Small strain mechanical properties of latex-based acrylic nanocomposite films

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ABSTRACT

A waterborne latex-based technique has been used to prepare acrylic films with laponite contents up to about 25 vol%. The laponite was attached to the surfaces of the latex particles, giving a cellular arrangement of laponite-rich regions at high laponite contents. Two regimes of reinforcement were observed, depending on whether T was above or below T_g, reinforcement at $T > T_g$ being significantly greater than predicted by micromechanical models. Modulated differential scanning calorimetry and dynamic mechanical analysis showed part of the organic content of the films not to contribute to the glass transition. This "rigid amorphous fraction" (RAF) was argued to correspond to intercalated regions of the matrix. However, the RAF alone was insufficient to account for the observed increases in stiffness at $T > T_g$. The mechanical response is therefore discussed in terms of a four-phase model, in which intercalated laponite stacks are embedded in a matrix with reduced mobility, forming a foam-like structure, in turn embedded in a matrix with the properties of the bulk polymer.

1. Introduction

There has been enormous interest in clay-based polymer nanocomposites since the discovery of significant mechanical and other property improvements in polyamides containing relatively low concentrations of exfoliated montmorillonite clay platelets [1]. Considerable effort has consequently been devoted to the synthesis and characterization of a wide variety of such materials [2–6]. Classical micromechanical models for particle reinforcement suggest the very high aspect ratios of the clay platelets to play an important role in increasing the tensile modulus with respect to that provided by equivalent volume fractions of equiaxed particles, particularly if the platelets are aligned with the tensile axis [7,8]. On the other hand, given the reduced absolute dimensions of the platelets (thicknesses of the order of 1 nm), and hence their relatively high surface area per unit volume, changes in the local physical response of the matrix associated with the platelet–matrix interface may also have a significant effect on global properties [9–13]. The reinforcement is therefore often considered to result from the immobilization of polymer chains at the platelet surfaces, either through chemical interactions with surface modified clays or entanglement with a surface modifier [14,15].

Experimental evidence for the existence of regions of immobilized matrix in polymer nanocomposites has been provided by nuclear magnetic resonance (NMR) [16–18], dynamic mechanical analysis (DMA) [19,20], and differential scanning calorimetry (DSC) [21–24]. In each case, the thickness of the layer of immobilized matrix at the filler particle surfaces is estimated to be between 1 and 5 nm.

The presence of clay platelets also generally results in large increases in melt viscosity, and a need to maintain melt processability may therefore limit clay contents when the degree of exfoliation is high [25]. Emulsion polymerization has been used in the past as an alternative to melt processing for the preparation of clay polymer nanocomposite latexes [26], but the clay contents investigated have tended to be relatively low [27–29]. However, film formation from latexes (coatings, paints etc.) depends primarily on the carrier fluid, the solids content of the latex and the presence of processing additives. Therefore, if latex particles with high clay contents can be prepared during the synthetic step, the associated increases in melt viscosity do not necessarily prevent film formation, although they may modify the conditions required for the preparation of homogeneous crack-free films. It has thus been shown to be possible to prepare films from nanocomposite latexes containing up to at least 50 wt% of laponite clay (about 25 vol%), i.e. loading levels comparable with those obtained by layer by layer deposition [30]. Rather than encapsulate the laponite within the latex particles, which remains technically difficult for high aspect

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ratio fillers [31,32], it is attached to the latex particle surfaces to give an "armored" morphology [33–36]. Provided that the latex particles are sufficiently small, and the laponite is initially well dispersed, a high degree of dispersion is maintained on film formation, even at relatively high clay volume fractions [33,37].

Our previous investigations have focused on the morphology and low strain mechanical properties of dried, consolidated films with a range of laponite contents prepared from model polystyrene (PS)/laponite latexes [33,37], whose armored morphology leads to a characteristic cellular arrangement of laponite-rich regions at laponite contents above about 10 wt%. A significant proportion of the organic matrix, referred to as the "rigid amorphous fraction" (RAF), is found not to contribute to the main glass transition in these films. However, the RAF is argued to be associated primarily with intercalation into stacks of individual laponite platelets, and is insufficient to account for the outstanding stiffness reinforcement observed at $T > T_g$. A model incorporating the cellular structure and the existence of additional regions of partly immobilized polymer has therefore been proposed to account for the behavior of these materials [33,37]. The aim of the present work is to establish the generality of the results obtained for the PS/laponite latexes by investigating a series of low T_g acrylic copolymer/laponite latexes, whose characteristics in the absence of laponite are closer to those of latexes currently used in practical coatings applications.

2. Experimental

To prepare the latexes, the required quantity of laponite (Laponite RD (Rockwood Additives)) was dispersed in water with a peptizing agent (sodium pyrophosphate (Aldrich), 10% by weight of laponite) and a surfactant (sodium dodecyl sulfate (SDS) (Acros Organics), 1% by weight of the final monomer content of all the latexes) and stirred for 2 h 5% macromonomer (poly(ethylene oxide) 1000 monomethyl ether methacrylate (Polysciences)) by weight of laponite was then added in order to render the laponite surface compatible with the acrylic copolymer matrix and promote attachment of the laponite to the polymer particles [26]. The functionalized laponite suspension was poured into a reactor and stirred under a nitrogen atmosphere. After degassing in nitrogen, the monomer (200 g/L, a 1:1 mixture by weight of methyl methacrylate (MA) and butyl acrylate (BA) (Aldrich)) and the initiator (2,2′ azobis(cyanopentanoic acid) (Wako Chemicals), 0.5% with respect to the monomer) were added to the suspension, and emulsion polymerization left to proceed at 70 °C for 4 h. The characteristics of the latexes obtained in this way are summarized in Table 1. When referring to the latexes in what follows, the laponite contents determined experimentally by ash tests will be used, which may differ significantly from the nominal laponite contents of the films, also given in Table 1. The particle diameters

were determined by transmission electron microscopy (TEM) to be approximately 80 nm in all cases. The latexes were diluted with distilled water in the presence of a negative stain (2 wt% phosphotungstic acid, PTA). The resulting suspensions were then spin coated onto carbon coated copper grids (1400 rps for 180 s) and observed with a Philips CM10 TEM operated at 80 kV. Dynamic light scattering (DLS) measurements were made using an LS 230 Coulter analyzer, after diluting the latexes 100-fold with distilled water. The relatively large particle sizes obtained by DLS for the latexes containing laponite were therefore attributed to particle agglomeration subsequent to polymerization.

The distribution of the laponite platelets in the latex dispersions was studied by embedding the latex in a water soluble melamine-based resin (Nanoplast FB 101 kit, Polysciences Inc.) in the ratio 2 parts of resin to 1 part of latex by weight, following the standard protocol provided by the supplier. The resulting solid blocks were then sectioned with an ultramicrotome (Reichert-Jung Ultracut E) equipped with a diamond knife (Diatome), and observed using a Philips CM20 TEM at 200 kV.

Consolidated acrylic/laponite nanocomposite films were prepared from the latexes by drying and sintering the resulting powder for 20 min at 100 °C under an applied compressive load ranging from 3 to 50 kN (Fontijne Holland Press), depending on the laponite content, to give optically transparent films of about 0.3 mm in thickness. The film morphologies were investigated by TEM (Philips CM10 at 80 kV) of microtomed sections prepared at room temperature, and by wide angle X-ray scattering (WAXS), using a Siemens Kristalloflex 805 diffractometer (Cu K$_\alpha$, λ = 1.54 Å). For dynamic mechanical analysis (DMA) (TA instruments Q800), rectangular specimens of dimensions 10 × 20 × 0.3 mm^3 cut from the consolidated films were scanned from $-50-150$ °C at 5 K/min and a measurement frequency of 1 Hz. 10 independent measurements were made for each material. Modulated differential scanning calorimetry (MDSC) (TA instruments Q100, calibrated with sapphire and indium standards) was used to measure the glass transition temperature, T_g, and the reversing heat capacity, C_p, as a function of T (5 mg/heating scans at 3 K/min and a modulation signal of ± 0.5 K with a period of 100 s).

Table 1
Characteristics of the acrylic/laponite latexes.

Initial (nominal) laponite content with respect to the monomer[a] [vol%]	Measured laponite content from ashing of the films [vol%]	Particle diameter from DLS [nm]	SDS content [gL⁻¹]	Solids content [%]	Conversion [%]
0	0	83	2	16.2	99
4.6	4.3	1200	2	16.6	89
9.8	10.3	1100	2	19.4	97
15.7	13.2	1400	2	20.4	98
30.3	23.2	1100	2	20.2	100

[a] Determined from the laponite weight percentage assuming a laponite density of 2.53 g cm⁻³ [38].
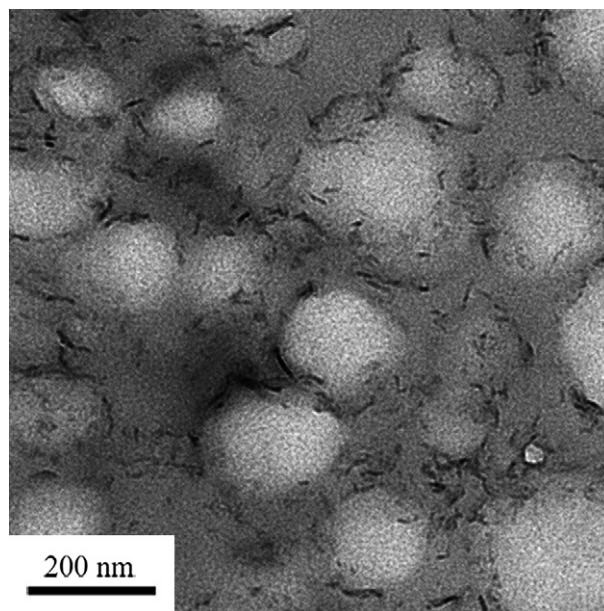
Fig. 1. TEM micrograph of an acrylic/4.3 vol% laponite latex embedded in melamine resin and sectioned at room temperature.