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Synthesis, structure, mechanical properties, and thermal stability of some polysulfone/organoclay nanocomposites

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Abstract

Polysulfone/organoclay nanocomposites were prepared via a solution dispersion technique, and were characterized by X-ray diffraction, transmission electron microscopy, stress–strain measurements in elongation, and thermogravimetric analysis. The X-ray and microscopy results demonstrated that at least at some compositions, the technique employed was successful in exfoliating and widely dispersing the clay platelets. The other measurements demonstrated considerable improvements in strength and modulus, and in thermal stability. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polysulfones; Montmorillonite; Exfoliated clays

1. Introduction

The major reason for the present interest in introducing clays into polymers at the nanoscale level is the pronounced improvements in properties one can obtain at surprisingly low clay contents. Examples of improvements are the increase in strength, modulus, thermal resistance, heat distortion temperature, and solvent resistance, and reductions in flammability. Since it is the very large surface areas attainable with these fillers that is of critical importance, the real breakthrough was in establishing the conditions for modifying the clay particles so that the layers could be separated (exfoliated), and then well dispersed into the polymeric medium. This was demonstrated by a group at the Toyota Laboratories, specifically for (i) Nylon-6 [1–8], a commercially important thermoplastic which was subsequently studied by other groups in similar experiments [9–22]. Additional work focused on several other polyamides [23–25], and eventually layered materials other than the clays were investigated.

Since work in this area has been accelerating at a considerable pace, it is useful to provide an unusually extensive list of references, in this case categorized according to the polymer being improved by the introduction of the clay and clay-like platelets. These polymers include (ii) poly(ethylene terephthalate) [26,27], poly(ε-caprolactone) [28–30], and unsaturated polyesters [31], (iii) polyurethanes [32–35], (iv) polystyrene [36–56], and styrene copolymers [57–63], (v) polypropylene [64–85], (vi) polyethylene [86–89], and polyethylene oligomers [90] or copolymers [91], (vii) poly(vinyl alcohol) [92,93], and poly(acrylamide) [94,95], (viii) poly(methyl methacrylate) [54,96–103], methyl methacrylate copolymers [104–106], and other polyacrylates [107–109], and poly(acrylic acid) [110], (ix) poly(ethylene oxide) [9,111–121], ethylene oxide copolymers [122,123], and poly(ethylene imine) [124], (x) epoxidized natural rubber [125,126], polybutadiene [127], butadiene copolymers [128–130], and poly(dimethylsiloxane) [131–136], (xi) polypyrrole [137], poly(vinyl pyrrolidone) [138,139], poly(vinyl pyrrolidinone) [140], poly(vinyl pyridine) [141], poly(vinyl pyridinium) salts [142] and poly(*N*-vinyl carbazole) [143], (xii) polyaniline [144–149], poly(*p*-phenylene vinylene) [150], and related polymers [151], (xiii) polyimides [152–165], and poly(amic acid) [166–168], (xiv) liquid-crystalline polymers [169,170], (xv) epoxy polymers [171–186], and phenolic resins [187], and (xvi) DNA [188] and met-hemoglobin [189].

There has also been a lot of interest in theory and simulations addressing the preparation and properties of these materials [13,190–202].

The present investigation is the second in a series attempting to use exfoliated clays to improve the properties of high-performance polymers, particularly those of importance in US Air Force applications. The first investigation

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focused on a rigid polymer, poly(bisphenyl ether triphenylphosphate) [170], a polymer of considerable interest because of its excellent high-temperature properties and nonflammability, features arising from the phenyl and phosphate groups, respectively, in the chain's repeat unit. The properties of this polymer were found to be significantly improved by the introduction and exfoliation of montmorillonite (MMT), using a solution dispersion technique. This particular clay has a layered structure consisting of two silica tetrahedral sheets with an edge-shared octahedral sheet of either aluminum or magnesium hydroxide. Stacking of layers of ca. 1 nm thickness mediated by a weak dipolar force leads to interlayers or galleries between the layers. The galleries are normally occupied by cations such as K^+, Na^+, Ca^{+2} or Mg^{+2}, but these were replaced in an alkylammonium ion-exchange reaction. The resulting organomodified clays were then successfully exfoliated and dispersed in the polymer, significantly improving its tensile modulus and thermal stability.

The same approach was applied here to a commercially available high-performance polymer, specifically a polysulfone. The one chosen is a clear, relatively rigid but tough polymer having a high glass-transition temperature, and has been extensively used in molded articles, particularly those requiring good electrical properties and hydrolytic stability.

2. Experimental

2.1. Materials

Pure MMT with a cation-exchange capacity [29] of 98 mequiv/100 g, and a nominal tactoid aggregate size of 40 μm was obtained from Southern Clay Products. The polysulfone (PSF) chosen was Udel P-1700 (BP Amoco), and the dodecylamine (Aldrich), dimethylacetamide (DMAc, Aldrich) and *N*-methylpyrrolidone (NMP, Aldrich) were all used as received.

2.2. Synthesis of the organoclay

Dodecylammonium exchanged clays were prepared as previously described [170]. A 500 ml quantity of 0.05 M dodecylammonium bromide in an ethanol:water (1:1) solution, and 2 g of the MMT were heated to 75°C and held there for 24 h. The exchanged clays thus prepared were repeatedly washed with the ethanol–water solution to remove Br^- ions, as evidenced by the absence of any white precipitate in the filtrate when tested with a 0.1N $AgNO_3$ solution. The product obtained was then vacuum-dried to a constant weight at ambient temperature. The resulting organoclays were ground into fine particles, and the 40 μm size fraction was collected using mechanical sieving.

2.3. Synthesis of the polysulfone/organoclay composites

PSF/organoclay composites were obtained by mixing the desired amount of the organoclay with PSF in DMAc at 80°C for 24 h. The compositions chosen corresponded to 1, 3, and 5 wt% of the modified clay. It is difficult to convert wt% into vol% for such composites, particularly for polymers which can crystallize and for clays which can affect the degrees of crystallinity (and thus the densities). Therefore, the corresponding values of the vol%, 0.78, 2.3, and 3.9, are only approximations. In any case, the resulting samples were poured into Teflon molds, and evaporation of the DMAc yielded homogeneous films.

2.4. X-ray diffraction

X-ray diffraction (XRD) patterns were obtained using an X-ray diffractometer (X'pert, Philips) equipped with Cu K_α radiation and a curved graphite crystal monochromator [170]. Diffraction data were collected at 0.01°/s steps between 0.5 and 20°, and were used to determine changes in gallery heights in the organoclay before and after polymer intercalation.

2.5. Transmission electron microscopy

This characterization was carried out to supplement the XRD measurements since it could show the relative positionings of the layers and the extent of their dispersion within the polymeric matrix.

The samples for the TEM were embedded in a capsule with a standard embedding agent polymerized at 60°C for 48 h. The resulting samples were ultrathin-sectioned using a microtome equipped with a diamond knife. The sections were 60–100 nm thick, and transmission electron micrographs were obtained on them with a Hitachi H-600 apparatus running at an acceleration voltage of 100 kV.

2.6. Mechanical properties in elongation

These samples were studied on an Instron 1122 type tensile machine with an extension rate 1 mm/min at ambient temperature [170]. Specimens for the mechanical property measurements had a dimension of $0.8 \times 10 \times 15$ mm^3, with dimensional deviations of ±0.01 mm.

2.7. Thermogravimetric analysis

TGA analyses were carried out under N_2 on a Rhometric STA 1500 thermogravimetric analyzer, using a heating rate of 10°C/min, from room temperature to 800°C.

3. Results and discussion

3.1. Structure by X-ray diffraction

The diffraction patterns of the pristine MMT, the organically modified MMT and the three polysulfone/organoclay nanocomposites are shown in Fig. 1. The primary silicate reflection at $2\theta = 4.92°$ in the organoclay corresponds to a d

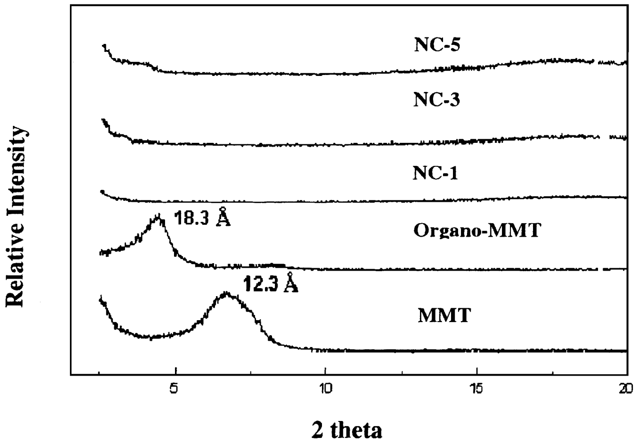

Fig. 1. XRD patterns for the montmorillonite clay itself, its organic modification, and three nanocomposites having 1, 3, and 5 wt% of the modified clay.

layer spacing of 18.3 Å which represents an increase of approximately 6 Å from the van der Waals height in the original Na^+ form of the MMT. There are no sharp reflections below $2\theta = 20°$ in the three nanocomposites, suggesting that there was some exfoliation of the organoclay in the composites.

3.2. Structure by transmission electron microscopy

Fig. 2 shows electron micrographs of ultrathin sections of the PSF-organoclay nanocomposites. The organoclay particles are clearly visible and, at least at some compositions, they were successfully exfoliated. The exfoliations seem to be largest at 1% loading and least at 5%. Specifically, there is some exfoliation into nanoscale layers which are separated by about 200 Å and dispersed rather well in the PSF matrix. As is frequently the case, the layers appear to be roughly parallel to one another [177]. Presumably, there is the usual problem of obtaining random arrangements of rigid rods or platelets above a rather small threshold concentration. There could also be a kinetic complication, specifically the relatively small entropic driving force for additional randomization not being sufficient to immediately overcome the high viscosity of the medium.

3.3. Mechanical properties

The stress–strain measurements in elongation indicated that the pure PSF had a tensile strength of 54 MPa, and a tensile modulus of 2.0 GPa. These results are compared with the corresponding results for the nanocomposites in Fig. 3 and in the first three columns of Table 1. Improvements have been seen in these two mechanical properties up to clay loadings of 3 wt%. The decreases for 5% seem consistent with the decreased exfoliation beyond the 3% loading, as mentioned above. The corresponding increases in toughness would be rather modest since there are no parallel increases in elongation to break, as shown by the values in the last column of the table.

Fig. 2. Transmission electron micrographs of the nanocomposites. The upper, middle, and lower portions correspond to 1, 3, and 5 wt% of the modified clay, respectively.

It may be useful to put these results into a much broader context, by comparing some of these mechanical property results with the corresponding results for other classes of polymers. This was done by scanning the extensive list of publications cited above and then taking rough averages of the increases in modulus at a loading of approximately 1%. Probably the weakest polymer used in clay nanocomposites is poly(dimethylsiloxane), and its modulus increased

Table 1
Mechanical properties of the polysulfone/organoclay nanocomposites

Sample	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)
NC-0[a]	54.2	2.00	48
NC-1	61.1	2.51	52
NC-3	75.8	2.65	43
NC-5	46.5	1.82	48

[a] The number in the sample designation indicates wt% organically modified montmorillonite in the nanocomposite.

approximately 100% when reinforced by the 1% clay. Poly(ethylene terephthalate) has inherently better properties, and its increase was about 75%. The present high-performance polysulfone showed an increase of approximately 25% as does Nylon-6. With increasingly improved mechanical properties (and increasing intractibility), the increases were generally 10% for typical polyimides, and only 5% for the rigid poly(bisphenyl ether triphenylphosphate) mentioned above. Perhaps, not surprisingly, the better the mechanical properties of the unfilled polymer, the more difficult it is to obtain substantial improvements in these properties.

3.4. Thermal stability

Fig. 4 shows the TGA results for the pure PSF and for the nanocomposites containing 1 and 5 wt% of the organoclay. Approximate decomposition temperatures of these three materials were 494, 498, and 513°C. There were thus significant increases in thermal stability resulting from the exfoliated clay platelets. This may be partly due to kinetic effects, with the platelets retarding diffusion of oxygen into the polymer matrix.

4. Conclusions

The conditions for exfoliating clay platelets in this polysulfone were established, and the resulting nanocomposites were found to have some improved properties. The fact that the clay platelets gave only modest improvements in the properties of this polymer may be analogous to some observations in the area of sol–gel technology [203,204]. There, the hydrolysis and condensation of an organosilicate, organotitanate, etc. are used for precipitating silica, titanates, and similar reinforcing agents into a polymer [205]. Again, improvements in mechanical properties of some high-performance polymers by these in situ particles were rather modest, specifically much less than those observed for relatively weak polymers such as poly(dimethylsiloxane) [206]. The central dogma may be that the properties of high-performance materials are so good that it is difficult to obtain further improvements, particularly simultaneous improvements in several properties. Also, the fact that such polymers are designed to be unreactive further complicates the situation with regard to getting good bonding between the reinforcing phase and the host polymeric matrix.

In any case, the present results may well encourage measurements of other properties, such as permeability, flame resistance, and resistance to solvents, and to hostile environments in general. It would be of particular interest to expand some of these materials into foams for structural applications. Having the clay platelets aligned in the struts and walls of a foam could well greatly improve its mechanical properties, such as compressive strength.

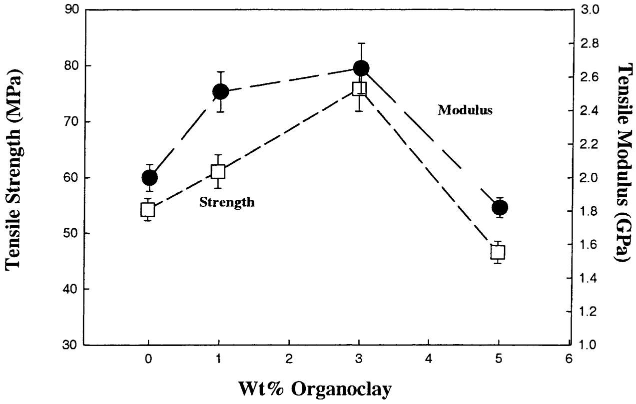

Fig. 3. Effects of modified clay content on the tensile strengths and moduli of the nanocomposites in elongation.

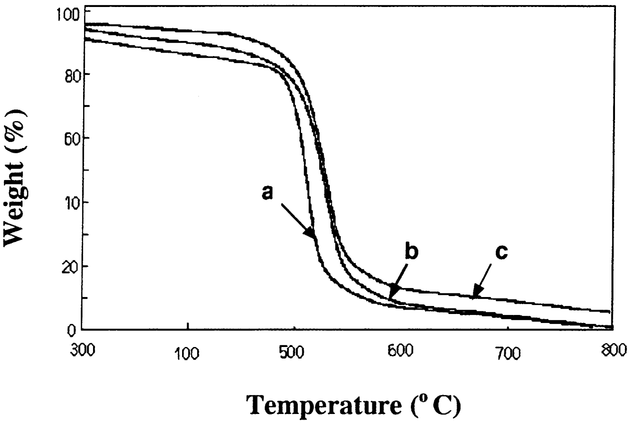

Fig. 4. Thermogravimetric results (relative weight loss as a function of temperature) for (a) pure polysulfone, (b) the 1% nanocomposite (NC-1), and (c) the 5% nanocomposite (NC-5).

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