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Preparation of a nanocomposite of polypropylene and smectite

Y. KUROKAWA
Faculty of Engineering, Gunma University, Kiryu, Gunma 376, Japan

H. YASUDA
Calp Corporation, Sodegaura, Chiba 299-02, Japan

A. OYA
Faculty of Engineering, Gunma University, Kiryu, Gunma 376, Japan

Platy clay mineral particles are a unique reinforcement material for resins. Montmorillonite-reinforced nylon with outstanding properties has been commercialized [1–3], and similar work is in progress for epoxy [4, 5], poly(ethylene oxide) [6], polystyrene [7] and other resins. In these studies, dispersion of the particles throughout the resin, finely and homogeneously, is the key to developing a high quality composite. A group of clay minerals called smectite has interesting properties as follows: (i) metal cations between the constituent smectite layers are replaced by other cations including an organic cation such as alkylammonium cations; and (ii) a polar molecule also intercalates between the constituent layers to coordinate the cation. The property of (i) was used to develop montmorillonite-reinforced nylon which is called a nano-composite because of dispersion of the delaminated montmorillonite layers throughout the nylon matrix [1–3]. Some studies in progress are using the property (ii) [4–7]. However, a high quality smectite-reinforced polypropylene (PP) has not been developed in spite of attracting much attention, because both properties (i) and (ii) cannot be applied for polypropylene (abbreviation: PP) with a small polarity. So the

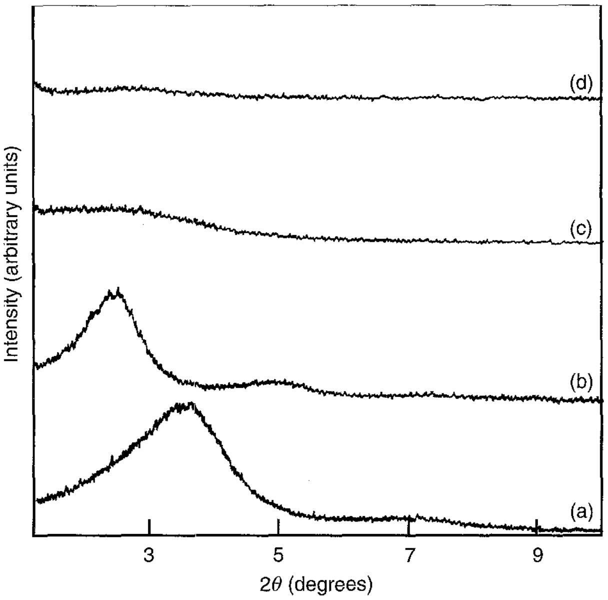

Figure 1 X-ray diffraction profiles of the samples: (a) SAN; (b) SPD; (c) SPD/m-PP after washing; (d) SPD/m-PP (10 min blend).

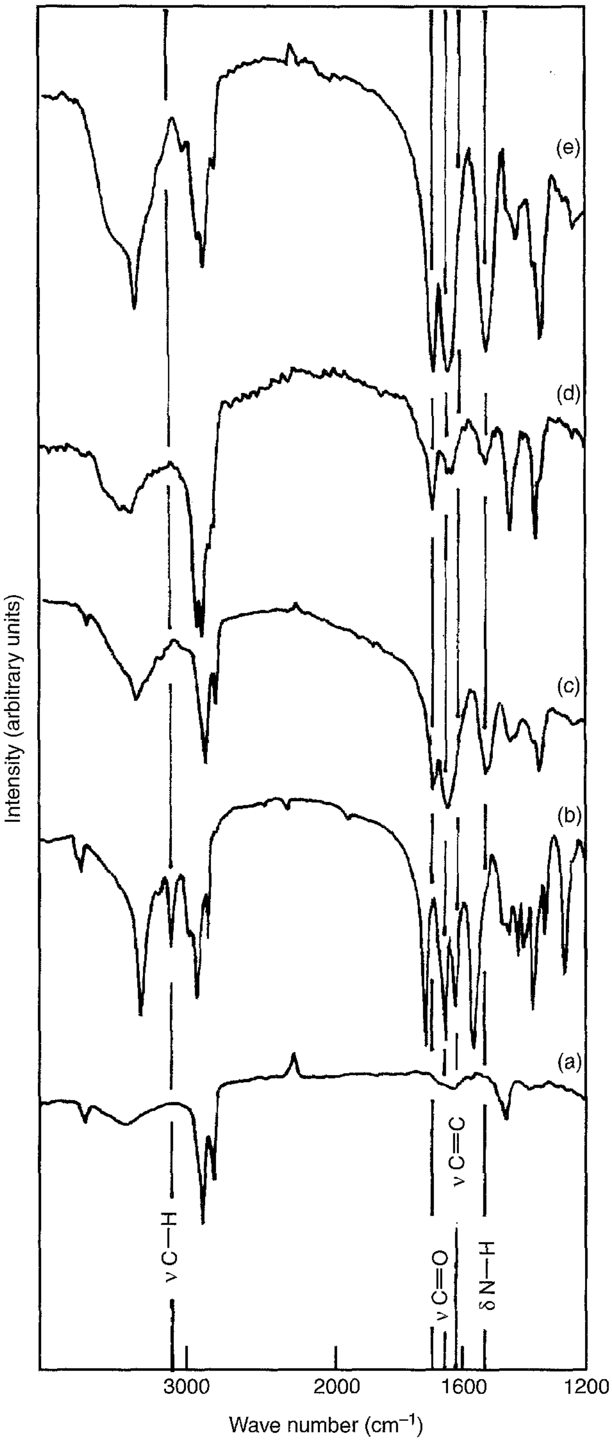

Figure 2 IR spectra of the samples: (a) SAN; (b) SD; (c) SPD; (d) SPD/m-PP after washing; (e) extract from SPD/m-PP.

authors thought to blend PP with smectite after dispersion in another resin with larger polarity and a high affinity for PP. Such a trial is reported in this letter.

A hydrophobic clay mineral (abbreviation: SAN) was supplied by Corp Chemical Co. Ltd. and has an ideal chemical formula of $[X^{+}{}_{0.33}(Mg_{2.67}Li_{0.33})Si_4O_{10}(OH)_2$, here X^{+} is $(CH_3)_3N^{+}R$ and $(CH_3)_2$

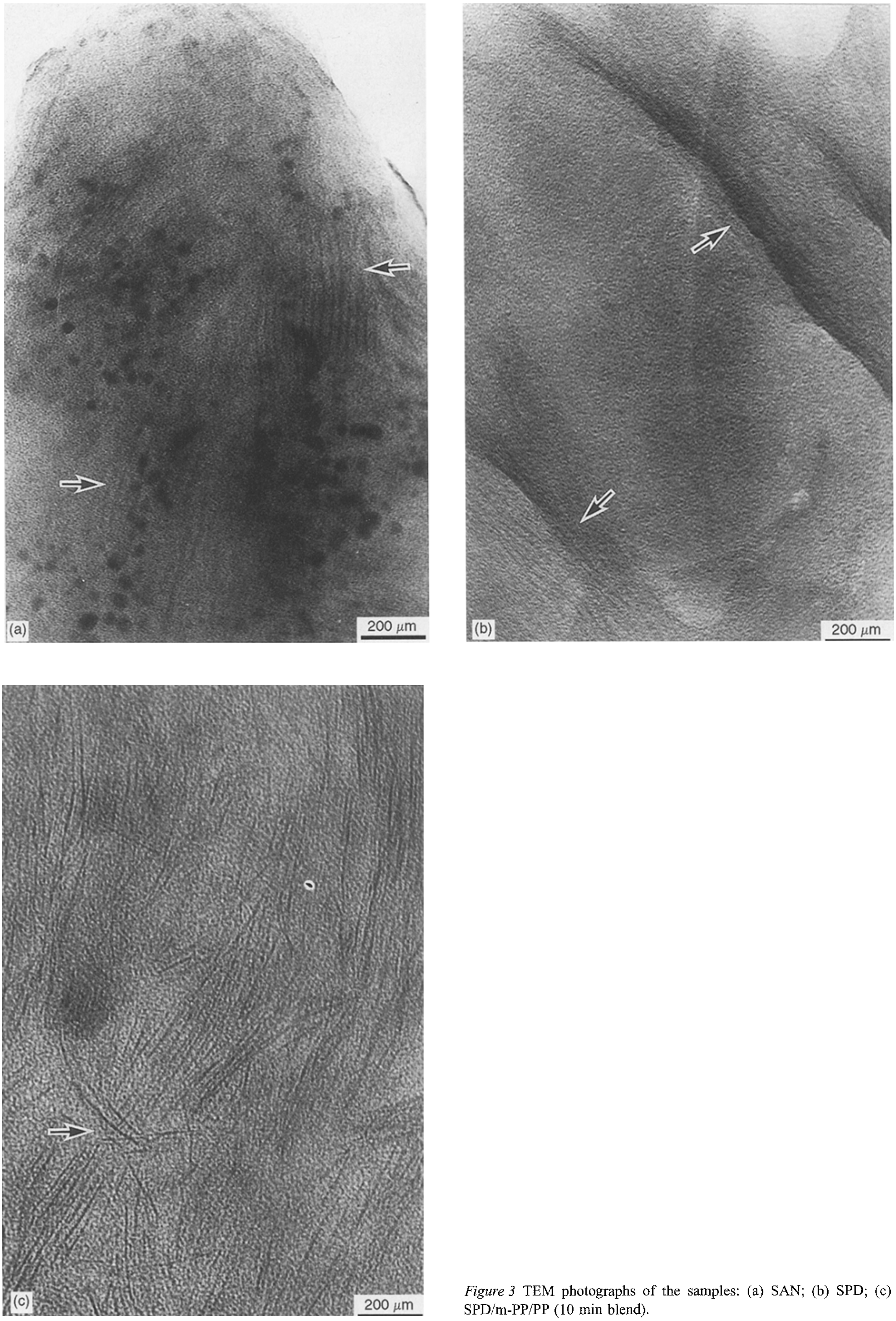

Figure 3 TEM photographs of the samples: (a) SAN; (b) SPD; (c) SPD/m-PP/PP (10 min blend).

N^+RR'; and $R=C_{16}$, $R'=C_{18}$]. 40 g of SAN was dispersed with 320 g of toluene at 20 °C for 24 h. 0.196 g of catalyst, 2,2′-azobis (isobutyronitorile) [$(CH_3)_2C(CN)N=NC(CN)(CH_3)_2$], was dissolved in 20 g of toluene. Both the toluene solutions were mixed, added to 180 g of toluene in which was dissolved 40 g of diacetone acrylamide [$CH_2=CHCONHC(CH_3)_2CH_2CO\ CH_3$: abbreviation: DAAM] and kept at 20 °C for 1 h for intercalation and then 75 °C for 24 h under N_2 atmosphere to polymerize the intercalated DAAM with the catalyst. A small amount of the sol was taken out and dried for X-ray diffraction and IR spectrum measurements. This sample will be abbreviated as SPD.

The sol after polymerization was mixed with 40 g of maleic acid (HOOCCH=CHCOOH)-modified polypropylene (abbreviation: m-PP) dissolved in 200 g of toluene at 100 °C for 1 h. The mixture after cooling to 60 °C was placed in methanol and washed with methanol repeatedly to remove unpolymerized DAAM using a homogenizer and centrifugal apparatus. The composite (abbreviation: SPD/m-PP) was further blended with PP to be 3 wt% of the filler content by using a Labo Plastmill (Toyo Seiki Co.) at 230 °C for 10 min, termed SPD/m-PP/PP.

Figure 1 shows X-ray diffraction profiles of the samples at various stages. The interlayer distance d_{001} of SPD became larger than that of SAN by 1.14 nm but the (0 0 1) diffraction peak was clearly observed, which suggests remaining of the ordered stacking of smectite layers in SPD. Such a clear diffraction peak disappeared in SPD/m-PP after washing with methanol and also in SPD/m-PP/PP. The stacking structure must have been delaminated in these samples. A d_{001} of around 3.5 nm, although not so accurate, was obtained for both samples by controlling X-ray diffraction conditions carefully.

Figure 2 shows the behaviour of DAAM by the various treatments. DAAM monomer intercalated in SAN (abbreviation: SD) has two characteristic absorptions at 3088 cm^{-1} (νC–H) and 1624 cm^{-1} (νC=C) which disappeared in SPD, showing occurrence of polymerization. It is certain that the polymerized DAAM exists between smectite layers of SPD, because of (i) the absorptions of νC=O(1710 cm^{-1} and 1680 cm^{-1}) and δN–H(1540 cm^{-1}) and (ii) a larger d_{001} for SPD than for SAN by 1.14 nm. The SPD/m-PP after washing with methanol gave weaker absorptions assigned to νC=O and δN–H, and the residue (the extract) obtained from the methanol washings after evaporation showed these absorptions strongly. About 65 wt% of the polymerized DAAM was removed from SPD/m-PP by methanol, but no change was observed in X-ray diffraction profiles. We think that m-PP was intercalated instead of the polymerized DAAM.

Figure 3 shows transmission electron micrography (TEM) photographs. The layered stacking structures (arrowed) in SAN have an average interlayer distance of 2.3 nm which coincides with that from the X-ray diffraction method. Black spots in this photograph could not be identified. The stacking structures (arrowed) in SPD showed about 3.6 nm of interlayer distance which also coincides with results from the X-ray diffraction method. The most interesting state was observed in SPD/m-PP/PP. The delaminated layers were dispersed finely and homogeneously throughout the matrix resulting in a nanocomposite in which the crossed layers arrowed were sometimes observed, suggesting an excellent delamination of the SAN layers. The smectite/PP nanocomposite contains about 5 wt% of m-PP and less than 2 wt% of polymerized DAAM. A study on the effects of these foreign components on the mechanical properties of composite is in progress and will be reported in the future.

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