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A carbocation substituted clay and its styrene nanocomposite

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Abstract

A substituted tropylium ion can be ion-exchanged onto montmorillonite to give a novel organically-modified clay. One can prepare a polystyrene nanocomposite of this clay by emulsion, but not bulk, polymerization. This is the first example of a clay that contains a carbocation and its use to prepare a polymer-clay nanocomposite. Both the clay and its nanocomposites exhibit outstanding thermal stability. Characterization by X-ray diffraction, transmission electron microscopy, cone calorimetry, thermogravimetric analysis and the evaluation of mechanical properties shows that a mixed intercalated-exfoliated nanocomposite is obtained.

Keywords

Polystyrene, Nanocomposite, Tropylium, Carbocation

1. Introduction

Polymer layered silicate nanocomposites have been a topic of great interest since the discovery by Toyota scientists in 1993 that a polyamide-6 nanocomposite containing 5% clay exhibits an increase in tensile strength, tensile modulus, flexural strength, flexural modulus and heat distortion temperature with only a small decrease in impact strength ^[1]. Further work has been carried out on a variety of polymer systems and this has shown that the formation of nanocomposites in general leads to enhanced material properties (noted above) for the polymers ^[2].

In order to enhance the compatibility between the clay and the organic polymer, one typically must ion-exchange the sodium counterion of the clay for an organophilic ion, usually an 'onium' ion. The most common treatments that have been used to produce the organically-modified clays are ammonium salts, and the normal recommendation is that this cation contains at least one long (C12 or greater) alkyl chain. The use of phosphonium salts and stibonium salts provides a marginal increase in thermal stability ^{[3], [4]}.

The formation of a nanocomposite requires that the clay be well-dispersed throughout the polymer matrix, if this criterion is not met, then the clay is acting as a filler and the material is described as a microcomposite or an immiscible nanocomposite. A nanocomposite is described as intercalated if the registry between the clay layers is maintained and it is called exfoliated, or delaminated, if this registry is lost. For some properties, notably flexural modulus and permeability, it is believed that an exfoliated system shows more enhanced properties while, for fire retardancy, there is apparently no difference in behavior between exfoliated and intercalated systems.

In this paper we describe the preparation of the first carbocation substituted clay and the use of this clay to prepare nanocomposite of polystyrene. The thermal stability of the clay is greatly enhanced compared to the normal, ammonium, organically-modified clays.

2. Experimental

2.1. Materials

The majority of chemicals used in this study, including cycloheptatriene, triphenylmethyl chloride, chlorostyrene, benzoyl peroxide (BPO), inhibitor removal reagents, PS (Melt flow index 200° C/5 kg, 7.5 g/10 min, Mw=230,000), were acquired from Aldrich Chemical Co. Pristine sodium montmorillonite was provided by Southern Clay Products, Inc.

2.2. Instrumentation

Thermogravimetric analysis (TGA) was performed on a Cahn TG-131 instrument under a flowing nitrogen atmosphere at a scan rate of 10 °C/min from 20 to 800 °C. All TGA results are the average of a minimum of three determinations; temperatures are reproducible to ±3 °C, while the error bars on the fraction of nonvolatile material is ±3%. Cone calorimetry was performed using an Atlas Cone 2 instrument according ASTM E 1354-92 at an incident flux of 35 or 50 KW/m² using a cone shaped heater. Exhaust flow was set at 24 L/s and the spark was continuous until the sample ignited. Cone samples were prepared by compression molding the sample (20–50 g) into square plaques using a heated press. Typical results from Cone calorimetry are reproducible to within about ±10%. These uncertainties are based on many runs in which thousands of samples have been combusted ^{[5], [6]}. X-ray diffraction was performed on a Rigaku Geiger Flex, 2-circle powder diffractometer; scans were taken from 2 theta 0.86–10, step size 0.1, and scan time per step of 10 seconds. Bright field transmission electron microscopy (TEM) images of the composites were obtained at 60 kV with a Zeiss 10c electron microscope or a JEOL 100CX electron microscope equipped with an AMT digital system. The samples were ultramicrotomed with a diamond knife on Riechert-Jung Ultra-Cut E microtome at room temperature on a

Sorvall MT-2B microtome at room temperature to give ~70 nm thick sections. The sections were transferred from the knife-edge to 600 hexagonal mesh Cu grids. The contrast between the layered silicates and the polymer phase was sufficient for imaging, so no heavy metal staining of sections prior to imaging is required. Mechanical properties were obtained using a SINTECH 10 (Systems Integration Technology, Inc.) computerized system for material testing at a crosshead speed of 0.2 in/min. The samples were prepared both by injection molding, using an Atlas model CS 183MMX mini max molder, and by stamping from a sheet; the reported values are the average of five determinations.

2.3. Tropylium perchlorate ^[7]

A 41.0 g portion of phosphorus pentachloride (197 mmol) and 10.0 g of 95% cycloheptatriene (103 mmol) were placed in a 500 ml round bottom flask together with 300 ml of carbon tetrachloride and magnetically stirred for 1 h, followed by 15 min of reflux. The precipitation was washed with carbon tetrachloride, then treated with 40 ml distilled H₂O and rinsed with ethanol. The aqueous ethanol layer was treated with a slight excess of 70% perchloric acid and 15.7 g (80% yield) of tropylium perchlorate was obtained. 1 H NMR: (CD₃CN) 9.21 ppm (s). IR spectrum was in good agreement with that previously reported ^[8]. UV: 220nm (s), 276nm(m).

2.4. 7-methoxycycloheptatriene ^[9]

To a vigorously stirred solution of 7.65 g of tropylium perchlorate (40 mmol) in 20 ml distilled water and 6 ml methanol in a 100 ml beaker was added 4 g of sodium bicarbonate. When no foam was visible, the oil layer was extracted with 20 ml ether. The ether layer was dried over magnesium sulfate and flask evaporated to give 3.6 g (70%) of the light yellow 7-methoxycycloheptatriene. 1 H NMR: (CDCl₃, ppm) 6.66 (dd, 2H), 6.19 (dd, 2H), 5.51 (dd, 2H), 3.62 (dd, 1H), 3.43 (s, 3H); IR: 3015, 2818, 1619, 1529, 1439, 1394, 1293, 1207, 1117, 1092, 1003, 740, 699, 625, 587 cm⁻¹ UV: 258nm(s).

2.5. Trityl perchlorate ^[10]

To a magnetically stirred solution of 28 g of trityl chloride (97 mmol) in 100 ml of anhydrous ether in a 250 ml round bottom flask was added dropwise 15 g of 70% perchloric acid (105 mmol). After 1 h of gentle stirring, the flask was placed on a rotary evaporator to remove all volatiles. The recovered material was dissolved in minimum amount of dry acetonitrile, then washed three times with dry hexanes and 31.0 g (90% yield) dark brown trityl perchlorate was obtained. 1 H NMR (CD₃CN, ppm): 7.36–7.14 (m); IR: 3059, 1486, 1445, 1088, 758, 697, 636 cm⁻¹ UV: 220 nm (s), 264 nm (m).

2.6. 7-styrylcycloheptatriene ^[11]

To a stirred solution of styrylmagnesium chloride (prepared from 0.72 g of magnesium turnings (30 mmol) and 2.78 g of p-chlorostyrene (20 mmol)) in 25 ml anhydrous tetrahydrofuran (THF) at 0 °C under a nitrogen atmosphere was added dropwise a solution of 2.48 g of 7-methoxycycloheptatriene (20 mmol) in 25 ml of anhydrous THF. After removal of the ice bath, the solution was stirred for 5 h, then heated to 50 °C for 1 h and the solution turned a dark blue. The solution was hydrolyzed with dilute HCl, then extracted with ether. The ether extract was washed with a solution of dilute sodium bicarbonate until it was neutral and then the ether layer was dried over magnesium sulfate. After evaporation of the ether, the residue was vacuum distilled, after the addition of a small amount of pyrocatechol. The recovered material, 2.33 g (60%) of 7-styrylcycloheptatriene (12 mmol), a yellow-brown liquid, was collected at 0.4–0.5 Torr and 100–110 °C. 1 H NMR (CDCl₃, ppm): 7.43 (d, 2H), 7.33 (d, 2H), 6.69–6.78 (m, 3H), 6.27 (dd, 2H), 5.75 (d, 1H), 5.42 (dd, 1H), 5.26 (d, 1H), 2.75 (dd, 1H); IR: 3018, 2927, 1630, 1612, 1513, 1494, 1450, 1408, 1202, 1017, 990, 907, 837, 777, 744, 700cm⁻¹ UV: 252 (s), 269(sh).

2.7. Styryltropylium perchlorate ^[11]

To a suspension of 3.60g (10.5 mmol) trityl perchlorate in 25 ml anhydrous acetonitrile was added 1.94g (10 mmol) 7-styrylcycloheptatriene, dissolved in 25 ml anhydrous THF. The mixture was gently stirred for 1 h. The solvent was removed under vacuum at room temperature and the residue was extracted with cyclohexane to remove the triphenylmethane. The solid was dissolved in 15 ml dry THF then collected by precipitating with ether. A total of 2.65 g (90% yield) was recovered. ¹H NMR (CD₃CN, ppm): 9.34 (d, 2H), 9.06 (m, 4H), 7.93 (d, 2H), 7.64 (d, 2H), 6.90 (dd, 1H), 6.20 (d, 1H), 5.54 (d, 1H); IR: 3022, 2928, 1653, 1598, 1511, 1493, 1447, 1373, 1260, 1097, 937, 833, 757, 701, 625 cm⁻¹ UV: 225 nm (s), 262 (m), 402 nm (w).

2.8. Bulk polymerization of styrene

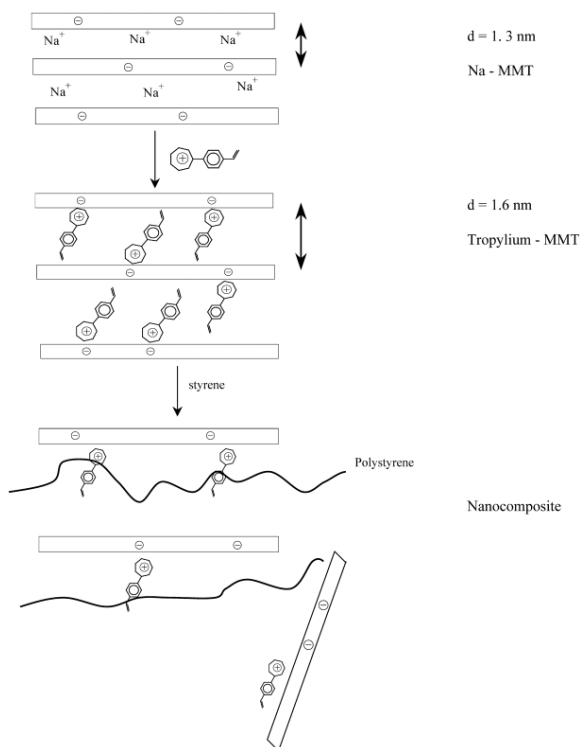
The bulk polymerization of styrene in the presence of the styryltropylium modified clay was carried out following an identical procedure to that which has been previously used. The clay (3%) was well-dispersed in the monomer, then heated to 65 °C in an oil bath in the presence of BPO as the initiator.

2.9. Emulsion polymerization of styrene

In a 500 ml round bottom flask was placed 3 g organically-modified clay, 0.3 g SDS and 200 g water. After this was agitated to ensure good dispersion of the clay, the flask was placed in an oil bath at 65 °C and 97 g of styrene was added along with 0.1 g KOH and 0.5 g potassium persulfate and the solution was heated for 6 h. After cooling, 20 ml of water and 0.5 g aluminum sulfate were added followed by 1 M HCl. Finally methanol was used to completely break the emulsion. The precipitate was washed three times with methanol and the polymer was then dried in a vacuum oven at 80 °C overnight.

3. Results and discussion

In order to prepare a nanocomposite by the combination of a clay and an organic polymer, the gallery space within the clay must be made sufficiently organophilic to permit the entry of the organic polymer. The usual treatment is to replace the inorganic ions by an ammonium ion that contains at least one long alkyl chain, which produces a clay that undergoes thermal degradation at about 200 °C, a temperature which is too low to enable melt blending with those polymers, such as polycarbonate, that must be processed at higher temperatures ^[12]. In an effort to generate a new organically-modified clay that has greater thermal stability than the common ammonium clays, we have investigated the replacement of the inorganic ions with a substituted tropylium ion ^[13]. The substituent of choice is a styryl group, since it has been shown that this substituent on an ammonium ion increases the possibility of nanocomposite formation ^[3]. Nanocomposites were formed by both bulk and emulsion polymerization of styrene in the presence of the clay. The synthetic scheme for the preparation of the substituted cation, the styryltropylium-modified clay and its styrene nanocomposite are shown in [Scheme 1](#).



Scheme 1. Preparation of styrene nanocomposite using styryltropylium clay.

3.1. X-ray diffraction

The XRD data for the clay and the nanocomposite material that is formed by both bulk and emulsion polymerization are shown in Fig. 1. A peak in the XRD trace of the styryltropylium-clay is observed at a 2θ value which corresponds to a d-spacing of 1.6 nm; the d-spacing in the sodium clay is 1.3 nm. Such an increase indicates that the styryltropylium cation does enter into the gallery space of the clay. When styrene is bulk-polymerized in the presence of this clay, the d-spacing does not change, indicating that a nanocomposite does not result from bulk-polymerization. However, when styrene is emulsion-polymerized in the presence of the clay, the peak completely vanishes, which could mean either that an exfoliated nanocomposite has been formed or else that the emulsion-polymerization process has disordered the clay.

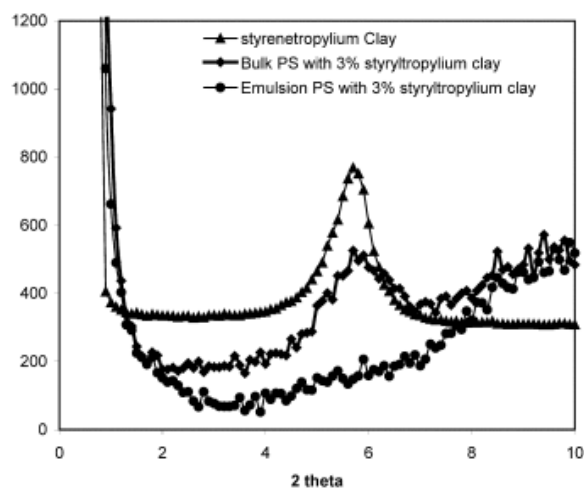


Fig. 1. XRD traces for styrenetropylium clay and its bulk and emulsion nanocomposites with styrene.

The presence of the tropylium ion and the aromatic rings in the nanocomposite is shown by the ultraviolet spectra, in which a red-shift of 70 nm is observed for the nanocomposites relative to the pure

tropylium cation. Rathore et al. ^[14] have shown that the formation of charge-transfer complexes between benzenoid donors and tropylium cations leads to new absorptions in a similar region of the UV-Vis spectrum.

3.2. Transmission electron microscopy

This technique is complementary to XRD and enables the observation of the actual images of the material. The low magnification TEM image for the bulk-polymerized material is shown in [Fig. 2](#); one can clearly see that clay tactoids are present, implying that the clay is not homogeneously dispersed throughout the polymer. In the TEM images of the emulsion-polymerized material, shown in [Fig. 3](#), one sees at low magnification that the clay is now well-dispersed throughout the polymer, a clear indication that a nanocomposite has been formed. In the high magnification image, one can see individual clay layers; some of these are in registry with other clay layers while others do not show registry. This material is most accurately described as a mixed intercalated-exfoliated nanocomposite.

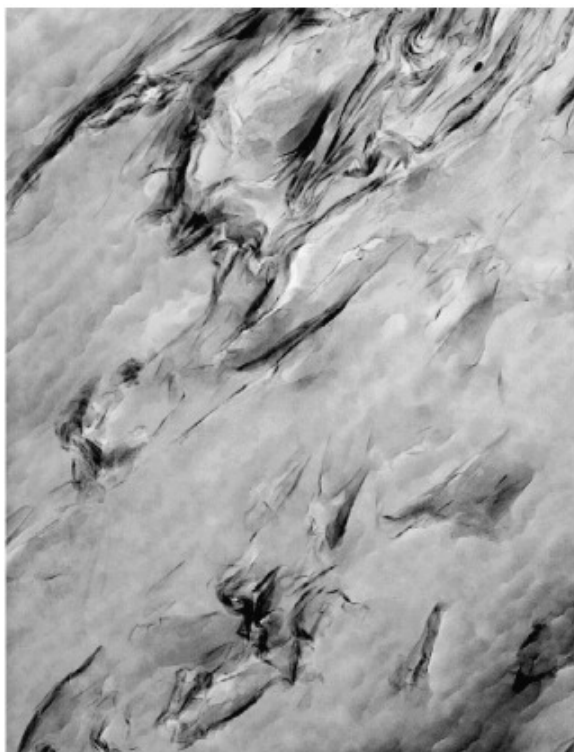


Fig. 2. [TEM image](#) at low magnification of bulk polymerized tropylium-polystyrene [nanocomposite](#).

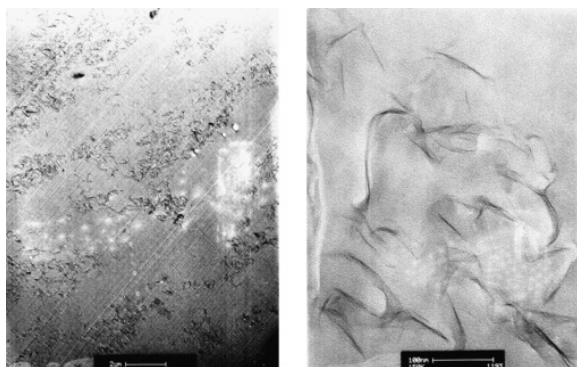


Fig. 3. [TEM image](#) at low (left) and high (right) magnification of emulsion-polymerized tropylium-polystyrene [nanocomposite](#).

3.3. Cone calorimetry

The technique of choice to evaluate the fire properties of materials is cone calorimetry. The parameters that are available from the cone include: the time to ignition, t_{ign} ; the heat release rate curve, (of particular interest is the peak of the heat release rate, PHRR); the total heat released; the specific extinction area, SEA, a measure of the amount of smoke that is emitted; and the mass loss rate, MLR. The normal observations that are made for styrene nanocomposites are the following: the time to ignition is normally lower for the nanocomposite than for the virgin polymer, i.e., the nanocomposite will ignite more easily than does the virgin polymer; the peak heat release rate is decreased by up to 60% for nanocomposites while it is essentially unchanged for microcomposites but the total heat evolved is the same; the mass loss rate is decreased and the SEA is slightly increased.

A significant reduction in PHRR is indicative of the formation of a nanocomposite but one cannot differentiate between intercalation or exfoliation; both intercalated and exfoliated nanocomposites seem to be equally effective [5], [6]. The data presented in Table 1, show that there is an insignificant reduction in PHRR for the bulk-polymerized system, in agreement with both XRD and TEM, it is an immiscible nanocomposite (microcomposite). The emulsion-polymerized sample, however, shows a more than 30% reduction in PHRR, which is large enough to validate that nanocomposite formation does occur. The plots of heat release rate, shown in Fig. 4, for polystyrene and the bulk- and emulsion-polymerized nanocomposite materials show clear differences between these materials. Additionally, the time to ignition decreases more for the bulk-polymerized material and the mass loss rate is higher.

Table 1. Cone calorimetric data for polystyrene and its bulk and emulsion polymerized nanocomposites

Composition	Pure PS (commercial)	Bulk PS with 3% clay	Emulsion PS with 3%clay
Ignition time (s)	51	29	45
PHRR (KW/m ²) (% reduction)	1400	1300 (7)	960 (32)
Average mass loss rate (g/s)	31	28	27
Average SEA (m ² /Kg)	1107	1093	1352
Total heat released (MJ/m ²)	97	88	86

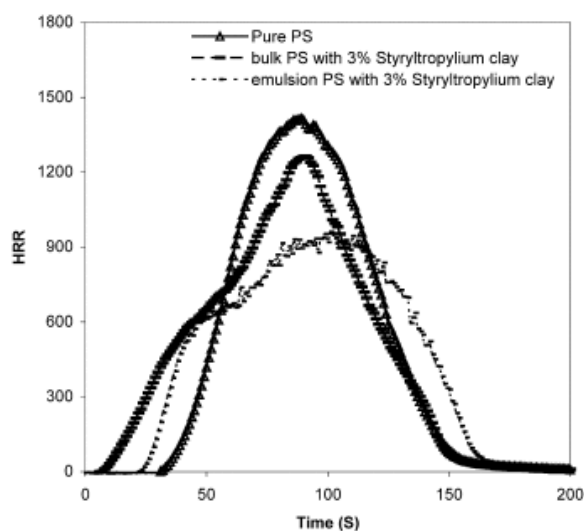


Fig. 4. Heat release rate data for polystyrene and its bulk and emulsion polymerized nanocomposites.

One of the goals of this work was to develop a clay that had higher thermal stability than the ammonium substituted organically-modified clay. Based on the ion-exchange capacity of the sodium clay, the tropylium clay

should contain 18% organic material. From the TGA curve, shown in Fig. 5 together with the curve for a commercial ammonium-substituted clay, one can see the enhanced thermal stability of the substituted tropylium cation clay; at 300 °C, 1% of the mass has been lost; at 400 °C, 2% has been lost; at 600 °C, 5% has been lost while at 800 °C, 12% has been lost.

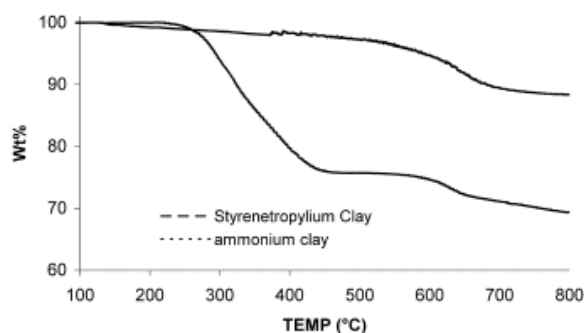


Fig. 5. TGA curves for styrenetropylium clay and an ammonium-substituted clay.

The TGA curves for both the bulk- and the emulsion-polymerized samples are shown in Fig. 6; the onset temperature of the thermal degradation, measured as the temperature at which 10% degradation occurs, increases by 15 °C for the bulk-polymerized material and by 27 °C for the emulsion-polymerized nanocomposite. As expected, the emulsion polymerized virgin polymer shows enhanced thermal stability relative to the bulk-polymerized material. The thermal stability of the emulsion-polymerized nanocomposite is clearly much higher than both the emulsion polymer and the bulk polymer or bulk nanocomposite. These values are a little higher than have been previously obtained for emulsion-polymerized polystyrene nanocomposites [15]. The increase in the onset temperature is about what has been observed previously for PS nanocomposites.

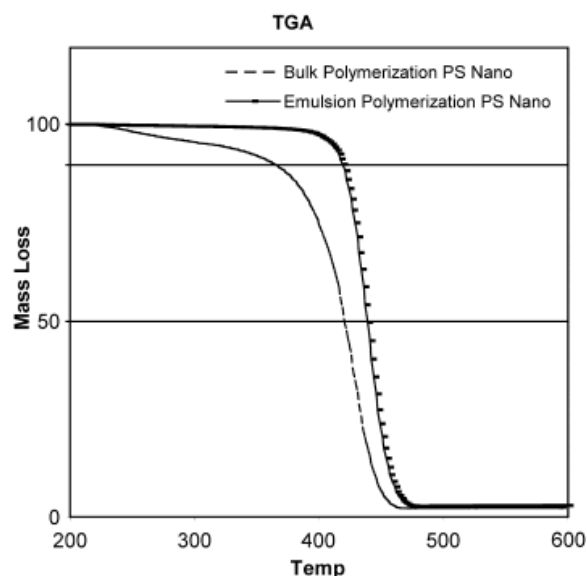


Fig. 6. TGA curves for bulk and emulsion polymerized polystyrene nanocomposites.

The effect on mechanical properties of the polymer due to the presence of the clay is always a matter of concern [2]. Young's modulus increases from 2.9 GPa in the emulsion-polymerized polystyrene to 4.2 GPa in the emulsion-polymerized nanocomposite.

4. Conclusions

For the first time, a carbocation has been ion-exchanged onto a clay and the clay used to prepare a polystyrene nanocomposite; both the clay and its nanocomposite have outstanding thermal stability. The

nanocomposite has been prepared by emulsion polymerization, and its mixed intercalated-exfoliated composition has been established by X-ray diffraction, transmission electron microscopy and cone calorimetry. It is quite possible that this new organically-modified clay may be useful for the preparation of nanocomposites of polymers which must be processed at temperatures which are above the thermal stability limit of the standard ammonium-substituted clays. Other tropylium ions, including the unsubstituted cation, are under current investigation.

Acknowledgments

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References

- [1] Y. Kojima, A. Usuki, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, O. Kamigaito. *J. Mater. Res.*, 8 (1993), pp. 1185-1189
- [2] M. Alexandre, P. Dubois. *Mater Sci Eng.*, R28 (2000), pp. 1-63
- [3] J. Zhu, A.B. Morgan, F.J. Lamelas, C.A. Wilkie. *Chem. Mater.*, 13 (2001), pp. 3774-3780
- [4] Wang D, Wilkie CA. *Polym Degrad Stab*, in press.
- [5] J.W. Gilman, T. Kashiwagi, M. Nyden, J.E.T. Brown, C.L. Jackson, S. Lomakin, E.P. Giannelis, E. Manias. S. Al-Malaika, A. Golovoy, C.A. Wilkie (Eds.), *Chemistry and technology of polymer additives*, Blackwell Scientific (1999), pp. 249-265
- [6] J.W. Gilman, T. Kashiwagi, E.P. Giannelis, E. Manias, S. Lomakin, J.D. Lichtenham, P. Jones. M. Le Bras, G. Camino, S. Bourbigot, R. Delobel (Eds.), *Fire retardancy of polymeric materials, the use of intumescence*, Royal Society of Chemistry, Cambridge (1998), pp. 203-221
- [7] C.A. 58 4339(a) 1963.
- [8] W.G. Fateley, B. Curnutte, E.R. Lippincott. *J. Chem. Phys.*, 26 (1957), pp. 1471-1481
- [9] K. Conrow. *J. Am. Chem. Soc.*, 83 (1961), pp. 2343-2350
- [10] H.J. Dauben Jr, L.R. Honnen, K.M. Harmon. *J. Org. Chem.*, 25 (1960), pp. 1442-1445
- [11] G. Manecke, E. Steudle. *Makromol Chem.*, 175 (1974), pp. 1371-1382
- [12] W. Xie, Z. Gao, W.-P. Pan, R. Vaia, D. Hunter, A. Singh. *Polym. Mater. Sci. Eng.*, 83 (2000), p. 284
- [13] Substituted tropylium ion was selected for study, rather than the more common triphenylmethyl cation, because tropylium is expected to have better thermal stability.
- [14] R. Rathore, S.V. Lindeman, J.K. Kochi. *J. Am. Chem. Soc.*, 1997 (1997), p. 119, 9393-9404
- [15] D. Wang, J. Zhu, Q. Yao, C.A. Wilkie. *Chem. Mater.*, 14 (2002), pp. 3837-3843