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## Macromolecular Nanotechnology

## Highly filled polystyrene–laponite nanocomposites prepared by emulsion polymerization

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## ABSTRACT

Polystyrene-based nanocomposite films containing up to 20 wt% laponite clay have been prepared by emulsion polymerization. Significant increases in the storage and tensile moduli were observed in both the glassy and rubbery state on laponite addition. However, whereas in the glassy state these increases were correlated with the extent of exfoliation of the laponite, in the rubbery state they were more dependent on the overall laponite content. These results are discussed in terms of the observed morphologies and micromechanical models for the reinforcing effect of rigid nano-sized filler particles.

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## 1. Introduction

Remarkable mechanical property improvements have been reported in polymer nanocomposites, but the effect of filler size and the role of the high specific interfacial area associated with nanofillers remain unclear [1–4]. In polymer/clay nanocomposites, maximum reinforcement is generally obtained with exfoliated rather than intercalated structures [5,6]. Stiffness reinforcement is already apparent at low clay contents [7–9], so that further increases in concentration might be expected to lead to even more marked effects [2,10–13]. However, clay contents are typically limited to 5–10 wt% [13–15] owing to difficulties in obtaining adequate dispersions and/or the high melt viscosity of the nanocomposites and their precursors [16]. Polystyrene (PS)/clay nanocomposites have been prepared by melt blending [12,17–20], bulk *in situ* polymerization

[9,21–23] and emulsion polymerization [14,24–26]. In this work, PS/synthetic laponite clay nanocomposites were obtained by an improved emulsion process, in which the interactions between the laponite and the PS are reinforced by modifying the laponite surface with a macromonomer. Such use of coupling agents has been described previously for a range of materials and preparation techniques [27–29]. Here, the styrene radicals react with the functionalized laponite as shown previously for polymer/silica nanocomposites [26,30,31]. This leads to a colloidal dispersion of PS particles with laponite platelets attached to their surfaces, which may be used to prepare PS films with laponite contents of up to at least 20 wt%. The morphology of these films and the effect of the laponite on their stiffness and strength are discussed in the light of micromechanical models and fractography.

## 2. Experimental section

The characteristics of the emulsions are given in Table 1. The laponite (Laponite RD, Rockwood Additives Ltd. UK)

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**Table 1**

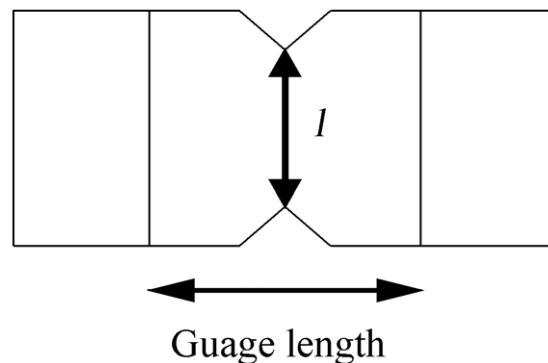
Formulations and characteristics of the emulsions.

Latex	Laponite content (g/L)	SDS content (g/L)	Laponite/monomer (wt%)	Solids content (%)	Conversion (%)	$D_p$ (nm)
L0	0	2	0	16.6	97.8	82
L5	10	2	5	17.5	99.2	86
L10	20	2	10	17.5	94.1	78
L20	40	2	20	18.1	89.1	72

was dispersed in water with a peptizing agent (sodium pyrophosphate, Aldrich, 10% by weight of laponite) and a surfactant (sodium dodecyl sulphate (SDS), Acros Organics) and stirred for 1–2 h. 5% macromonomer (poly(ethylene oxide) 1000 monomethyl ether methacrylate, Polysciences) by weight of laponite was added to promote attachment of the laponite to the PS [26,30,31]. The functionalized laponite suspension was introduced to a reactor and stirred under  $N_2$ . After degassing, styrene (Aldrich, 300 g/L) and the initiator (2,2' azobis(cyanopentanoic acid), Wako Chemicals, 0.5% with respect to the monomer) were added to the suspension and polymerization allowed to proceed at 70 °C for 4 h. Latexes containing 0 wt% laponite (L0), and approximately 5 wt% laponite (L5), 10 wt% laponite (L10) and 20 wt% laponite (L20) with respect to the PS were prepared in this way. The particle diameters ( $D_p$ ) from dynamic light scattering (DLS) are given in Table 1. Solid films were obtained by compression molding the dried latexes (Fontijne Holland Press) at 160 °C to give transparent films of 0.3 mm in thickness. The weight average PS molar mass,  $M_w$ , was determined by gel permeation chromatography (GPC) to be  $1.2 \times 10^6$  g/mol. The polydispersity was 3.23.

To evaluate PS particle size distributions by scanning electron microscopy (SEM, Philips XL30), the latexes were spin coated onto a steel substrate at 1460 rev/min for 180 s and then carbon coated. The distribution of the laponite in the latexes was investigated by transmission electron microscopy (TEM, Philips CM20), by either (i) spin coating the diluted latex (20 times in water) onto carbon covered copper grids or (ii) embedding the latex in a water soluble resin (Nanoplast FB 101 kit, Polysciences Inc., ratio 2 parts of resin to 1 part of latex by weight, following the supplier's protocol); the resulting solid blocks were then sectioned with an ultramicrotome (Reichert-Jung Ultracut E) equipped with a diamond knife (Diatome). The size distribution of the as-received laponite particles was determined by TEM of a 0.1 wt% aqueous suspension deposited on a carbon covered copper TEM grid and stained with ammonium molybdate and bacitracine. The film morphologies were investigated by TEM of microtomed sections and X-ray diffraction (XRD) (Siemens Kristalloflex 805, Cu  $K_\alpha$ ,  $\lambda = 1.54$  Å).

Dynamic mechanical analysis (DMA, TA instruments Q100) temperature scans were made on  $10 \times 20 \times 0.3$  mm<sup>3</sup> rectangular specimens cut from the films (10 K/min, 1 Hz). Differential scanning calorimetry (DSC, TA instruments Q100) was used to measure the glass transition temperature,  $T_g$  (5 mg, 15 K/min). Tensile tests were carried out at room temperature on double edge-notched tensile (DENT) specimens cut from the films as shown in Fig. 1, using a miniature tensile test machine (Minimat, Polymer Labs) at a speed of 0.1 mm/min. The ligament



**Fig. 1.** Double edge-notched tensile (DENT) specimen geometry used for the tensile tests.

length,  $l$  (see Fig. 1) was varied from 2 to 5 mm following the essential work of fracture (EWF)-based protocol for the study of thin film fracture properties [32].

### 3. Results

The mean PS particle diameter was determined by SEM to be  $80 \pm 30$  nm for all the latexes, consistent with the DLS results (Table 1). The form of the as-received laponite platelets was irregular, and a mean effective particle diameter of 54 nm was therefore defined from measurements of the mean minimum and maximum lateral dimensions of 80 individual particles determined by TEM. Figs. 2 and 3 show TEM images of latexes L10 and L20 obtained using the embedding technique, and of the dried latexes (L0, L10 and L20), respectively. Although laponite platelets were occasionally encountered in the aqueous phase of the latex, they showed the expected strong tendency to adhere to the surface of the PS particles.

Given that the laponite platelets are extensively bound to the polymer particle surfaces, they are expected to remain at, or close to the original inter-particle boundaries during the compaction step, implying a cellular arrangement of the laponite particles to persist in the absence of extensive matrix flow. Fig. 4 shows TEM images of sections from pressed films prepared from latexes L5, L10 and L20. The dispersion of the laponite in the PS matrix was relatively uniform at the scale of these micrographs. However, as shown in Fig. 4(d–f), the laponite was only partially exfoliated, even at the lowest concentrations (L5). This was confirmed by XRD, all the nanocomposite films showing a diffraction peak at  $2\theta$  of approximately  $6^\circ$ , i.e. a layer spacing,  $d_{001}$ , of about 1.48 nm, which compares with about 1 nm for the unmodified laponite, and 1.32 nm for

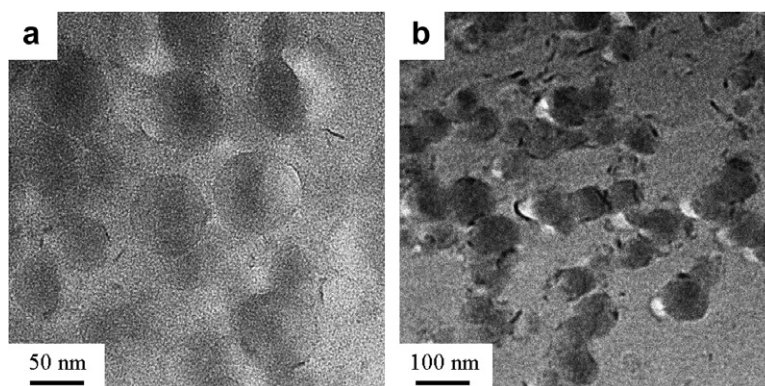


Fig. 2. TEM images of thin sections of (a) L10 and (b) L20 latexes embedded in melamine resin. Laponite particles are indicated by the arrows.

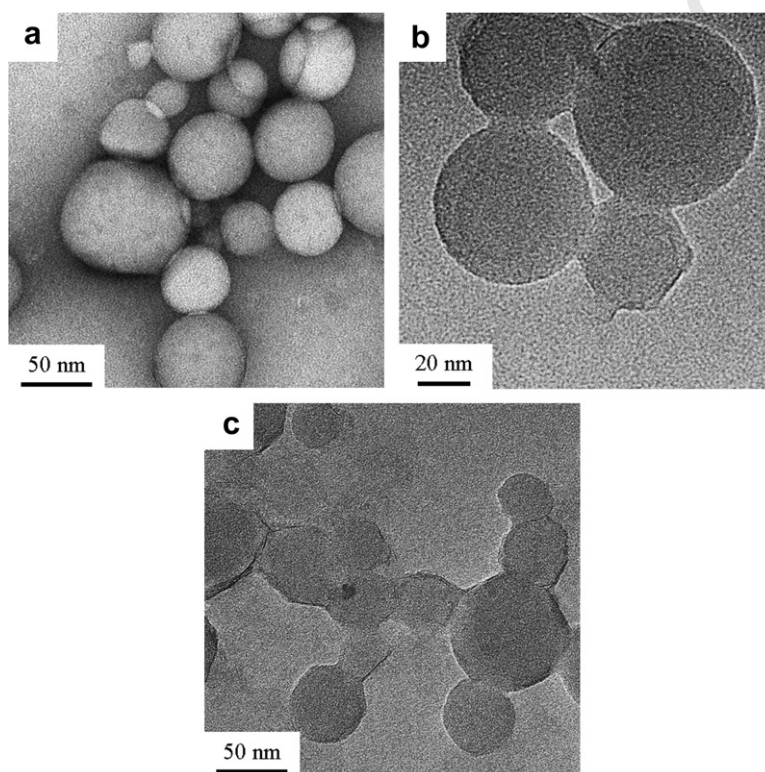


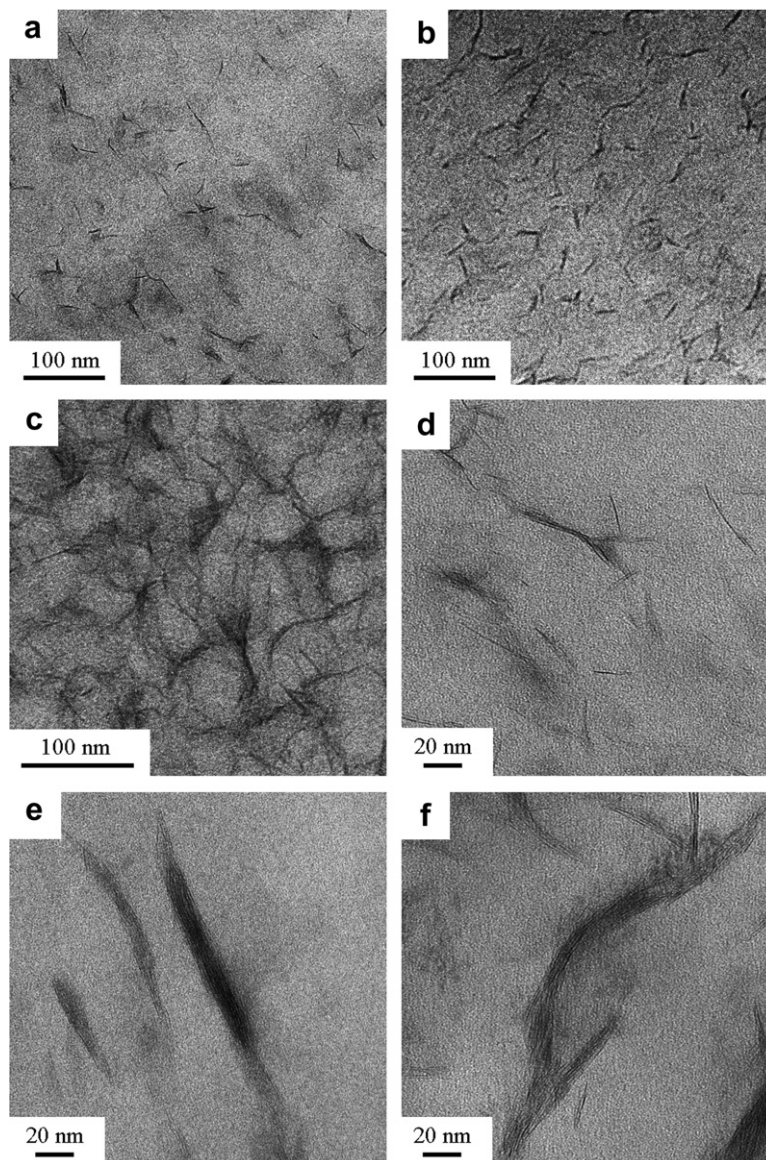
Fig. 3. TEM images of latexes deposited on carbon films by spin coating: (a) L0; (b) L10; (c), L20.

160 the laponite treated with the macromonomer, regardless of  
 161 the surfactant and laponite concentration, suggesting sig-  
 162 nificant intercalation by the PS. The lower magnification  
 163 TEM images confirmed the cellular arrangement of the lap-  
 164 onite particles in L10 and L20 (Fig. 4(b-c)), with a cell size  
 165 corresponding closely to the original latex particle  
 166 diameter.

167 As shown in Fig. 5, changes in the storage modulus,  $E'$ ,  
 168 were observed in both the glassy and rubbery states on  
 169 laponite addition, along with small shifts in  $T_g$ , the temper-  
 170 ature corresponding to the peak in  $\tan \delta$  associated with  
 171 the  $\alpha$  transition (Table 2). However, although  $E'$  increased

strongly and monotonically with laponite content in the  
 rubbery state, the films containing 5 wt% laponite (L5)  
 showed higher  $E'$  in the glassy state than both the unmod-  
 ified latex (L0) and films containing higher laponite con-  
 centrations (L10 and L20). Moreover,  $T_g$  also showed the  
 largest increase in the films prepared from L5. Consistent  
 results were obtained by DSC, with the largest increase in  
 $T_g$  again being observed in the films prepared from L5  
 (Table 2).

Typical stress (force normalized with respect to the lig-  
 ament cross-sectional area) displacement curves from  
 DENT specimens with a ligament length of 3 mm are



**Fig. 4.** TEM micrographs of thin sections from consolidated films prepared from (a) L5; (b) L10 and (c) L20. (d–f) show higher magnification images of the films in (a–c), respectively.

shown in Fig. 6. Failure was brittle in all cases, and full section yielding was not observed prior to crack onset, invalidating the EWF approach. Moreover, the scatter in the data made it impossible to identify any systematic dependence of the effective tensile strength, defined as the maximum force divided by the ligament cross-sectional area, on  $l$  and hence, for the purposes of comparison, results are given in Table 3 for the mean tensile strength for all  $l$ , the mean elongation at break (maximum total specimen strain) and the apparent stiffness (initial slope of the force normalized with respect to the ligament cross-sectional area vs. the total specimen strain). According to these definitions, films containing 10 and 20 wt% laponite (L10 and L20) showed reduced tensile strength and elongation at break compared with the unmodified films (L0), although

their apparent stiffness increased. On the other hand, films containing 5 wt% laponite (L5) showed not only the highest stiffness, consistent with the DMA results, but also the highest tensile strength.

#### 4. Discussion

Increases in stiffness on clay addition to styrenic polymers obtained using the synthetic techniques referred to in the introduction, with different types of clay and clay modification, have been widely reported [14,18,19,21,22,–24,25]. Relatively small increases in  $E'$  in the glassy state in the presence of the clay coupled with very large increases in the rubbery state are also reported in many of

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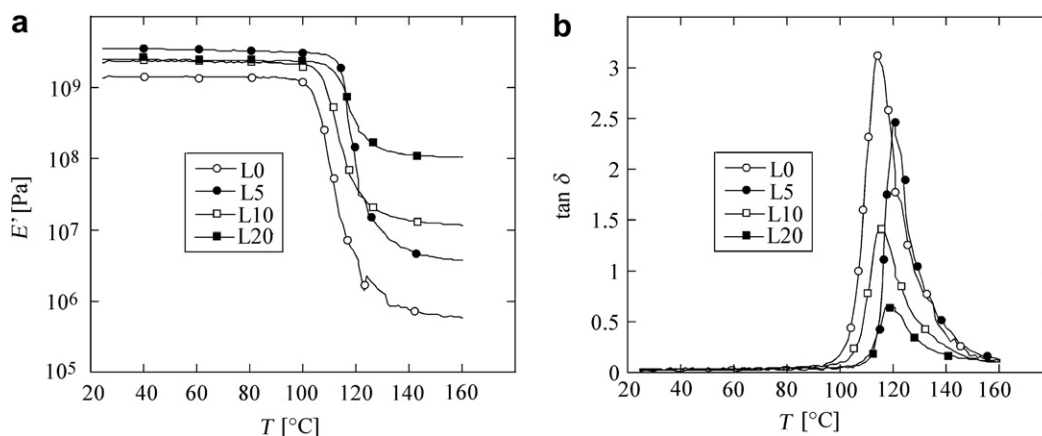


Fig. 5. (a)  $E'$  and (b)  $\tan \delta$  in consolidated films prepared from L0, L5, L10 and L20.

Table 2

$E'$  in the glassy and rubbery state (160 °C) and transition temperatures for the consolidated films.

Latex	$E'$ (glassy state) (GPa)	$E'$ (rubbery state) (MPa)	$T_x$ (°C)	$T_g$ (°C)
L0	1.4	0.8	116	103
L5	3.4	3.1	121	114
L10	1.9	10.2	118	106
L20	2.0	102	119	111

Table 3

Tensile properties of DENT specimens from the consolidated films.

Latex	Tensile strength (MPa)	Elongation at break (%)	Nominal stiffness (GPa)
L0	26 ± 7	2.54 ± 0.73	1.49 ± 0.42
L5	42 ± 13	1.21 ± 0.46	3.55 ± 1
L10	16 ± 8	0.83 ± 0.32	2.02 ± 0.60
L20	12 ± 5	0.68 ± 0.23	1.98 ± 0.62

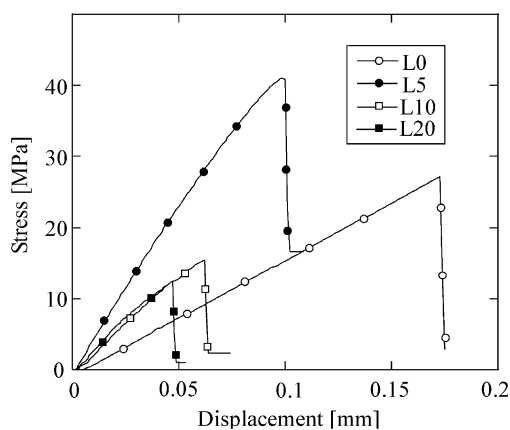


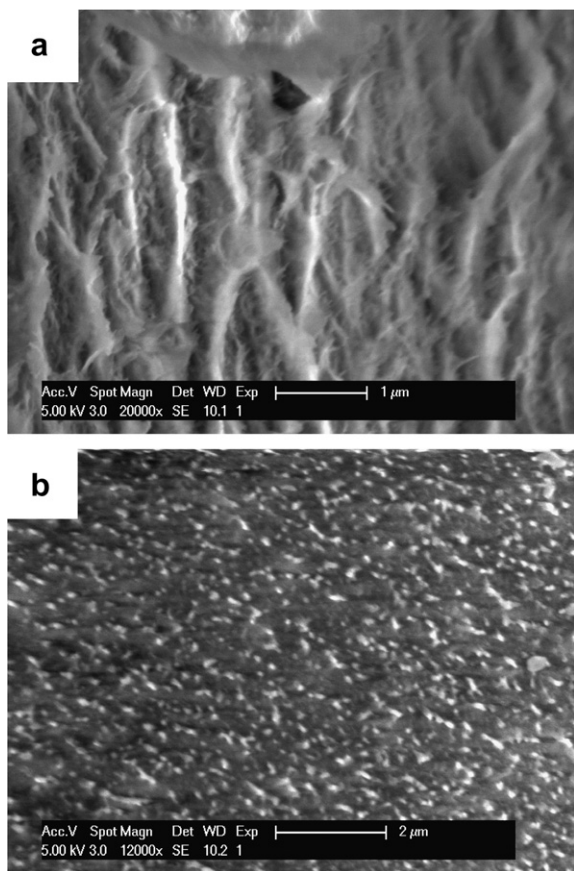
Fig. 6. Stress–displacement curves from tensile tests on DENT specimens from consolidated films prepared from L0, L5, L10 and L20 with a ligament length of 3 mm.

215 these systems [18,19,21,25]. This general trend towards increased stiffness has been explained in terms of both classical mechanical reinforcement by the relatively rigid clay platelets, and restricted mobility in the polymer matrix, often associated with an interphase at the clay platelet surfaces and/or to chain confinement effect in the interlayer galleries of intercalated clay stacks [14,15]. However, quantitative explanations for the very different degrees of reinforcement in the glassy and rubbery states are generally lacking.

The relationship between the clay content and  $T_g$  also remains unclear. In general, the higher the clay concentration, the higher  $T_g$ , [14,21,24,33] but decreases in  $T_g$  have also been reported, which may result from a plasticizing effect, e.g. due to the presence of surfactants in the modified clays or reduced matrix molar masses [22,25,34]. In the present case, the effective surfactant content was constant throughout (see Table 1) and the molar masses were high, consistent with the observed increases in  $T_g$  with laponite content, which were therefore assumed to be essentially due to restricted mobility near the transition.

The observed storage moduli obtained from DMA were compared with values calculated using the Halpin–Tsai and Mori–Tanaka models and estimates of the morphological parameters associated with the laponite particles. Rather than consider single laponite platelets as the reinforcing elements, which is unrealistic in view of the TEM and XRD observations, the mean dimensions and aspect ratios (diameter/thickness) of the laponite aggregates were estimated from TEM micrographs for each type of composite film comprising images of 120 aggregates, assuming these to represent diametral sections. Mean aspect ratios of 21.77, 6.45 and 5.46 were determined in this way for L5, L10 and L20, respectively. A mean aggregate volume,  $V_{\text{aggr}}$ , and the volume of polymer matrix per aggregate,  $V_{\text{pol}}$ , were also estimated as described elsewhere [35]. The aggregate volume fraction was determined from

$$\phi = \frac{V_{\text{aggr}}}{V_{\text{aggr}} + V_{\text{pol}}} \quad (1)$$



**Fig. 7.** SEM micrographs of the fracture surfaces from DENT specimens of (a) a consolidated film prepared from L0 and (b) a consolidated film prepared from L20.

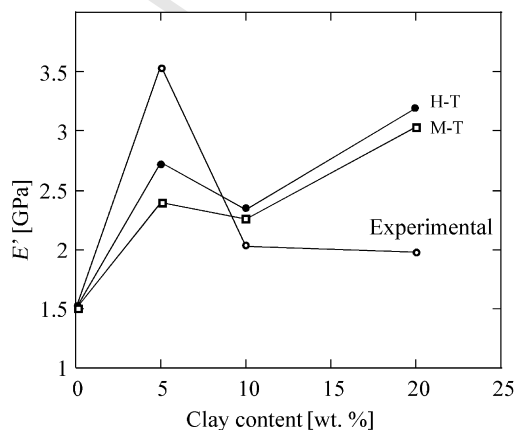
The modulus of the laponite aggregates was calculated following Sheng et al. [36] assuming the properties of the polymer in the interlayer galleries to be isotropic and identical to those of the matrix. The Young's modulus of the laponite,  $E_f$ , was taken to be 178 GPa and the Poisson's ratios of the laponite and the polymer were 0.15 and 0.33, respectively [37–39]. The Halpin–Tsai equations

$$E_1 = E_m \left( \frac{1 + \zeta \eta \phi}{1 - \eta \phi} \right), \quad \text{with } \zeta = 2\alpha, \quad \text{and } \eta = \left( \frac{E_f}{E_m} - 1 \right) / \left( \frac{E_f}{E_m} + \zeta \right) \quad (2)$$

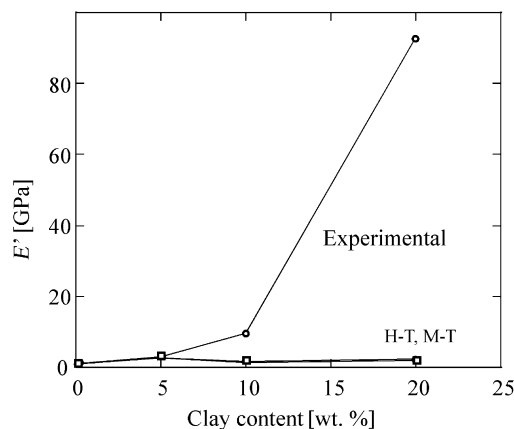
where  $E_m$  is the matrix modulus, were then used to evaluate the elastic modulus of the nanocomposites as follows: Eq. (2) gives the in-plane aggregate modulus,  $E_1$ , and the out-of-plane modulus,  $E_3$ , may be obtained by substituting  $\zeta = 2$  in Eq. (2). Assuming an isotropic orientation distribution for the aggregates, the overall modulus  $E$  is then estimated to be  $0.49E_1 + 0.51E_3$  [40]. The Mori–Tanaka model was applied using the simplified Hui–Shia formulation [41], assuming the same aggregate aspect ratio and composition as for the previous calculations. The resulting predictions for  $E$  in the glassy state are shown in Fig. 8, indicating order of magnitude agreement with the data

in this regime. Moreover, the model calculations reproduced qualitatively the peak in modulus at 5 wt% laponite, which was ascribed to the relatively high degree of exfoliation in this case, and hence the high effective particle aspect ratios.

At  $T > T_g$ , simple geometrical models were inadequate, underestimating the reinforcing effect of 20 wt% laponite by about 2 orders of magnitude, as shown in Fig. 9 (the Poisson's ratio of the matrix was taken to be 0.48 in the rubbery state [42]). The large increases in the  $E'$  might in principle be accounted for by the presence of a filler or filler-polymer network [43–49]. The existence of a supramolecular structure has been inferred previously from rheological studies of PS/montmorillonite composites obtained by emulsion polymerization [46]. In the present case, rheological studies were inconclusive owing to the relatively high matrix molar mass, which made it difficult to access the terminal zone experimentally. However, as described in the results section, TEM provided some direct evidence of a cellular arrangement of the laponite aggregates arising from their tendency to adhere to the surfaces of the latex particles in the precursor suspensions. In the



**Fig. 8.** Comparison of experimental  $E'$  at room temperature with values calculated from the Halpin–Tsai (H–T) and Mori–Tanaka (M–T) models.



**Fig. 9.** Comparison of experimental  $E'$  at 160 °C with values calculated from the Halpin–Tsai (H–T) and Mori–Tanaka (M–T) models.

303 dried latexes, the laponite may therefore be considered to  
 304 form a more or less complete shell around the latex parti-  
 305 cles, depending on its concentration and dispersion. By  
 306 considering a laponite platelet (or agglomerate) to be  
 307 equivalent to a flexible disc of 54 nm in diameter, complete  
 308 coverage may be shown to correspond to a uniform distri-  
 309 bution of about 9 platelets per latex particle. Individual  
 310 laponite platelets are approximately 1 nm thick, so taking  
 311 the density of PS to be  $1.05 \text{ g cm}^{-3}$  and that of laponite  
 312 to be  $2.08 \text{ g cm}^{-3}$ , there would be roughly 3, 6 and 12  
 313 platelets per particle for latexes L5, L10 and L20, respec-  
 314 tively, in the event of full exfoliation. Thus, at the parti-  
 315 cle-particle interfaces in the films, which are shared by  
 316 adjoining particles, an average of about 6, 12 and 24 plate-  
 317 lets is predicted to be associated with each original parti-  
 318 cle. It follows that whereas a fully exfoliated morphology  
 319 is at least possible in films cast from latex L5, the total  
 320 interfacial area is insufficient to accommodate a single  
 321 layer of laponite platelets in films cast from latexes L10  
 322 and L20, and stacking of the platelets is inevitable, regard-  
 323 less of the initial state of exfoliation of the laponite.

324 In practice, complete exfoliation was not achieved, even  
 325 in the L5-based films, as shown by TEM and XRD, and the  
 326 observed agglomerate sizes in all the films were greater  
 327 than required by the above packing considerations, with  
 328 number average thicknesses of 8.4 and 9.9 nm being esti-  
 329 mated from TEM for L10 and L20, respectively, i.e. agglom-  
 330 erates of 6–7 laponite layers, or an effective particle  
 331 thickness of 6–7 nm. Under these conditions, full coverage  
 332 of the latex particles is unlikely, and indeed it is not clear  
 333 that percolation of inter-particle contacts was achieved at  
 334 any concentration. The percolation threshold for contacts  
 335 between (overlapping) discs placed randomly on a 2D sur-  
 336 face corresponds to a surface coverage  $\varphi_c = 0.676$  and a to-  
 337 tal disc area per unit surface of 1.12 [50,52]. For an  
 338 effective particle aspect ratio of 9 ( $= 54/6$ ), the total volume  
 339 fraction of laponite corresponding to percolation would be  
 340 about 25%, i.e. greater than the concentrations under con-  
 341 sideration here. It is therefore proposed that the nanocom-  
 342 posites be modeled as a closed-cell PS/laponite foam  
 343 whose wall thickness,  $t$ , is of the order of the mean aggre-  
 344 gate thickness, and whose cell diameter,  $D$ , is equal to the  
 345 latex particle diameter. All the laponite present in any  
 346 given nanocomposite is assumed to be concentrated in the  
 347 cell walls, and the cells are filled with pure PS matrix,  
 348 which is taken to behave as an incompressible solid in  
 349 the rubbery state, with modulus  $E_m$ . For  $E \gg E_m$ , the overall  
 350 stiffness is then approximated by

$$353 \quad E \approx \left(\frac{t}{D}\right)^2 \left\{ 1 + \left(\frac{t}{D}\right)^2 \right\} E_f + O(E_m) \approx \left(\frac{t}{D}\right)^2 E_f + E_m \quad (3)$$

354 Q2 where  $E_f$  is the modulus of the cell walls [52]. The Halpin-  
 355 Tsai model was used to predict  $E_f$  from the local concentra-  
 356 tion of laponite in the cell walls and assuming a homoge-  
 357 neous dispersion of the laponite platelets with  $\alpha = 54$   
 358 ( $t = 2.5, 8.4$  and  $9.9$  nm for L5, L10 and L20, respectively,  
 359 leading to laponite concentrations of approximately 27,  
 360 17 and 30 vol%). However, if the matrix modulus in the cell  
 361 walls is taken to be that of the unmodified PS in the rub-  
 362 bery state, i.e.  $E_m = 0.8 \text{ MPa}$  (see Table 2),  $E$  is estimated

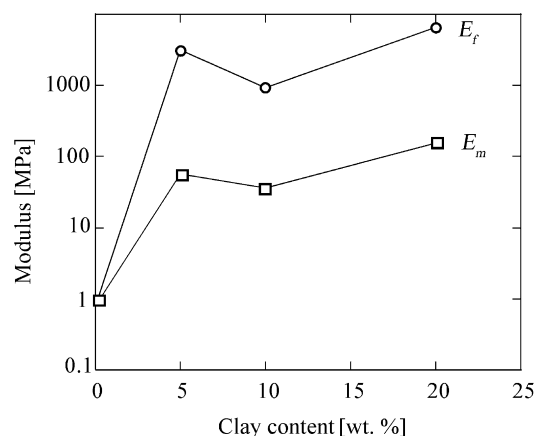


Fig. 10. Values of  $E_f$  and  $E_m$  required to fit the experimental data for the rubbery modulus via the foam model as described in the text.

to remain of the order of  $E_m$  for all the overall laponite con-  
 centrations, consistent with Eq. (2), but clearly inconsis-  
 tent with the data. On the other hand, although the small  
 measured shifts in  $T_g$  suggested little influence of the lapo-  
 nite on the global matrix properties, this may not be true  
 of the cell walls. Indeed, at 30 vol% laponite (the estimated  
 concentration in the cell walls for L20), the mean platelet  
 spacing is inferred to be of the order of 2 nm locally, which  
 is comparable with independent calorimetric estimates of  
 the thickness of immobilized layers in semicrystalline  
 polymers and polymer-clay nanocomposites in which  
 there is a strong interaction between the matrix and the  
 clay [53,54]. The effect of any such immobilization on the  
 local matrix stiffness is difficult to quantify *a priori*, but it  
 is possible to back-calculate the values of  $E_f$  and the corre-  
 sponding values of  $E_m$  required to account for the experi-  
 mental values of  $E$  in terms of Eq. (3) for the different  
 nanocomposites. As shown in Fig. 10, this implies the aver-  
 age local matrix modulus to increase by approximately 2  
 orders of magnitude in the cell walls, whilst remaining be-  
 low its value for  $T < T_g$ , which appears reasonable, given  
 that the presence of an immobilized layer is not necessary  
 to account for the elastic response below  $T_g$ .

#### 4.1. Tensile strength

As indicated in Table 3, addition of 5 wt% laponite re-  
 sulted in a small increase in the tensile strength of the  
 notched specimens, but there was a progressive reduction  
 as the laponite content was raised further. The peak in fracture  
 resistance at 5 wt% laponite was consistent with the trends in  
 $E'$  in the glassy state, and it was therefore inferred  
 that exfoliation is also an important factor for the high strain  
 properties. Previous observations of a decrease in elongation  
 at break and the tensile strength with clay content in styrenic  
 polymer-based nanocomposites, have been accounted for in  
 terms of poor adhesion between the clay and the polymeric  
 matrix [14,17,19,23]. It follows that where improvements in  
 matrix clay adhesion have been achieved by suitable surface  
 functionalization of the clay platelets, the tensile strength is  
 increases in well-dispersed



systems at low clay contents [21]. A possible explanation for the present non-monotonic behavior might therefore be weaknesses associated with the relatively large laponite agglomerates observed at high laponite contents. SEM images showed fibrillation during failure of the unmodified matrix (Fig. 7(a)), consistent with crazing and/or locally ductile behaviour, whereas a network of well defined “tufts” was visible at the fracture surfaces of the highly filled films (Fig. 7(b)). It was not possible to identify the locus of failure unambiguously from such images, but preliminary *in situ* observations by TEM of microdeformation in thin films prepared from the different nanocomposites have indicated the onset of failure in the nanocomposites with high laponite contents to be associated with the formation of localized deformation zones containing cavities with diameters comparable with those of the original PS latex particles [55]. Based on the foam model invoked in the previous section, it is inferred that the initial damage mechanism at high laponite contents is plastic growth of cavities within the PS-rich regions. Crack advance is then assumed to proceed by rupture of the intervening ligaments corresponding to the cell walls, accounting for the residues on the fracture surface visible in Fig. 7(b). The decrease in fracture resistance in L10 and L20 may be at least in part due to reduced plasticity in these ligaments with respect to that of unmodified PS. In the relatively highly exfoliated L5-based films, in which the cellular structure was less in evidence, crazing remained the dominant deformation mode, as in the pure PS matrix, so that the laponite was presumably able to act as a reinforcement e.g. by introducing local stress concentrations to the vicinity of the crack tip, resulting in delocalization of the crack-tip damage zone and increased energy dissipation.

## 5. Conclusion

An emulsion polymerization route has been used to obtain loadings of up to 20 wt% of **well-dispersed** laponite clay in solid PS films. DMA indicated the laponite to result in modest stiffness reinforcement for  $T < T_g$ , whereas for  $T > T_g$ , the stiffness reinforcement was significantly greater. The behavior in the rubbery state has been modeled assuming a continuous foam-like cellular arrangement of regions relatively rich in laponite particles, corresponding to the original particle surfaces. It is argued that the local matrix modulus in the vicinity of the laponite particles must be significantly higher than that of the PS, implying local restrictions on the matrix mobility. At high laponite contents, the local reduction in matrix mobility associated with the increases in rubbery modulus may also lead to decreased ductility, accounting for the observed decreases in fracture resistance. Future work will focus on the microdeformation mechanisms associated with fracture at different laponite loadings, and the range of laponite contents will be extended to higher concentrations in order to provide better defined cellular morphologies and a basis for more detailed investigation of the foam model.

## 6. Uncited reference

Q1 [51].

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