PREPARATION AND CHARACTERIZATION OF POLYIMIDE NANOCOMPOSITES

SUMMARY OF RESEARCH

NASA Grant NAG-1-2314

June 15, 2000, to June 14, 2002

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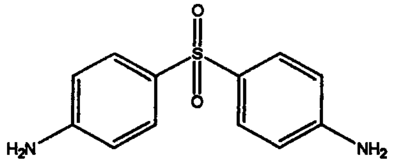
Introduction

Many properties of polymeric materials can be enhanced by dispersing small quantities of clay nanocomposites throughout the polymer. Among the enhancements are increases in modulus and resistance to erosion by atomic oxygen and reductions in thermal expansivity, gas permeability, and flammability.

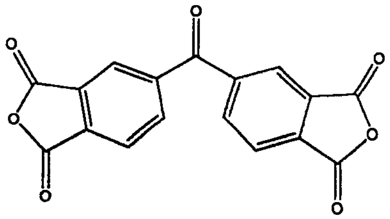
To achieve the full extent of enhancement with these polymer-clay nanocomposites, the clay nanoparticles, which have thicknesses of only one-to-several nanometers and lengths and widths of hundreds of nanometers to micrometers, must be exfoliated one from another and then individually dispersed throughout the polymer. This dispersion is achieved only after alkali metal cations (usually Na^+) that reside on the surfaces of the nanoparticles have been replaced by organocations (typically a quaternary amine cation). This renders the surface of the nanoparticle a more hospitable interface for the organic polymer matrix. Following the cation exchange, the organio clay is either mixed directly into the polymer or is dispersed in monomer which is later polymerized around the nanoparticle.

Systems with 4,4′-DDS + BTDA and 3,3′-DDS + BTDA

Several polyimides were investigated as potential matrices for clay nanocomposites. The polyamic acids formed by the reactions of benzophenonetetracarboxylic dianhydride (**BTDA**) with *p*-aminophenylsulfone (**4,4′-DDS**) and with *m*-aminophenylsulfone (**3,3′-DDS**) were prepared in 1-methyl-2-pyrrolidinone (**NMP**). Their solution viscosities were measured and are reported below. In some cases organoclay (SCPX-2003 from Southern Clay Products, montmorillonite clay modified with a quarternary ammonium salt containing a long-chain tallow group) was added to the solution.



4,4′-DDS



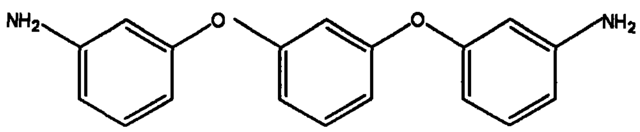
BTDA

Even tthough the viscosity data suggested low molecular weights, films were prepared from the 4,4′-DDS + BTDA and 3,3′-DDS + BTDA polyamic acid solutions by casting the solutions on plate glass and heating to 300°C. The films were not strong. Those prepared from the *meta* isomer of DDS seemed to be of slightly better quality than those from the *para*. However, neither system seemed viable enough to justify further study.

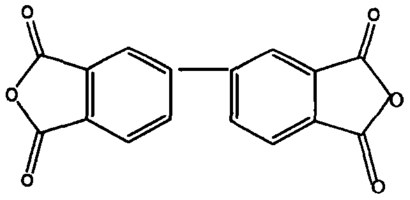
Polyamic acid	% SCPX-2003 Clay	Reaction Time (hr)	Viscosity (dL/g)
4,4′-DDS + BTDA	0	42	0.37
	0	75	0.13
	0	90	0.16
	3	< 24	0.18
	5	73	0.24
	5	96	0.26
	5	120	0.23
3,3′-DDS + BTDA	0	< 24	0.15, 0.16
	0	44	0.19

Systems with APB + BPDA

The same procedure was used to synthesize the polyamic acid and subsequently the polyimide from 1,3-bis(3-aminophenoxy)benzene (**APB**) and 3,3′,4,4′-biphenyltetracarboxylic dianhydride (**BPDA**).



APB

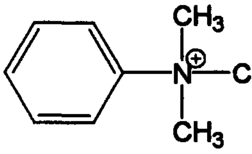


BPDA

Polyimide films were prepared from the APB + BPDA polyamic acid. Also, in some preparations SCPX-2003-clay was added to the polyamic acid at 3, 5, and 8 wt-% loadings. Clay nanocomposite films were made and tested. Only the 8% films cracked when folded. The other films (*i.e.*, neat, 3% and 5%) were judged to have high enough molecular weight and sufficient strength to be suitable for further study.

Reduced-Charge Montmorillonites

To render the clay more organophilic, the surface concentration of the replaceable cations was reduced. These cations (predominantly Na^+) serve as gegenions for negatively charged oxygens at the surface of the silicate. The Na^+ and other surface ions were replaced with Li^+ by washing the clay with 1 M. LiCl solution three times. This Li^+-saturated montmorillonite was then freeze dried, and heated to either 120, 130, or 250°C for 24 hours. In the heating, the small Li^+–unlike the larger Na^+–is able to penetrate the silicate surface and become imbedded in the silicate lattice. The result is a clay whose surface charge depends on the heat treatment, as reported by Bujdak and Komadel.[1] The fully charged montmorillonite that was not subjected to the Li^+ treatment is designated as **FCM**; whereas the reduced-charge clays are identified as **RCM-120**, **RCM-130**, and **RCM-250**.



TMPA

These Li^+ clays, *i.e.*, the reduced-charge montmorillites, were washed with 1 M. NaCl three times to restore some Na^+ ions to the silicate surface, while leaving behind those non-exchangeable Li^+ ions which had penetrated the silicate lattice. These are referred to as **RCM-120-Na**, *etc*. Some of these samples were then washed three times with trimethylphenylammonium (**TMPA**) chloride, thereby replacing Na^+ ions with TMPA ions. A quaternary amine with an aromatic substituent was selected over fully aliphatic amines because the latter do not withstand the high curing temperatures (*ca.* 300°C) required in the imidization step.[2] With organic ions partially coating their surfaces, these reduced charged organoclays, with are designated **RCM-120-TMPA**, *etc*., are expected to have more favorable interactions with the polyimide matrix in the nanocomposite.

Cation Exchange Capacity

The cation exchange capacity (**CEC**) is used as a measure of the number of exchangeable cations (alkali metal or alkaline earth ions in naturally occurring clays) which reside on the surface of the silicate sheets. For example, Southern Clay Products reports CEC = 0.93 meq/g for its cloisite clay (montmorillonite with Na^+ on its surface) alkali metal or alkaline earth ions.

The CECs of the FCM, RCM-120-Na, RCM-130-Na, and RCM-250-Na clays were obtained using atomic absorption to determine the quantity of Na^+ ions freed when they were exchanged with TMPA. The FCM-TMPA and RCM-250-TMPA clays were also subjected to elemental analyses for silicon, lithium, and organic carbon. Their CECs were determined from the

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[1] Bujdak, J., and Komadel, P., *J. Phys. Chem.*, **101**, 9065 (1997).

[2] Delozier, D. M., Orwoll, R. A., Cahoon, J. F., Johnston, N. J., Smith, J. G., Jr., and Connell, J. W., *Polymer*, **43**, 813 (2002).

elemental ratios of silicon to organic carbon. The results, found in Table II, show a decreasing surface coverage as the processing temperature of the Li^+-clay was increased.

Table II. Cation exchange capacities comparing the fully charged and reduced-charge clays; CECs were measured with two different techniques.

	Cation Exchange Capacities (meq/g)	
Clay	**Atomic Absorption**	**Elemental Analysis**
FCM-TMPA	0.72	0.78
RCM-120-TMPA	0.54	–
RCM-130-TMPA	0.65	--
RCM-250-TMPA	0.24	0.35

X-Ray Diffraction Analysis

The RCM-250-TMPA was compared with RCM-250-Na in X-ray (Cu-K_α radiation) diffraction (XRD) studies. As shown in Fig 1, the measurements give evidence that the TMPA

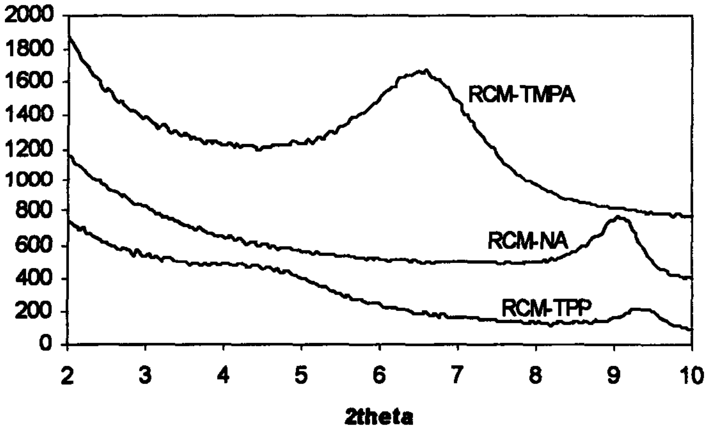

Figure 1. XRD Patterns of RCM-NA, RCM-TMPA, and RCM-TPP

cation successfully expanded the collapsed clay layers that had been treated at 250°C. Similarly, Bujdak *et al.*[3] found that montmorillonite, which had undergone charge reduction at 210°C, exhibited an x-ray peak at $2\theta = 9\text{-}10°$. They attributed the peak to collapsed layers. The RCM-250-Na exhibits a peak in the same location; however, after being washed with TMPA, the clay (RCM-250-TMPA) exhibited a peak at $2\theta = 6.5$. This shift suggests that TMPA re-expanded at least of the some of the collapsed interlayers, although the breadth of the peak suggests that a mixture of collapsed and expanded layers may exist.

Also shown in Figure 1 is the XRD pattern for RCM-250 that had been exchanged with tetraphenyl phosphonium (**TPP**) ions. The RCM-250-TPP diffraction pattern shows two peaks, one consistent with collapsed layers as seen in the RCM-250-Na and another peak at $2\theta \approx 4.7°$, consistent with the placement of TPP in the interlayer, suggesting that TPP only minimally expanded collapsed layers in the clay.

Fig. 2 shows XRD data for RCM-250-Na by itself and a polyimide film synthesized from 4,4′-oxydianiline (**ODA**) and BTDA with 3 wt-% loading of RCM-250-Na. The shift in the peak to lower 2θ suggests that the ODA-BTDA system either expands collapsed interlayers or intercalates the clay, possibly for the same reasons that TMPA appears to expand collapsed interlayers.

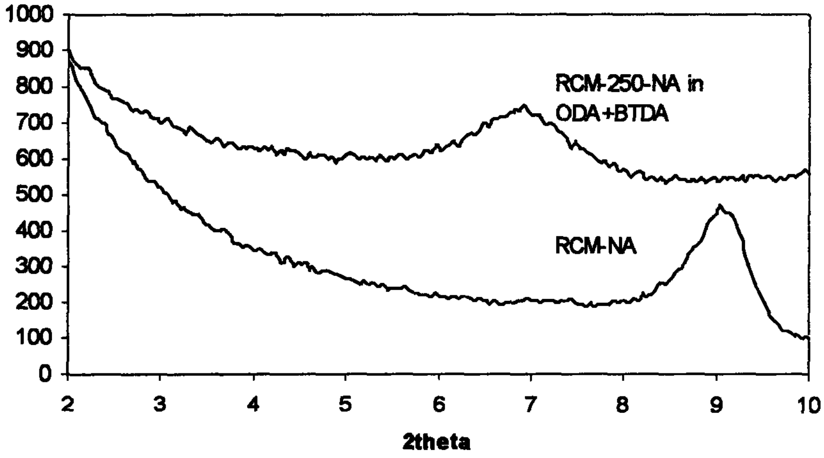

Figure 2. XRD for RCM-250-NA and 3% RCM-250-NA in ODA+BTDA

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[3] Bujdak, J., Hackett, E., Giannelis, E., *Chem. Mat.*, **12**, 2168 (2000).

Thermal-Gravimetric Analyses

Fig 3 shows the thermal-gravimetric analysis (TGA) of various modified clays. All clays withstood 400°C and up in both air and nitrogen, a sufficient temperature for the completion of a polyimide cure cycle at 300°C without significant degradation of the clay.

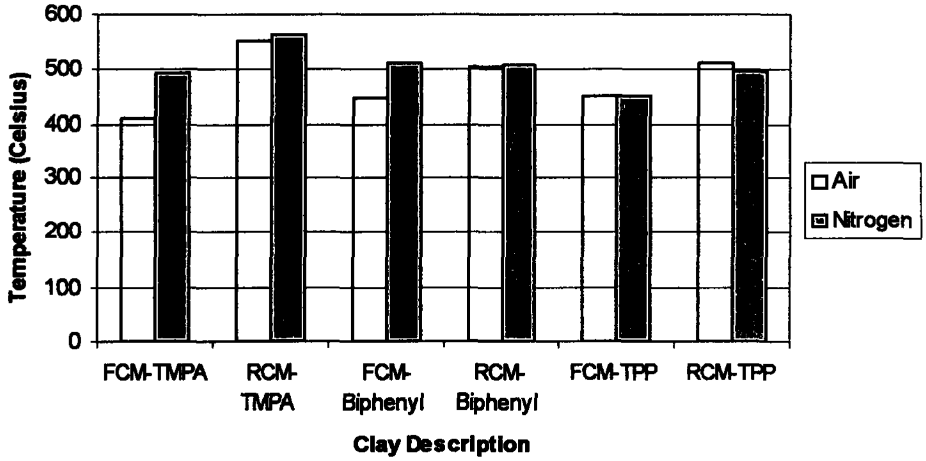

Figure 3. Temperatures for 5% weight loss of various RCM-250, organically modified montmorillonites

Tensile Moduli

Figs 4 and 5 show the tensile moduli of various FCM and RCM-250 organoclays at 3 wt-% loadings in both the ODA+BTDA and APB+BPDA polymer systems with each bar based on

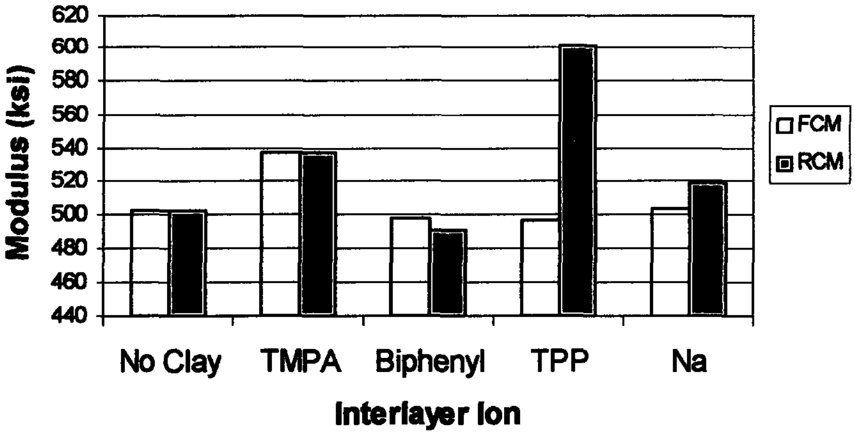

Figure 4. Modulus for various interlayer ions in 3% FCM and RCM-250 ODA+BTDA Polymer Films

five runs from one film. In addition to the TMPA, TPP, and Na^+ ions, the trimethylbiphenyl ammonioum ion (**biphenyl**) was included in these measurements. A significant difference in modulus between FCM and RCM-250 materials was observed only in ODA+BTDA TPP clays and APB+BPDA biphenyl clays. Why these particular ions interacted better with the particular polymer system is yet to be understood.

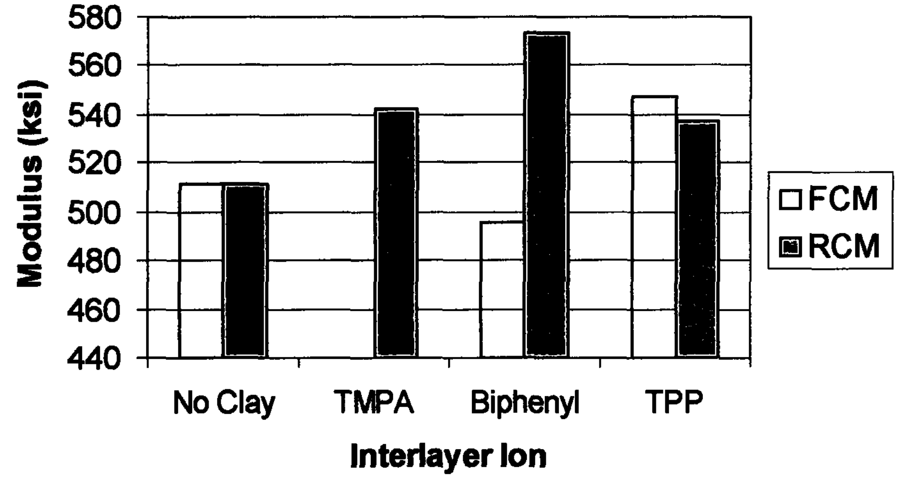

Figure 5. Modulus for various interlayer ions in 3% FCM and RCM-250 APB+BPDA Polymer Films