mechanical mixing, but the mechanical properties were not improved remarkably. The trimethylsilylation conferred no favourable effect on the mechanical properties of the composite.

1. Introduction

There have been many works concerning clay mineral-reinforced plastics [1–5], but the number in industrial use is quite small. The reinforcing effect of the clay mineral filler is thought to be enhanced by the following factors; (i) the stacked layers in a clay mineral particle are separated as finely as possible in a plastic matrix to increase the aspect ratio of the filler particle [6, 7] and (ii) the clay mineral surface is modified to have a high affinity with the plastic matrix [8, 9]. Fukushima *et al.* succeeded in dispersing the finely separated montmorillonite flakes in nylon by the use of a unique technique [10, 11]. The resulting composite exhibited some interesting prominent properties but its practical applications are seriously limited by its high price. Thus we have attempted to develop a clay mineral-reinforced conventional plastic using a simple technique, which is characterized by: (i) mixing both clay mineral and plastic after dissolving in an organic solvent, and (ii) surface treatment of the clay mineral by trimethylsilylation. The structures and some fundamental properties of the resulting composites have been described.

2. Experimental procedure

2.1. Materials

A hydrophobic smectite (SAN) was supplied by Corp Chemical Ind. Co. together with a hydrophilic smectite (SWN) as a reference. Their analytical data and some properties are shown in Table I. The idealized chemical formula of the SWN is $Na_{0.33}^{+}(Mg_{2.67}Li_{0.33})Si_4O_{10}(OH)_2$. The SAN was derived from the SWN by exchanging Na^+ with $[(CH_3)_3NR]^+$ in which R is $-C_{16}H_{33}$ and $-C_{18}H_{37}$. The ratio between both the quaternary ammonium cations in the SAN is not clear. Polypropylene (PP) was supplied by Calp Corporation; details of the PP are not clear. Methyltrimethoxysilane, $CH_3Si(OCH_3)_3$ (MTMS), was used as a surface modifier to improve the affinity between the filler and the PP matrix.

2.2. Preparation procedures

A transparent sol was obtained by dissolving 10 wt % SAN, after drying at 60 °C, into toluene. At higher temperature, the SAN changed from white to pale brown. The MTMS was added to the sol, in an amount equal to one-third of the sol weight, followed by stirring at 110 °C for 6 h to produce trimethylsilylate (MTMS treatment). During this process, $CH_3(OCH_3)_3Si$ reacts with hydroxyl (–HO) groups on the SAN particle surface to form $CH_3(OCH_3)_2Si–O–SAN$. The MTMS-treated SAN, after removal of toluene under a reduced pressure, was heated at 180 °C for 1 h to remove unreacted –OH groups from the SAN surface to improve the affinity.

The MTMS-treated SAN was again dissolved in toluene to give a 13 wt % SAN content, mixed with the PP (20 wt % of total weight) and stirred at 120 °C for 30 min. The solution was then cooled to 60 °C with

---

* Author to whom all correspondence should be addressed.

0022–2461

TABLE I Properties of SWN and SAN

	SWN		SAN	
Chemical analysis (wt %)	Si	25.4	SiO_2	38.6
	Mg	16.8	MgO	18.7
	F	-	F	-
	Li	0.5	Li_2O_3	1.0
	Na	2.0	Na_2O	0.0
	Fe	0.0	Fe_2O_3	-
	Al	0.1	Al_2O_3	0.2
			C	31.7
True density ($g\,ml^{-1}$)	2.13		–	
Specific surface area (m^2g^{-1})	160		–	
MB adsorption (Meq $100\,g^{-1}$)	101		–	
pH (1 wt % soln)	10.48		–	

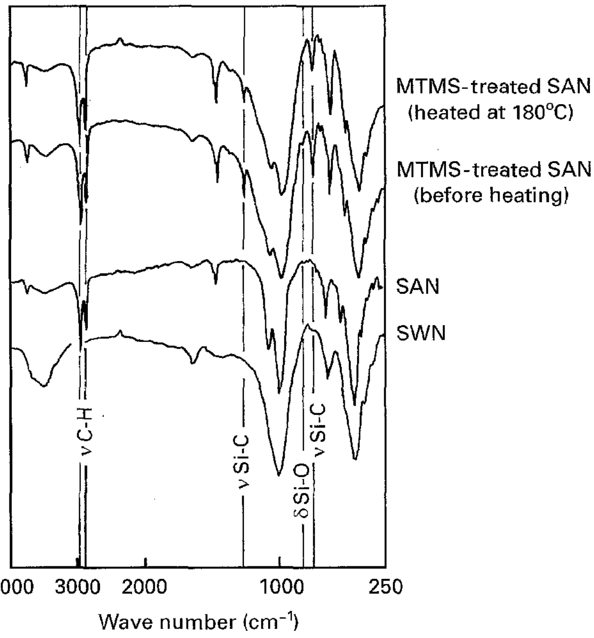

Figure 1 Infrared spectra of SWN and SAN before and after treatments.

stirring, dropped into methanol and finally washed with methanol repeatedly to remove the unreacted MTMS. The MTMS-treated SAN/PP composite thus prepared was used as a "master batch".

The master batch after drying was kneaded with the PP and shaped under $35\,kg\,cm^{-2}$ at 210 °C using an injection-moulding machine (Nissei-Jushi Kogyo FS-150). The MTMS-treated SAN content in the composite was adjusted to 3 wt %. As references, two samples were prepared in addition to the PP with no filler. They are two PP reinforced by the SAN without MTMS treatment and the SWN, respectively. The former was prepared by almost the same procedures described above, but the latter was blended mechanically without the solvent.

2.3. Measurements

The infrared spectrum was taken by a conventional KBr-tablet method. Powder X-ray diffraction was carried out by using CuK_α radiation. The fracture surface of the sample was observed using a scanning electron microscope (SEM) and an electron-probe X-ray microanalyser (EPMA). Bending and tensile strength were measured using a Bendgraph (Toyo Sokki Co.) and a Strograph (Toyo Sokki Co.) according to ASTM-D790 and ASTM-D638, respectively. Total light transmission was measured by use of a colour computer (Suga Shikenki Co. SH-3) according to Japan Industrial Standard K7105.

3. Results

3.1. Infrared spectra

Fig. 1 shows IR spectra of the SAN before and after MTMS treatment, in which some characteristic absorptions alone are assigned. The absorptions assigned to ν-CH ($2848\,cm^{-1}$, $2920\,cm^{-1}$) were observed in the SAN but not in the SWN, which shows that the SAN includes the quaternary ammonium cations. It is also clear from the appearance of absorptions at $780\,cm^{-1}$ (ν-Si–C), $1270\,cm^{-1}$ (ν-Si–C) and $856\,cm^{-1}$ (δ-Si–O) in the MTMS-treated SAN, that the MTMS treatment was successfully carried out. The absorption of δ-Si–O (possibly assigned to δ-Si–OH) in the MTMS-treated SAN, disappeared after heating to 180 °C.

3.2. X-ray diffraction

Fig. 2 shows X-ray diffraction profiles of the SAN before and after dissolving in toluene. The SAN showed a strong (0 0 1) diffraction peak with a *d*-spacing of 2.26 nm. After dissolving in toluene (SAN content 7.8 wt %), the strong (0 0 1) peak of the SAN disappeared and a broad peak around 18° (2θ CuK_α) appeared instead. Here thin polyethylene–telephthalate film (trade name: Myler Film) was used to keep the sol in a simple holder. The SAN/toluene xerogel (SAN content 96 wt %) showed a strong (0 0 1) diffraction peak of which the *d*-spacing is 2.12 nm, together with some unknown peaks. In order to obtain further information on this structure, the X-ray diffraction angle for the SAN/toluene sol was extended to lower angles. As shown in Fig. 3, three peaks were observed at angles lower than ~ 5°. Because the *d*-values were 5.19 nm (1), 2.54 nm (2) and 1.64 nm (3), they were identified as (0 0 1) (0 0 2) and (0 0 3) peaks from the expanded layered structure, respectively.

3.3. Mechanical properties

Fig. 4 shows load/elongation curves of the PP plates with and without the fillers, in which no difference was observed among the curves. Some mechanical properties are listed in Table II. The fillers did not influence the tensile properties favourably, different from the case of bending properties. The SAN without MTMS treatment gave the most favourable reinforcing effect.

3.4. Dispersion state of filler in PP

Table II includes the total light transmission value which reflects intimately the dispersion state of filler

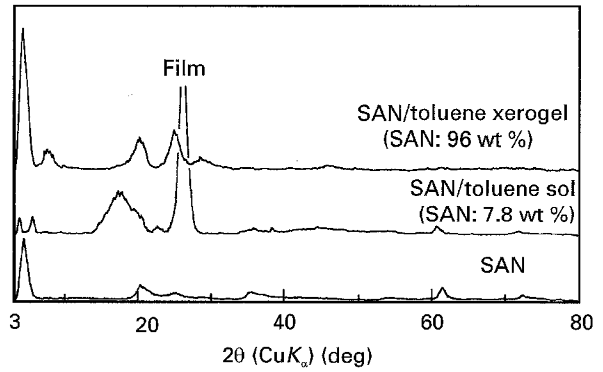

Figure 2 X-ray diffraction profiles of SAN, SAN/toluene sol and SAN/toluene xerogel.

particles in the matrix PP. The MTMS-treated SAN gave a relatively large value which is near to that of the PP without filler. The lowest value was obtained in the case of SWN/PP, which can be explained reasonably by using mechanical blending without a solvent.

Fig. 5 shows EPMA photographs of the PP with and without filler, in which white spots indicate silicon in the clay mineral. The SWN/PP sample contained large SWN particles, as suggested from it small total light transmission value. The SAN particles in the other two specimens dispersed more homogeneously throughout the PP matrix.

4. Discussion

The SAN is confirmed to be trimethylsilylated by the appearance of absorptions assigned to v-Si–C, and the resulting MTMS-treated SAN dispersed more finely in the PP than the SAN without the treatment, as suggested from its larger total light transmission value. Nevertheless, the mechanical properties of the former composite were superior to those of the latter, as shown in Table II, which is completely different from our expectations. We have no data showing the affinity, but guess that the predominant effects will appear when the MTMS-treated SAN particle is separated into the more thin flake-like particles because of its increasing interfacial contact area with the PP matrix. Such a state also results in an increase of the aspect ratio of the filler particle, leading to enhancement of mechanical properties of the composite [6].

The problem is how to separate the SAN particle in the PP as finely as possible by a simple technique as is used here. The SAN dissolved readily in toluene resulting in a transparent sol. However, it still retained the stacking layered structure with a large interlayer spacing of ~ 5 nm. This structure returned to

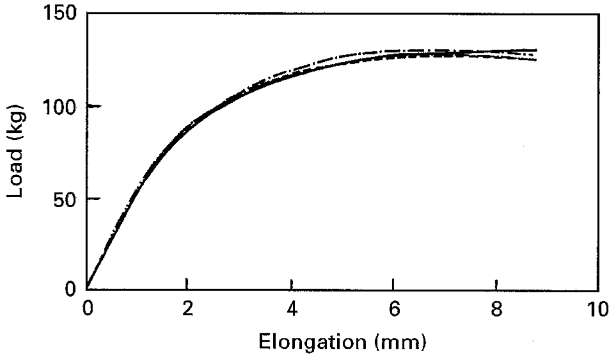

Figure 4 Load/elongation curves of PP plates with and without fillers: (——) No additive, (– – –) SWN, (—·—) SAN, (—··—) MTMS-treated SAN.

TABLE II Properties of PP with and without reinforcement

	PP	SWN/PP	SAN/PP	MTMS-SAN/PP
Total light transmission (%)	80.1	49.4	66.2	76.0
Tensile strength (MPa)	35.9	34.4	36.1	34.3
Tensile modulus (MPa)	1570	1630	1720	1620
Bending strength (MPa)	40.3	42.8	45.3	43.1
Bending modulus (MPa)	1490	1640	1800	1650

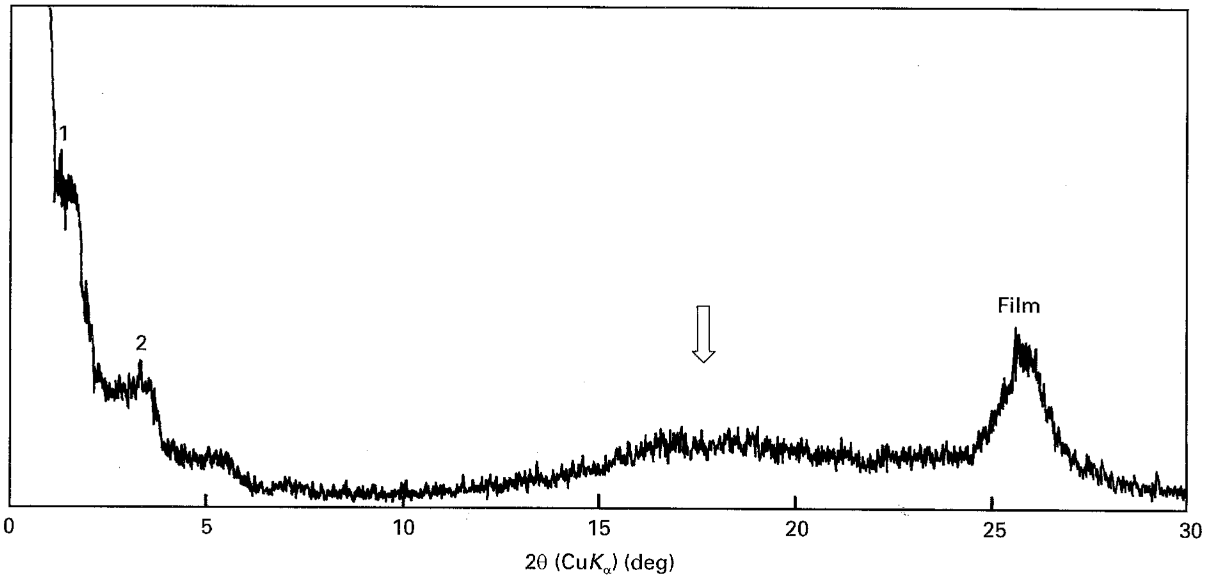

Figure 3 X-ray diffraction profile of SAN/toluene sol (SAN content 10 wt %).

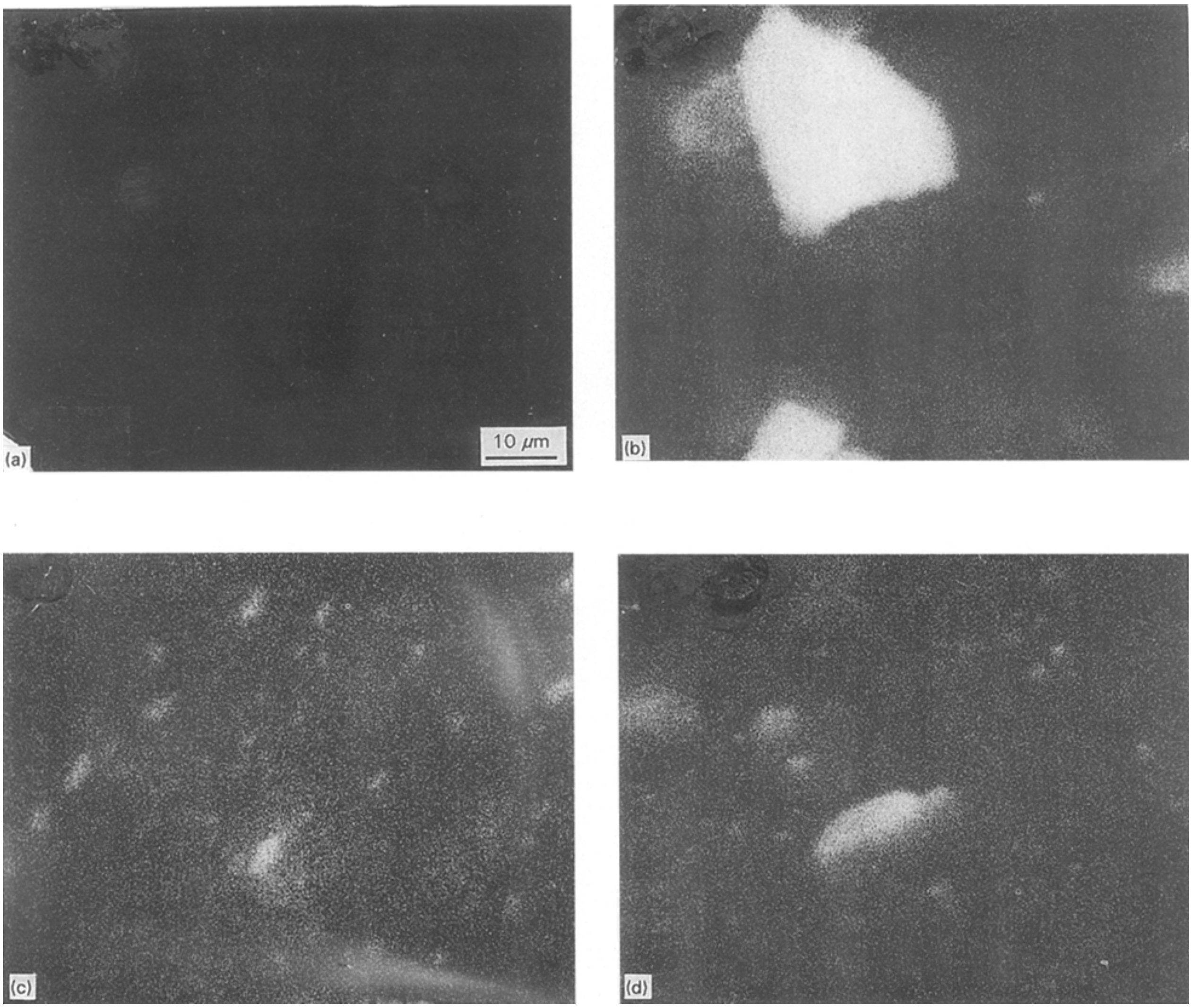

Figure 5 EPMA photographs of PP before and after treatment. (a) PP, (b) SWN/PP, (c) SAN/PP, (d) MTMS-treated SAN/PP.

the original stacking structure after removal of the toluene.

We expected that the PP molecules would be incorporated into the interlayer space expanded by the toluene, and remain there after removal of the toluene, but this was not the result. It is not clear whether the PP molecule could not enter into the interlayer space, or if, once entered, the PP molecule was removed from the interlayer space together with the toluene.

The dispersion state of the SAN by the present method was superior to that by the conventional mechanical blending technique. Nevertheless, there was almost no difference in their mechanical properties. The far finer separation of the SAN particle, if possible into an individual layer, is required to improve mechanical properties of the resulting composite.

References

1. J. C. WITTMANN and B. LOTZ, *J. Mater. Sci.* **21** (1986) 659.
2. M. YOSHIKAWA, T. SATOH, S. INUBUSHI, T. IKEDA and S. TAZUKE, *J. Mater. Sci. Lett.* **5** (1986) 1239.
3. A. GUPTA and M. PATEL, *ibid.* **7** (1988) 1021.
4. S. INUBUSHI, T. IKEDA, S. TAZUKE, T. SATOH, Y. TERADA and Y. KUMAGAI, *J. Mater. Sci.* **23** (1988) 1182.
5. A. TRIPATHI, A. K. TRIPATHI and P. K. C. PILLAI, *J. Mater. Sci. Mater. Electron.* **1** (1990) 143.
6. G. E. PADAWER and N. BEECHER, *Polym. Eng. Sci.* **10** (1970) 185.
7. J. LUSIS, R. T. WOODHAMS and M. XANTHOS, *ibid.* **13** (1973) 139.
8. S. CAI, G. JI, J. FANG and G. XUE, *Angew. Macromol. Chem.* **179** (1990) 77.
9. A. GARTON, S. W. KIM and D. M. WILES, *J. Polym. Sci. Polym. Lett. Ed.* **20** (1982) 273.
10. Y. FUKUSHIMA, T. KURAUCHI and O. KAMIGAITO, *J. Mater. Res.* **8** (1993) 1185.
11. Y. FUKUSHIMA, A. OKADA, M. KAWASUMI, T. KURAUCHI and O. KAMIGAITO, *Clay Mineral.* **23** (1988) 27.

Received 4 July
and accepted 15 December 1995