Polymer Bulletin 41, 107–113 (1998)

Polymer Bulletin

Morphology of polymer/silicate nanocomposites

High density polyethylene and a nitrile copolymer

H. G. Jeon, H.-T. Jung, S. W. Lee, S. D. Hudson

Department of Macromolecular Science, Case Western Reserve University, Cleveland,
OH 44106, USA

Received: 24 April 1998/Accepted: 8 May 1998

Summary

Nanoscale composites of a modified silicate with either high-density polyethylene (HDPE) or a nitrile copolymer have been examined. Hydrophilic silicate clay was intercalated by ion exchange reaction of alkylammonium ions. X-ray diffraction (XRD) and transmission electron microscopy (TEM) results revealed that so-modified silicate layers were finely dispersed in these polymeric matrices. Instead of being individually dispersed, most layers were found in thin stacks comprising several swollen layers. Greater dispersion was found in the nitrile copolymer rather than in HDPE, suggesting differences in the degree of physical interaction with the modified clay. Lamellar crystals of HDPE formed parallel to the silicate layers.

Introduction

Because of the highly anisometric planar geometry of clay minerals comprising layered silicates and the potential for their molecular level dispersion, there has been considerable interest in the properties of polymer-clay hybrids. They exhibit physical and chemical properties that differ significantly from that of their bulk counterparts. Silicate clays layers are bound together by a layer of sodium ions, and are naturally hydrophilic (1). Most organophilic clays are prepared by ion exchange and adsorption of small organic molecules into the spacing (2). Various amines are suitable for this purpose.

According to previous reports, when modified silicate layers were finely dispersed in nylon 6 (3-6), polypropylene (7), polystyrene (8), polyimide (9) and epoxy resin (10), mechanical, thermal and barrier properties were improved significantly. For example, molecular composites of nylon 6 and modified clay have excellent mechanical properties as compared with nylon 6, improving stiffness without sacrificing toughness. Superior thermal expansion and dielectric properties were obtained for polyimide nanocomposites. The impact resistance and the heat distortion temperature of epoxy resin were enhanced by dispersion of nanoscale silicate particles.

In this paper, two commercially important polymers are investigated: HDPE (High Density Polyethylene) and a nitrile copolymer, which are ideal for the fabrication of a variety of films and containers for packaging and industrial applications. Because the thickness of the silicate filler is less than typical polyethylene lamellae, the silicate layers might affect the semicrystalline morphology and the properties of HDPE. The nitrile copolymer (Barex 210 E) may be used for gas barrier applications, and the barrier and thermal properties are expected to be enhanced by incorporation of a nanoscale platelet filler. Here we investigate the dispersability of modified silicate layers in these polymer matrices and the orientation of HDPE lamellae with respect to that of the silicate layers.

Experimental

The nanoscale filler used in this study was sodium montmorillonite (Kunipia F, Kunimene Industries. Co. Ltd.) with cation-exchange capacity of 119 meq/100g, and the exchangeable cations are Na^+ (81.5%), Ca^{2+} (14.4%), and K^+ (0.9%). The dimensions of the silicate sheets in this montmorillonite are reportedly 200 nm in length and width and 1 nm in thickness. The nitrile copolymer (trade name: Barex 210E) and high density polyethylene were supplied by BP Chemicals and used as matrix polymers.

The montmorillonite was intercalated with dodecylamine to render the clay organophilic, following a method reported earlier (11, 12). The montmorillonite and water were mixed at high temperature. This dispersion of montmorillonite was added to a solution of the ammonium salt of dodecylamine, prepared by mixing of dodecylamine, concentrated hydrochloric acid and water. The precipitate was isolated by filtration, and washed several times with hot water to remove the residue of ammonium salt of dodecylamine. The product was then filtered and dried.

X-ray powder diffractograms were recorded using a Philips X-ray diffractometer, equipped with a Ni-filtered Cu $K\alpha$ radiation source. The diffracted beam was monochromated before detection.

In order to characterize the silicate particle size and shape, dilute (~0.1 - 1 wt. %) solutions of the modified silicate in suitable solvents were prepared. Even more concentrated solutions (up to 3 wt.%) in benzonitrile were transparent, and DMAc dispersions were only slightly cloudy. The silicate particles were deposited from solution onto a freshly cleaved mica sheet, and the solvent was evaporated. After platinum shadowing at 26° and carbon coating, the film was floated off the mica using distilled water, and retrieved onto Cu grids. Transmission electron micrographs were obtained with a JEOL JEM-100SX using acceleration voltage of 100 kV

Polymer composites were prepared by solution blending. A 1:4 ratio of the modified silicate and HDPE was dissolved in a co-solvent of the xylene and benzonitrile (80:20wt%) at 110°C for 30 minutes. The clear solution was precipitated in a large amount of vigorously stirred THF. The precipitated powder was filtered by a fine glass filter and washed several times with THF to remove the residues of xylene and benzonitrile. The powdered product was placed in a vacuum oven at 70°C for 7 hours, before vacuum compression molding at 130°C. The nitrile copolymer was mixed with 15 wt.% of the modified silicate in DMF, and then DMF was evaporated at 80°C for 24 hours in the vacuum oven. The film product was obtained for characterization.

The stain for HDPE was prepared by dissolving 2% (w/v) solution of $RuCl_3{\cdot}3H_2O$ in sodium hypochlorite for 3 hours (13). After staining the sample, it was sectioned at room temperature using an RMC MT-7000 ultramicrotome.

Results and discussion

Figure 1 shows the x-ray diffractogram of Na-montmorillonite and the product prepared from the ion exchange reaction of Na-montmorillonite and dodecylamine. The basal layer spacing was obtained from (001) peak position. After intercalating the montmorillonite with alkylamine, there was no remnant of the original 11.8Å spacing of Na-

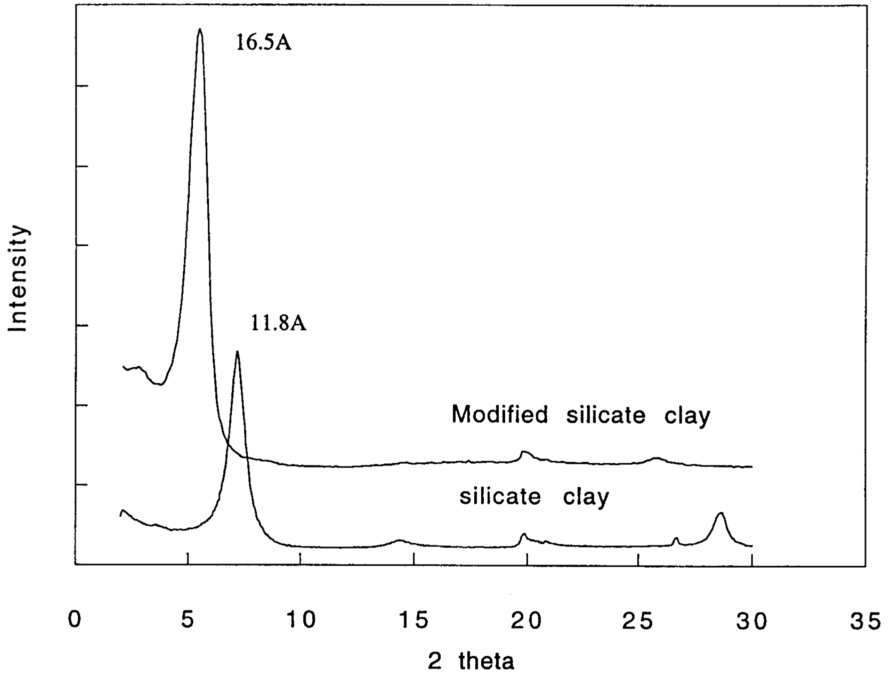

Figure 1. X-ray diffractograms of Na-montmorillonite (as received) and modified montmorillonite.

montmorillonite, and the basal spacing had increased by 4.7Å. Thus, it is indicated that Na-montmorillonite was successfully intercalated with dodecylamine. Since a monolayer of water separates the layers in the original Na-montmorillonite and occupies a space of ~ 2.0 Å, the interlayer spacing when dodecylamine is present is ~ 6.7 Å. This value indicates that the alkyl chain is neither lying flat on the clay surface, nor extending perpendicular from it. Instead it suggests that chains are packed in a tilted arrangement with respect to the silicate surface.

Electron microscopic study demonstrates that the modified silicate layers are well dispersed in benzonitrile on a molecular level, as shown in Figure 2. The thickness of modified silicate can be measured from the length of its shadow. The majority of the particles are ~ 5 nm in thickness, consisting of approximately 2 to 5 silicate layers. Several large particles have a thickness of nearly 20 nm, comprising approximately 10 layers. The irregular shape of the particles further indicates stacking and aggregation of individual layers. Therefore, although the solutions in organic solvent were transparent, small aggregates exist and the silicate layers are not *individually* dispersed.

The longest shadows in this micrograph disclose something of the distorted shape of the silicate particles in solution. These shadows extend from portions of the particles that are folded. The ultra-thin sheet-like particles are sufficiently flexible in solution that some larger particles collapse during deposition in a folded configuration onto the substrate. Because the layers have finite stiffness, the fold is not sharp, but has a small,

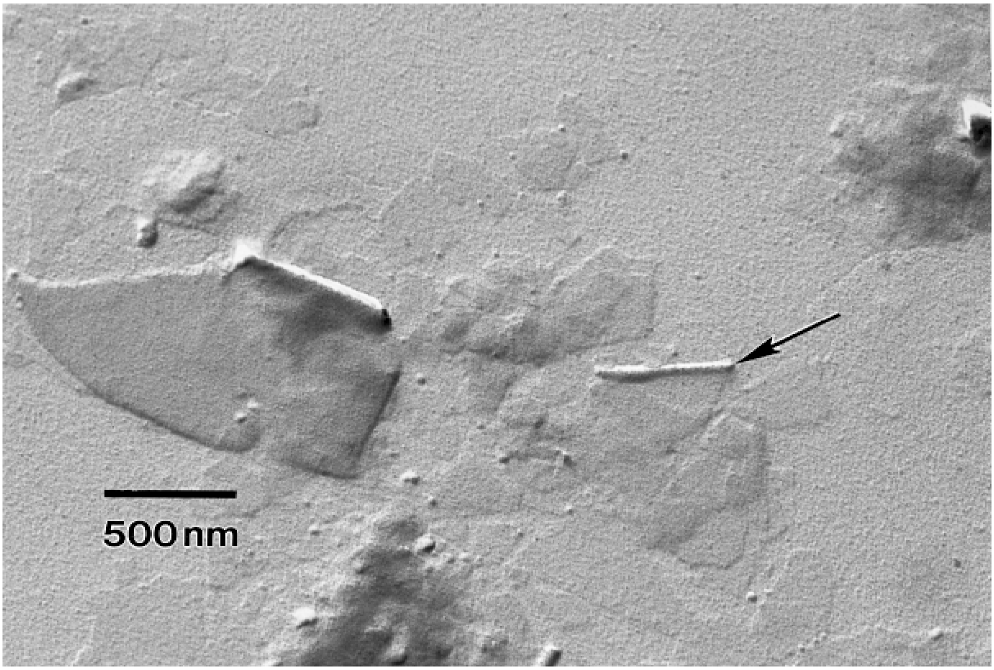

Figure 2. TEM micrograph of modified silicate layers deposited from benzonitrile solution. The arrow marks a folded silicate particle.

finite curvature. In summary, these silicate layers are not rigid plates, as subsequent observation will also show.

Figure 3 shows x-ray diffractograms of modified silicate composites of HDPE (20 wt.% filler) and of the nitrile copolymer (15 wt.% filler). The layer spacing of the modified silicate in the nitrile copolymer system is greater than in the HDPE system, suggesting that the nitrile copolymer is more compatible with the modified silicate interface. This difference is reasonable considering the potential for dipole interactions between the nitrile copolymer and the modified silicate. Little mixing of attached alkyl chains and polyethylene is evident from the minimal increase in the layer spacing.

A TEM micrograph of a section of nitrile copolymer/15 wt.% modified silicate composite is shown in Figure 4. The thick dark lines are assemblies of silicate sheets, viewed edge-on; the individual silicate sheets are imaged and the assembly has a regular, fringed appearance. Many of the silicate particles have an undulated conformation, and the fringes associated with individual layers also undulate. The specimen shows that some silicate layers are individually distributed in the nitrile copolymer matrix (see Fig. 4) while most of them are stacked in groups of approximately 5 - 8. No larger-scale stacks were observed. The particles also are generally horizontal in the Figure—apparently a result of the compression molding operation. The fine dispersion of highly asymmetric particles as shown is expected to improve the barrier properties of such films, since the diffusing path of gas molecules must have increased tortuosity.

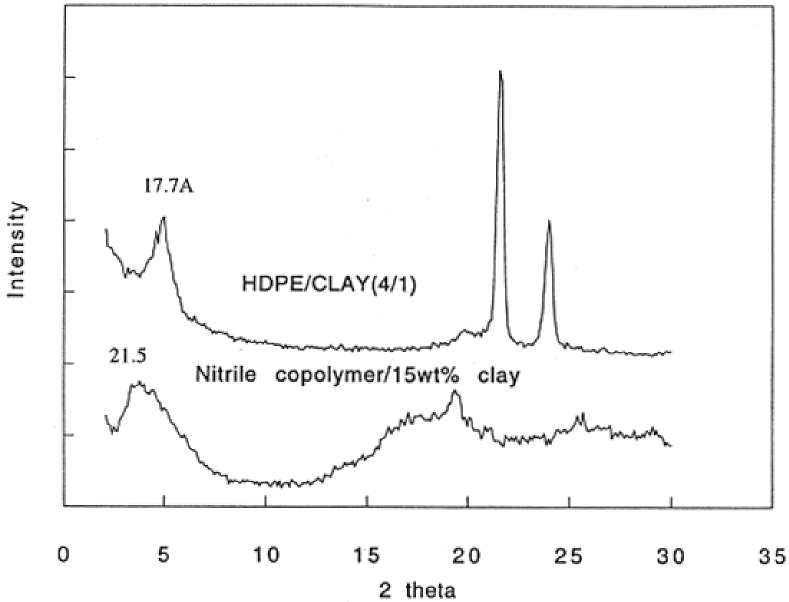

Figure 3. X-ray diffractograms of modified montmorillonite, HDPE and nitrile copolymer composite systems. A high degree of crystallinity of the HDPE is evident.

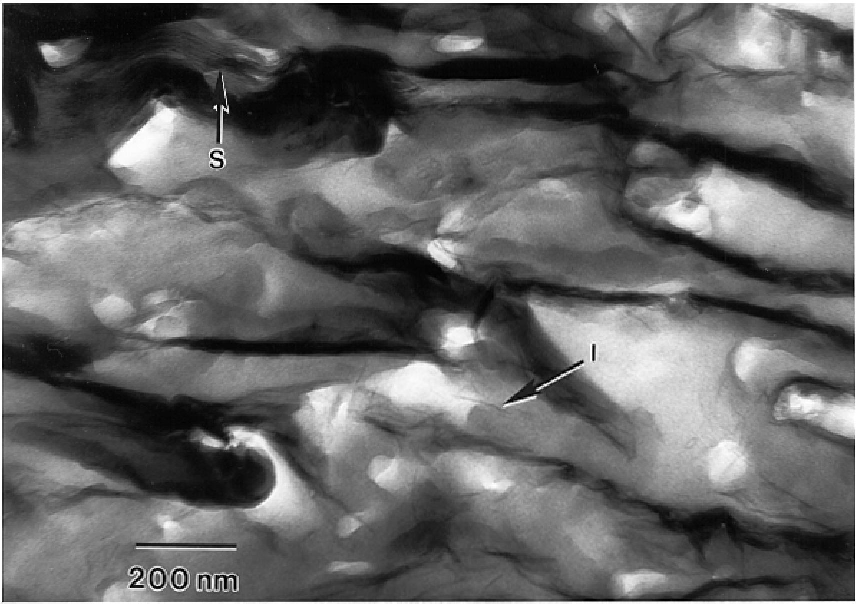

Figure 4. TEM micrograph of the nitrile copolymer filled with 15 wt. % modified montmorillonite. Examples of individual and stacked silicate layers are marked I and S, respectively.

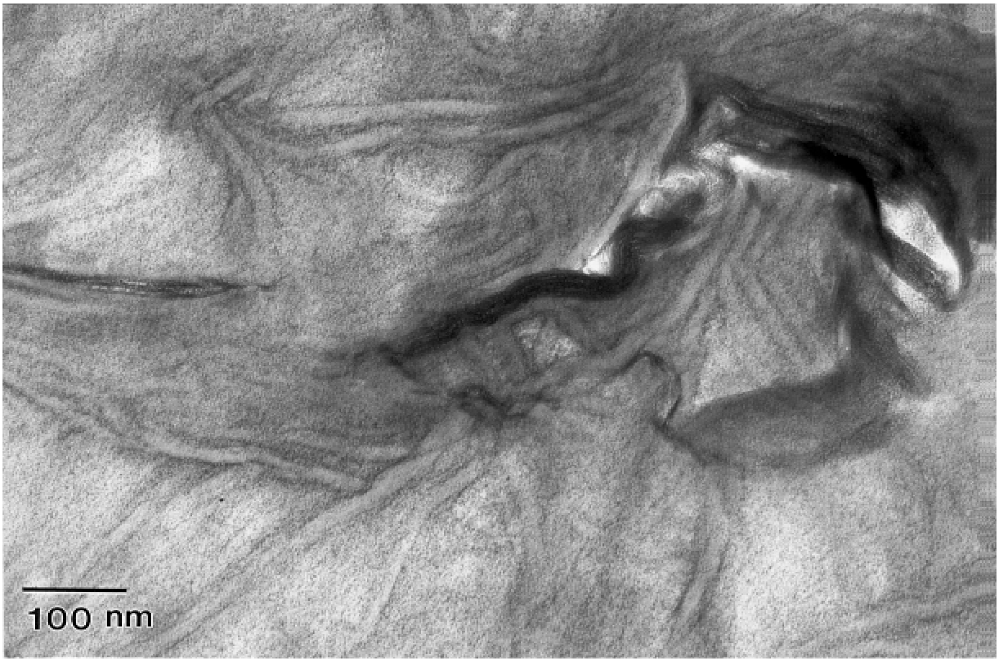

Figure 5. TEM micrograph of an ultrathin section of HDPE filled with 20 wt. % modified montmorillonite. Stacked particles are undulated and mutually parallel to the polyethylene lamellar crystals.

A similar morphology is observed for compression-molded specimens of HDPE/modified silicate composites (Figure 5). The thick dark lines again represent the stacked modified silicate layers, and the abundant thin dark lines are selectively stained, amorphous chain-folded regions of HDPE at lamellar crystal interfaces (13). The stacking of the silicate layers into larger particles actually facilitates their identification, and the relative crystal orientations can be determined. The silicate layers and the nearest neighbor polymer lamellae are parallel to one another. Moreover, those polymer lamellae that are not parallel to the silicate layers are bent sharply, so that they are parallel where they touch one another. Within a silicate particle stack, the individual layers can be identified in the Figure, and some swelling at the edges of stacks is apparent, as the layers splay from one another. Consistent with poorer swelling of these stacks by HDPE, the silicate stacks are typically thicker in this system, in comparison to the nitrile copolymer nanocomposite.

Although the lamellar form of the HDPE crystals is ordinary, it is significant that these lamellae are parallel to the silicate surface. This result is expected to have possibility of improving mechanical properties of HDPE using the nanoscale fillers. If polyethylene chains can be grafted onto the silicate layers, dispersability is expected to improve. Moreover, such chains should act as tie chains between polymer crystals, thus impeding crack growth. This concept is investigated and discussed in another publication.

Conclusion

We investigated the morphology of modified silicate filler in the HDPE and nitrile copolymer matrices. The hydrophilic clay was successfully intercalated with dodecylamine by ion exchange reaction. These modified silicates could be finely dispersed in benzonitrile. TEM characterization showed the layers to be aggregated in thin stacks, consisting of a few (two to five) individual layers. Comparison of silicate layer spacings in nanocomposites with the polymer matrices by wide angle x-ray diffraction and TEM microscopy indicate that the modified silicate layer is slightly more dispersed in the nitrile copolymer system than in the HDPE system. HDPE crystalline lamellae, similar to those found in pure HDPE samples, in the nanocomposites are parallel to the silicate layers. Owing to their dispersion and morphology, the enhancement of barrier and mechanical properties for the nanocomposite systems is expected.

Acknowledgments

We thank the Edison Polymer Innovation Corporation, BP Chemicals, Inc., NSF CMMC, and ACS PRF #31333-G7 for financial support of this work.

References

1. Brindly GW, Brown G (1980) The crystal structures of clay minerals and their x-ray identification. London
2. Wilson AD, Prosser HJ (1983) Developments in ionic polymers-2, Chap.2. Elsevier, New York
3. Okada A, Kawasumi M, Kamigaito O (1990) Mat. Res. Soc. Symp. Proc. 171
4. Kojima Y, et al. (1993) J. Polym. Sci. Polym. Chem. 31: 983
5. Kojima Y, et al. (1993) J. Mater.Res. 8: 1185-1189
6. Kojima Y, et al.(1994) J. Polym. Sci. Polym. Phys. 32: 625
7. Kawasumi M, Hasegawa N, Kato M, Usuki A, Okada A (1997) Macromolecules 30: 6333
8. Kato C, Kuroda K, Takahara H (1981) Clay Clay Min. 29: 294
9. Yano K, Usuki A, Okada A, Kurauchi T, Kamigaito O (1993) J. Polym.Sci. Polym. Chem. 31: 2493
10. Moet A, Akelah A (1993) Mater. Lett. 18: 97
11. Wang MS, Pinnavaia TJ (1994) Chem. Mater. 6: 468
12. Weiss A, Holm C, Platikanov D (1993) Coll. Polym. Sci. 271: 891
13. Montezinos D, Wells BG, Burns JL (1985) J. Polym. Sci. Polym. Lett. 23: 421