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SOME CLAY NANOCOMPOSITES BASED ON A HIGH-TEMPERATURE, HIGH-PERFORMANCE POLYMER

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ABSTRACT

The techniques of reinforcing relatively tractible polymers by means of intercalated and exfoliated clay particles are applied here to the more challenging case of a necessarily less tractible high-performance polymer. The polymer, poly(biphenyl ether triphenylphosphate), was chosen because of its earlier characterization in U.S. Air Force programs developing such composites. Conditions were found in which the polymer intercalated and exfoliated a montmorillonite clay, and the resulting nanocomposites were characterized with regard to their structures, thermal properties, and mechanical properties. As was found in previous investigations of high-performance materials, it was possible to improve a few properties, but then only at the cost of undesirable changes in other properties. In the present case, it was at least somewhat possible to increase thermal stability and to significantly increase extension moduli.

Key Words: Clay nanocomposites; High-performance polymers; Intercalated and exfoliated clay particles; Mechanical properties; Organic–inorganic hybrid materials; Poly(biphenyl ether triphenylphosphate)

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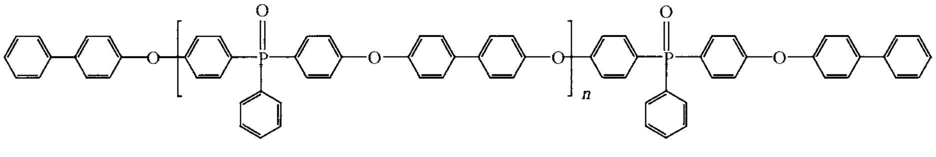
INTRODUCTION

In recent years, polymer–clay composites have attracted a great deal of interest among researchers. These hybrid organic–inorganic nanocomposites frequently exhibit exceptional properties, with only modest loadings of the clay filler giving large increases in properties such as the strength, modulus, thermal resistance, and heat distortion temperature. The basic feature of this approach is to separate and disperse the clay platelets, with the dispersions ranging from simple intercalation to total exfoliation of the layers. Since polyamide–clay composites were first synthesized by a Toyota research group (1,2), there have been numerous such nanocomposites prepared using clays and related layered materials. These have included a wide variety of other polymers, including polystyrene (3,4), poly(ethylene oxide) (4,5), polypropylene (6–9), poly(dimethylsiloxane) (10,11), polycaprolactone (12), polyurethanes (13,14), methylmethacrylate copolymers (15), styrene–acrylonitrile copolymers (16), polyisobutylene–bromomethylstyrene copolymers (17), unsaturated polyesters (18), polyimides (19,20), and epoxy resins (21–23). There has also been a lot of interest in theory and simulations addressing the preparation and properties of these materials (24–31).

The hydrophilic interlayer cations in a clay such as montmorillonite are usually Na^+ or K^+ and generally have to be replaced by organic species, such as alkylammonium cations, to obtain the desired nanometer-scale dispersions. The dispersions are generally obtained by intercalation of the polymer or prepolymerized monomer into the clay galleries, in solution or in the melt, followed by exfoliation of the clay layers, if desired.

Some of the most impressive improvements in mechanical properties have been obtained with polymers that are much in need of modification in this regard, for example, poly(dimethylsiloxane). These polymers are generally also relatively tractible, which simplifies the processing steps. The present investigation is rather different, in that it attempts to apply these techniques to the more challenging case of a necessarily less tractible high-performance polymer. Specifically, poly(biphenyl ether triphenylphosphate) (PBETP) was chosen for this investigation because of its earlier characterization in U.S. Air Force programs developing such high-temperature polymers. Its structure is shown in Scheme 1. This polymer is of particular interest because it has very good high-temperature resistance and nonflammability, due to the presence of the phenyl groups and phosphate moieties, respectively, on its backbone.

Some composites have been made earlier from some of these Air Force polymers. In some cases, a ceramic-like phase was generated by a sol–gel reaction



Scheme 1. Molecular structure of the PBETP polymer.

within the polymer, giving improvements in some mechanical properties (32–34). In other cases, the in situ generated phase was more rubber-like and was introduced to improve other properties (35,36).

The route chosen for preparation of these composites was solution intercalation of the polymer into the modified clays, using dimethyl acetamide (DMAc) as the dispersing medium. The resulting materials were characterized with regard to their glass transition temperatures T_g, thermal stabilities, and mechanical properties in simple extension.

EXPERIMENTAL

Materials

The clay used was a Na^+-type montmorillonite generously supplied by Southern Clay Products, Inc. The PBETP was synthesized at the Polymer Branch of the Wright Patterson Air Force Base, using methods described elsewhere (35,36).

Five organic clay modifiers, specifically *n*-octyltrimethyl ammonium chloride, *n*-decyltrimethyl ammonium bromide, *n*-dodecyldimethylethyl ammonium bromide, *n*-tetradecyltrimethylammonium chloride, and *n*-dioctadecyldimethyl ammonium chloride, were purchased from the Fluka Company, as was the DMAc solvent. All were used as received.

Preparation of Modified Clays

In a typical preparation, 5 g of *n*-decyltrimethylammonium bromide and 100 mL of water were placed into a 250-mL beaker, and the resulting solution heated to 80°C. Ten grams of clay were then dispersed in 200 mL of water at 80°C. The clay dispersion thus obtained was added to the solution of the *n*-decyltrimethylammonium bromide, and the resulting mixture was stirred vigorously for 1 h. A white precipitate was isolated by filtration, placed into a 500-mL beaker with 400 mL hot water, and stirred for 1 h. This process was repeated twice to remove the residue of *n*-decyltrimethylammonium bromide. The product was then filtrated and dried. This organophilic clay was termed "C10-Clay," with the number specifying the number of carbon atoms in the hydrocarbon chain in the alkylammonium salt used to modify the clay. Four other organophilic clays were prepared from the other ammonium salts and given designations in the same manner, with all five being described in the first two columns of Table 1.

Preparation of PBETP–Clay Composites

Preliminary experiments were carried out to determine which of these modified clays were best for intercalating the PBETP into the clay layers in the DMAc dispersion medium. The relevant results are shown in the last column of Table 1.

Table 1. The Dispersibility of the Modified Clays in DMAc

Designation	Organic Modifier	Dispersibility
C8	*n*-Octyltrimethyl ammonium chloride	None
C10	*n*-Decyltrimethyl ammonium bromide	Good
C12	*n*-Dodecyldimethylethyl ammonium bromide	Partial
C14	*n*-Tetradecyltrimethyl ammonium chloride	None
C18	*n*-Dioctadecyldimethyl ammonium chloride	None

The modifier that worked best was *n*-decyltrimethylammonium bromide, with *n*-dodecyldimethylethylammonium bromide possibly acceptable as well. It seemed that the hydrocarbon chain length had to be greater than 8, but probably less than 12, to make the corresponding modified clay dispersible in the DMAc. The focus of the remaining part of the investigation, therefore, was on the C10-Clay and the C12-Clay composites.

In a specific composite preparation, a mixture of 0.08 g C10-Clay and 20 g DMAc was stirred vigorously at 100°C for 12 h, yielding a 0.5 wt.-% DMAc dispersion of the clay. This was then mixed with 80 g of a 0.5 wt.-% DMAc solution of the PBETP polymer. After 48 h of stirring at 80°C, the mixture was poured into a Petri dish and dried in a vacuum oven at 100°C for 4 days. A yellowish translucent film was obtained. Some of the other modified clays were used in a similar manner to prepare additional composites.

Characterization

X-ray diffraction (XRD) analyses were performed using a Philips diffractometer and Cu K_α radiation. The diffraction software used was PC-APD.

Differential scanning calorimetry (DSC) was performed using a Perkin Elmer DSC system at a heating rate of 10°C/min, under a nitrogen atmosphere. These measurements were used to estimate values of T_g.

Thermogravimetric analysis (TGA) measurements were carried out on a Universal V2.6D TA instrument at a heating rate of 20°C/min, under a nitrogen atmosphere, after initial isothermal equilibration at 100°C for 5 min.

Moduli, ultimate strengths, and maximum extensibilities were measured using an Instron mechanical tester (model 1122) at room temperature. The samples had dimensions of approximately $40 \times 5 \times 0.2$ mm^3, and the lengths of the samples between the clamps were 20 mm. The extensions were carried out at a cross-head speed of approximately 5 mm/min.

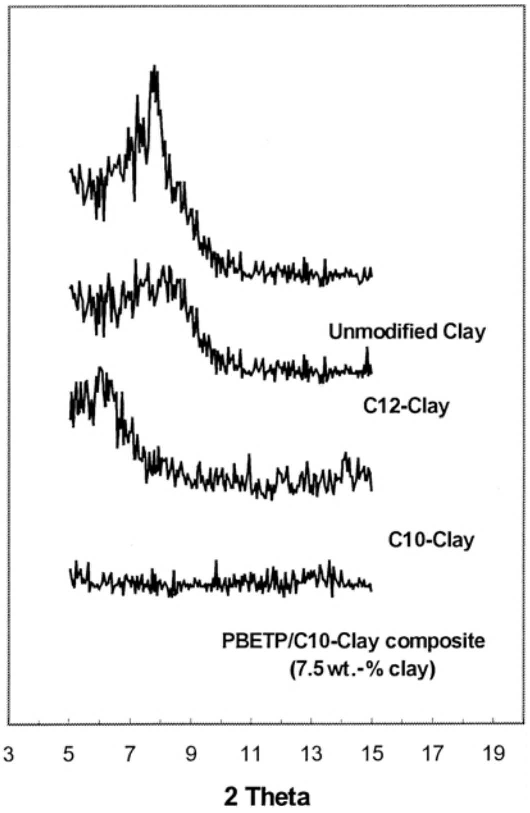


Figure 1. X-ray diffraction curves for the clay, two modified clays, and one of the modified clay composites.

RESULTS AND DISCUSSION

Dispersion of the Clay Platelets

Figure 1 presents some XRD curves, specifically for the unmodified clay, the C12-Clay and C10-Clay, and a PBETP/C10-Clay composite (with 7.5 wt.-% clay). It shows that the clay itself and the two modified clays have peaks in the angular 2θ region corresponding to 7.8, 7.2, and 5.9 degrees, respectively. Therefore, their interlayer spacings are 11.7, 12.3, and 15.0 Å, respectively. The latter two values represent the increase in this spacing over the 11.7-Å value due to intercalcalation of the organoammonium salts into the galleries of the clay. It shows that *n*-decyltrimethylammonium bromide is more effective than the *n*-dodecyldimethylethylammonium bromide for increasing the silicate interlayer spacing of the clay, although the latter had earlier been regarded the more effective clay-modified agent for dispersing the clay into DMAc (19). The difference prossibly results from the clays coming from different sources. Because of the present results, *n*-decyltrimethylammonium was used to prepare the PBETP–clay composites used in further evaluations.

Figure 1 also shows the XRD curve for the PBETP/C10-Clay composite having 7.5 wt.-% of the modified filler. No peak can be seen in the angular scan from 5 to 15°. This demonstrates that the clay has been successfully exfoliated into the polymer matrix.

Thermal Analyses

The DSC curves for PBETP, and the PBETP/Clay composites at clay contents of 3.8 and 7.5%, all showed the same value of T_g (235°C), but the transition zone became less well-defined on increase in the clay content. This smearing out of the glass transition region is unusual at such low filler contents.

Some of the TGA results are shown in Figure 2. The curves for the two PBETP/Clay composites show two weight–loss steps. The first, occurring at $\sim$220°C, is quite small and believed to be the loss of the organic ammonium salt. The second is presumably due to decomposition of the PBETP. With regard to the second process, the initial weight-loss temperatures for the two PBETP/Clay composites were 575°C and 580°C, respectively, which are at least somewhat higher than the 568°C value for the pure polymer. There is, thus, at least some enhancement of thermal stability due to the presence of the exfoliated clay platelets.

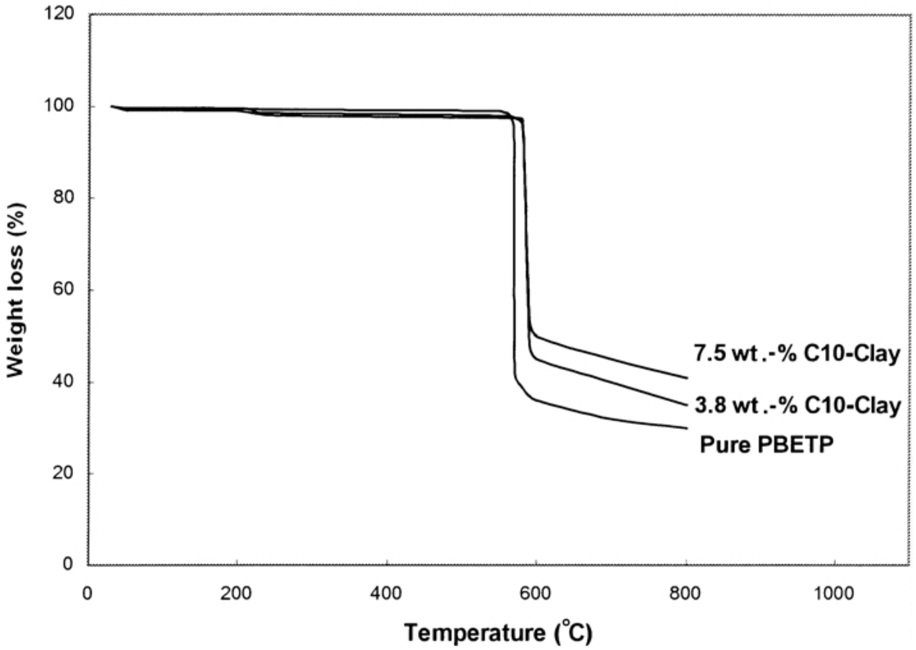


Figure 2. Thermogravimetric analysis curves for the PBETP polymer and some PBETP/C10-Clay composites: a) pure PBETP; b) 3.8 wt.-% C10-Clay composite; and c) 7.5 wt.-% C10-Clay composite.

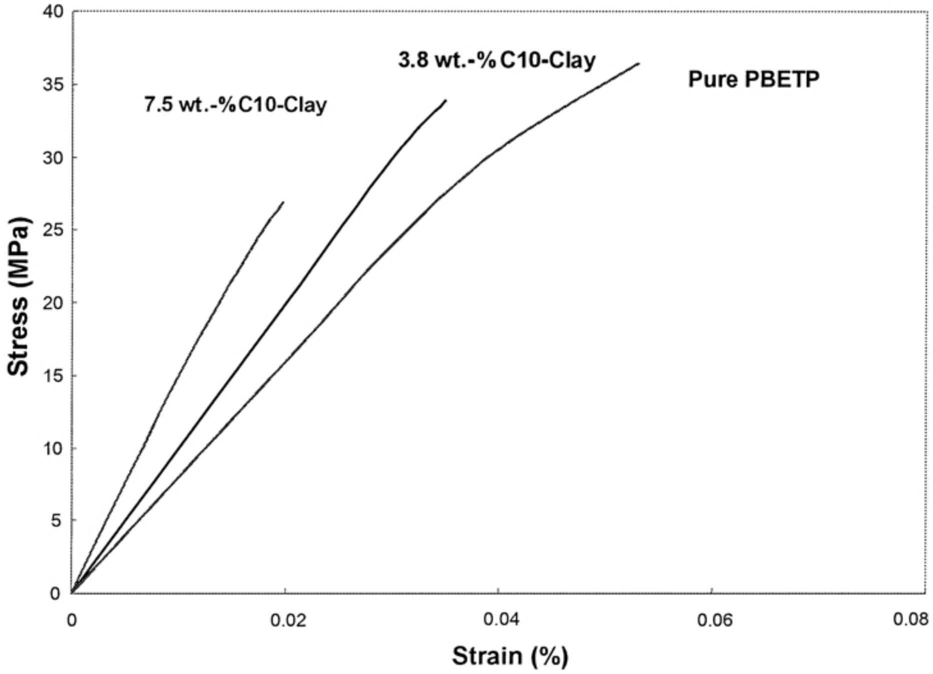


Figure 3. Stress–strain curves for the same three materials described in Figure 2.

Mechanical Properties

Figure 3 shows the stress–strain isotherms for the PBETP and for the same two PBETP/Clay composites described above. Increase in clay content is seen to give significant increases in the elongation moduli (initial slopes of the curves). The increases are significant, particularly in view of the small amounts of filler present and the already large moduli of this high-performance polymer. As is usual in the case of polymers already having superb properties, such improvements come at the cost of decreases in other properties such as the ultimate strength and extensibility. As was concluded elsewhere (32–36), it is very hard to improve the already excellent properties of high-temperature, high-performance polymers, particularly because many of them lack the reactivity that is required for good bonding between the polymer and the reinforcing phases.

CONCLUSION

As is obvious from the above results, quite small amounts of organically modified clays can have a very significant affect on the properties of a typical high-performance polymer. The conclusions reached seem to be consistent with what is becoming the central dogma in this area: It is very hard to improve the properties of high-performance polymers because their properties are already very good and because, by design, they do not have the reactivity that would help bond them onto reinforcing particles of any type. With regard to this desired interfacial bonding, future work should include some of the high-performance polymers that have been functionalized for this purpose or some of the widely available bonding agents (35,36).

Further improvements in the properties studied here would certainly encourage measurements of other properties, such as permeability, flame resistance, and resistance to solvents and to hostile environments in general.

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REFERENCES

1. Kojima, Y.; Usuki, A.; Kawasumi, M.; Fukushima, Y.; Okada, A.; Kurauchi, T.; Kamigaito, O. J. Mat. Res. **1993**, *8*, 1185.
2. Usuki, A.; Koiwai, A.; Kojima, Y.; Kawasumi, M.; Okada, A.; Kurauchi, T.; Kamigaito, O. J. Appl. Polym. Sci. **1995**, *55*, 119.
3. Vaia, R.A.; Ishii, H.; Giannelis, E.P. Chem. Mater. **1993**, *5*, 1694.
4. Giannelis, E.P. Adv. Mater. **1996**, *8*, 29.
5. Vaia, R.A.; Sauer, B.B.; Tse, O.K.; Giannelis, E.P. J. Polym. Sci. Polym. Phys. Ed. **1997**, *35*, 59.
6. Furuichi, N.; Kurokawa, Y.; Fujita, K.; Oya, A.; Yasuda, H.; Kiso, M. J. Mat. Sci. **1996**, *31*, 4307.
7. Kato, M.; Usuki, A.; Okada, A. J. Appl. Polym. Sci. **1997**, *66*, 1781.
8. Kurokawa, Y.; Yasuda, H.; Kashiwagi, M.; Oyo, A. J. Mat. Sci. Lett. **1997**, *16*, 1670.
9. Hasegawa, N.; Kawasumi, M.; Kato, M.; Usuki, A.; Okada, A. J. Appl. Polym. Sci. **1998**, *67*, 87.
10. Burnside, S.D.; Giannelis, E.P. Chem. Mater. **1995**, *7*, 1597.
11. Burnside, S.D.; Giannelis, E.P. J. Polym. Sci., Polym. Phys. Ed. **2000**, *38*, 1595.
12. Messersmith, P.B.; Giannelis, E.P. J. Polym. Sci., Polym. Chem. Ed. **1995**, *33*, 1047.
13. Wang, M.S.; Pinnavaia, T.J. Chem. Mater. **1998**, *10*, 3769.
14. Chen, T.-K.; Tien, Y.-I.; Wei, K.-H. Polymer, **2000**, *41*, 1345.
15. Dietsche, F.; Thomann, Y.; Thomann, R.; Mulhaupt, R. J. Appl. Polym. Sci. **2000**, *75*, 396.
16. Noh, M.H.; Lee, D.C. J. Appl. Polym. Sci. **1999**, *74*, 2811.
17. Burnside, S.D.; Wang, H.-C.; Giannelis, E.P. Chem. Mater. **1999**, *11*, 1055.
18. Kornmann, X.; Berglund, L.A.; Sterte, J.; Giannelis, E.P. Polym. Eng. Sci. **1998**, *38*, 1351.
19. Yano, K.; Usuki, A.; Okada, A.; Kurauchi, T.; Kamigaito, O. J. Polym. Sci., Polym. Chem. Ed. **1993**, *31*, 2493.
20. Okada, A.; Usuki, A. Mater. Sci. Eng. **1995**, *C3*, 109.

21. Usuki, A.; Mizutani, T.; Fukushima, Y.; Fujimoto, M.; Fukumori, K.; Kojima, Y.; Sato, N.; Okada, A.; Kurauchi, T.; Kamigaito, O. U.S. Patent 4,889,885, 1989.
22. Shi, H.; Lan, T.; Pinnavaia, T.J. Chem. Mater. **1996**, *8*, 1584.
23. Massam, J.; Pinnavaia, T.J. In *Chemical and Pyrolytic Routes to Nonostructured Powders and Their Industrial Application*; Beaucage, G.; Burns, G.; Hua, D.-W.; Mark, J.E., Eds.; Materials Research Society: Warrendale, PA, 1998; Vol. 520, 223.
24. Giannelis, E.P.; Krishnamoorti, R.; Manias, E. Adv. Polym. Sci. **1999**, *138*, 107.
25. Vaia, R.A.; Giannelis, E.P. Macromolecules **1997**, *30*, 7990.
26. Vaia, R.A.; Giannelis, E.P. Macromolecules **1997**, *30*, 8000.
27. Balazs, A.C.; Singh, C.; Zhulina, E.; Lyatskaya, Y. Acc. Chem. Res. **1999**, *32*, 651.
28. Ginsburg, V.V.; Singh, C.; Balazs, A.C. Macromolecules **2000**, *33*, 1089.
29. Kuznetsov, D.; Balazs, A.C. J. Chem. Phys. **2000**, *112*, 4365.
30. Singh, C.; Balazs, A.C. Polym. Int. **2000**, *49*, 469.
31. Lee, J.Y.; Baljon, A.R.C.; Sogah, D.Y.; Loring, R.F. J. Chem. Phys. **2000**, *112*, 9112.
32. Mark, J.E. Polym. Eng. Sci. **1996**, *36*, 2905.
33. Erman, B; Mark, J.E. *Structures and Properties of Rubberlike Networks*; Oxford University Press: New York, 1997.
34. Mark, J.E. In *Ceramic Transitions*, Third International Symposium on Sol-Gel Science and Technology; Klein, L.C., Ed.; American Ceramic Society: Westerville, OH, 1998.
35. Kumudinie, C.; Premachandra, J.K.; Mark, J.E.; Unroe, M.R.; Arnold, F.E. Polym. Prepr. **1998**, *39* (1), 571.
36. Kumudinie, C.; Premachandra, J.K.; Mark, J.E.; Dang, T.D.; Unroe, M.R.; Arnold, F.E. Polymer **2001**, *42*.

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