Available online at www.sciencedirect.com

Polymer 46 (2005) 8011–8017

polymer

www.elsevier.com/locate/polymer

Rheological and mechanical properties of percolated cyanate ester nanocomposites

Tim J. Wooster[a,b,*], Simmi Abrol[b], Douglas R. MacFarlane[a]

[a]Amorphous Materials Group, School of Chemistry, Monash University, Wellington Road, Clayton, Vic. 3800, Australia
[b]Materials Laboratory, Robert BOSCH Australia Pty Ltd, Cnr Center and McNaughton Roads, Clayton, Vic. 3168, Australia

Received 25 January 2005; received in revised form 25 May 2005; accepted 27 June 2005
Available online 19 July 2005

Abstract

The rheological properties and mechanical properties of percolated cyanate ester monomer/layered silicate mixtures are reported. A number of different cation exchanged montmorillonites were examined in an effort to achieve maximal montmorillonite delamination. The dispersion throughout the cyanate ester of a montmorillonite with phenylated ammonium cations (2MBHT MMT) results in the formation of a percolated network. The rheology of this percolated network undergoes a viscous liquid to elastic solid transition at 4 wt% montmorillonite. The percolation of the montmorillonite in the cyanate ester results in a significant improvement in crack resistance (80%) without a sacrifice of flexural strength.

Keywords: Cyanate ester; Montmorillonite; Rheology

1. Introduction

Cyanate ester thermosetting polymers have received increasing attention over the past 10 years for use in high temperature applications [1–7]. These polymers have outstanding adhesive, thermal, mechanical and in particular electrical properties [1–4,6–8]. Their excellent properties have meant that cyanate esters have been used in diverse applications including: Electrical encapsulation, aircraft interiors, structural materials for aerospace and as high temperature adhesives [1,2,5–7]. Whilst cyanate esters are one of the toughest thermosetting polymers (K_{Ic} 0.6–0.7 MPa m^{-1}) [2], the applications they are used in require improved crack resistance [1–3,5–8].

A number of different modifiers have been used to improve the crack resistance of cyanate esters [3]. These additives include reactive and nonreactive elastomers [9–14], a variety of engineering thermoplastics [10,15–21] and rigid inorganic particles [22]. One additive that has not received as much attention are layered silicates. The addition of layered silicates (montmorillonite, bentonite, etc.) to polymers often results in greatly improved properties over the native polymer or traditional composites [23–26]. Material properties that can be enhanced include: Flammability, thermal stability, resistance to gas permeability and mechanical properties such as modulus and crack resistance [23–26]. The success of the layered silicate additive has been found to be dependent on the degree of layer delamination and the nature of the composite formed [23–26].

The addition of a layered silicate to a polymer can result in three different silicate morphologies; macrocomposite, intercalated tactoids (where the polymer is sandwiched between layers), and exfoliated/delaminated structures (where the polymer causes individual montmorillonite layers to completely separate) [23–26]. Maximal property enhancement is achieved when an exfoliated morphology is achieved in the polymer layered-silicate composite [23–26].

Layered silicates are attractive additives for cyanate esters not only because they can increase crack resistance but also because they decrease mass transport through the cyanate ester, which might further enhance their moisture and flame resistance characteristics [23–26]. The majority

---

* Corresponding author. Present Address: CSIRO, 671 Sneydes Road, Werribee, Vic. 3030, Australia. Tel.: +61 3 9731 3251; fax: +61 3 9731 3250.

E-mail address: timothy.wooster@csiro.au (T.J. Wooster).

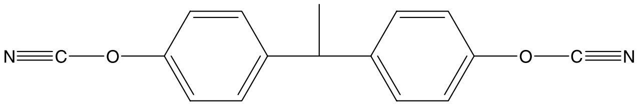
0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.06.106

of the work on cyanate ester layered silicates has been conducted by Dean and co-workers [27–29]. They have focused on bisphenol A dicyanate ester mixed with MT2EtOH montmorillonite clay [27–29]. These materials, like those synthesised by Kim et al. [30] using this montmorillonite and bisphenol E dicyanate ester, invariably formed intercalated structures [27–29]. The effect of this clay on cyanate ester composite layer structure [27–31], mechanical properties [27], thermal expansion [27,30], crack resistance [27], and thermal stability [27] has been studied. However, the effect of this and other cation-exchanged montmorillonites on cyanate ester monomer rheology has not been explored in detail.

The dynamic rheology of MMT/liquid suspensions has been extensively studied in many systems [32] (including: Epoxy, nylon 6 [33], polypropylene [34,35], polyamide [36], and polyurethanes [37]) except cyanate esters.[1] This work has found that these mixtures exhibit two types of rheology, at low silicate contents the systems behave as viscous liquids (storage modulus, $G' <$ loss modulus, G'') at higher contents the silicate layers percolate and form a continuous structural network, at this point the rheology is that of a elastic solid ($G' > G''$) [38–41]. The exact percolation limit is dependent on which end of the morphology spectrum the mixture lies [38–41]. Mixtures that are at the exfoliated end of the spectrum exhibit percolation at very low MMT contents (6 wt%) [32,42]. The higher the affinity of the MMT for the polymer the more exfoliation that will occur and the lower the percolation limit [23,25,43]. Therefore, study of the rheology of cyanate ester montmorillonite mixtures will give an indication of the success of layer separation and allow correct choice of montmorillonite to achieve optimal enhancement of mechanical properties.

2. Experimental

Cyanate ester montmorillonite mixtures were created from the cyanate ester monomer 1,1-bis(4-cyanatophenyl) ethane [bisphenol E dicyanate ester] (I) used as supplied (purity < 99%) by Lonza. Cyanate ester composites were obtained using copper(II) acetylacetonate and nonyl phenol as polymerisation catalysts: These were used as supplied (purity < 99.5%) by Aldrich Chemical Company. The montmorillonite silicates used were: Na montmorillonite (Na MMT), a quaternary ammonium cation exchanged montmorillonite, a dimethylbenzylhydrogenatetallow quaternary ammonium cation exchanged montmorillonite (2MBHT MMT), and a methyltallow-bis-2-hydroxyethyl quaternary ammonium cation exchanged montmorillonite (MT2EtOH MMT) used as supplied by Southern Clay Products.



(I)

The montmorillonite was dispersed throughout the monomer using a solvent exfoliation–adsorption method. The montmorillonite was suspended in a 30:70 mixture of liquid cyanate ester monomer and chloroform and sonicated for 30 min. The solvent was then removed from this mixture at 100 °C with stirring (spin bar). This mixture was then subjected to high shear mixing at 2000 rpm using an impeller. The final amount of solvent was removed by spreading the mixture as a thin film over a metal plate and vacuum degassed at 100 °C overnight. Mass spectroscopy and gel permeation chromatography analysis of these mixtures confirmed that no polymerisation had taken place during degassing/mixing. Solvent removal was confirmed using TG analysis, liquid monomer montmorillonite exhibiting no mass loss until MMT initiated polymerisation.

2.1. Flexural testing

Cyanate ester composite flexural properties were evaluated using an Instron 4045 mechanical tester. A three-point bend rig with all contact points having a 1 mm radius of curvature was used. Tests were conducted at 23 ± 2 °C with a cross-head speed of 1 mm min^{-1} and at least four specimens per composition were tested. ASTM specifications (D 790) [44] were followed in all tests with samples of the following dimensions, (30 × 6 × 2 mm, length × width × depth). Composite flexural strength, σ_f, was calculated using Eq. (1) [44].

$$\sigma_f = \frac{3FS}{2wd^2} \tag{1}$$

where F, applied force at breaking point; S, span between bottom two points (no greater than 20 mm); w, specimen width; and d, specimen depth. This test also allowed evaluation of composite flexural modulus, E_f, calculated using Eq. (2) [44].

$$E_f = \frac{\Delta F S^3}{4wd^3} \tag{2}$$

where ΔF is the gradient in the linear region of the load/displacement plot.

2.2. Fracture testing

Composite fracture behaviour was tested under mode I conditions using a double torsion test rig, which has been described in detail elsewhere [45]. Samples used were cast from brass/stainless steel split molds (38 × 19 × 2 mm) with

---

[1] Whilst Ganguli et al. [27,28] performed a chemorheological study of MMT cyanate ester mixtures they focused on the gel point of mixtures and did not quantify the effect of MMT surface treatment or content on liquid monomer rheology.

a groove 0.58 mm deep molded along the centre of the samples' long axis. A 5 mm long, 0.8 mm wide starting notch was machined (using a high speed diamond tipped cutting wheel) at one end of the groove and was sharpened using a razor blade prior to testing (Fig. 3).

A crosshead speed of 0.05 mm min^{-1} was used for these tests. Fracture toughness was calculated using well-established methods [46]; where unstable crack propagation took place, an average was taken of the initiation and release loads. Composite fracture energy was calculated from the fracture toughness, Young's modulus and an assumed Poisson's ratio of 0.35 using well-established equations [46].

2.3. Rheological testing

All rheological experiments were performed using a Haake Rheostress 1 that was routinely calibrated by the supplier using Brookfield viscosity standards. All experiments were conducted at 32 ± 0.5 °C. Dynamic frequency experiments were conducted using a parallel plate geometry (diameter 60, 1 mm gap). A stress of 2 Pa was applied over a frequency range of 0.1–10 Hz.

3. Results and discussion

3.1. Melt rheology

The rheology of polymer layered silicate suspensions has been shown to be dependent on the amount of silicate exposed to the polymer (influenced by silicate dispersion, silicate content and physicochemical interactions between the monomer and the silicate surface). If the montmorillonite content is kept constant, the primary factor determining the viscosity of a cyanate ester/layered silicate suspension will be silicate delamination. Thus the viscosity of 5 wt% M^+MMT^-/bisphenol E dicyanate ester mixtures should give an indication of the extent of MMT delamination. The viscosity of such dispersions was investigated using dynamic oscillatory rheology (Figs. 1 and 2, also summarised in Table 1).

In Figs. 1 and 2, it can be seen that 4HT MMT addition causes a minimal increase in viscosity, G' and G''. This indicates that this mixture resides at the tactoid/intercalate end of the nanocomposite morphology spectrum. The G'' of this mixture is much larger than the G' indicating that the viscoelastic properties of this material is dominated by viscous liquid behaviour. This is understandable given the predominantly aliphatic nature of this MMT cation. It has been demonstrated that cyanate esters are predominantly incompatible with aliphatic based surface treatments [47].

The addition of MT2EtOH MMT to the cyanate ester monomer results in a larger increase in viscosity than the 4HT MMT. The viscosity increase indicates there is more layer separation within this mixture. However, the viscosity increase is much lower than is observed in 5 wt% MMT/polymer systems that are predominantly delaminated [32,34,36]. Again the G'' of this mixture is much higher than the G', indicating that the viscoelastic properties of this material are dominated by viscous liquid behaviour. The substitution of two alcohol groups onto the cation appears to increase affinity for the cyanate ester monomer, but only enough to facilitate monomer permeation into the gallery and possibly some minor, but not extensive, montmorillonite delamination.

Unlike 4HT MMT and MT2EtOH MMT, the addition of 2MBHT MMT to the cyanate ester monomer results in a significant increase in mixture viscosity. 2MBHT MMT addition also results in a significant increase in G'. In this mixture, G' is slightly larger than G'' indicating that the viscoelastic behaviour of this mixture is dominated by

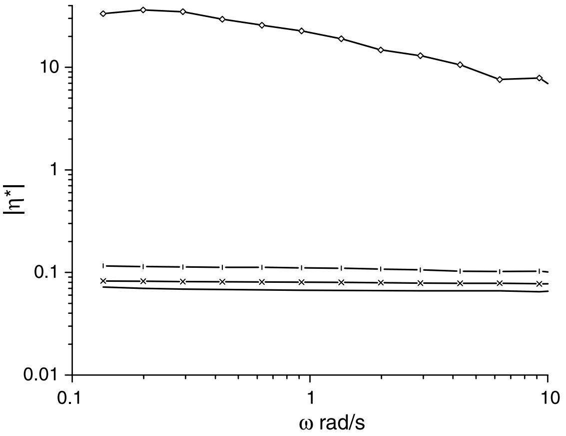


Fig. 1. Complex viscosity of 5 wt% M^+MMT^-/bisphenol E dicyanate ester mixtures; (I) No MMT (solid line), (II) 5 wt% 4HT MMT (line with cross), 5 wt% MT2EtOH MMT (line with stripe), and 5 wt% 2MBHT MMT (line with diamond).

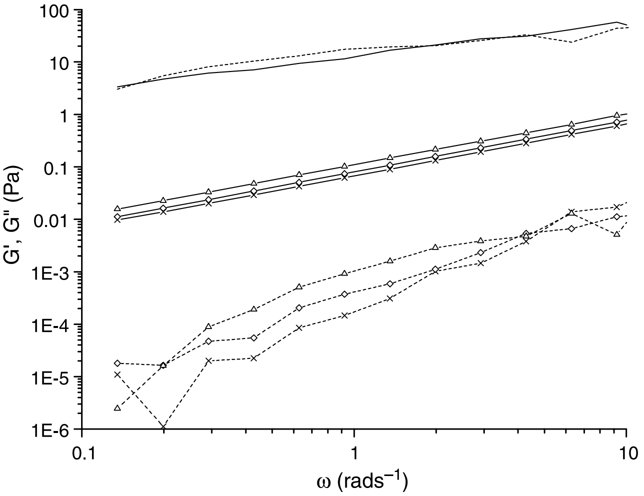


Fig. 2. Effect of montmorillonite content on (A) the complex viscosity and (B) the loss (G', dashed line) and storage (G'', solid line) moduli of (I) bisphenol E dicyanate ester monomer (line, cross), with (II) 5 wt% 4HT MMT (line, diamond), (III) 5 wt% MT2EtOH MMT (line, triangle) and (IV) 5 wt% 2MBHT MMT (line no symbol).

Table 1
Complex viscosity of various 5 wt% $M^{+}MMT^{-}$/bisphenol E dicyanate ester mixtures

Sample	$\|\eta^{*}\|$ (at 0.2 rad s^{-1})
Base monomer	70 cPa s
5 wt% 4HT MMT	82 cPa s
5 wt% MT2EtOH MMT	114 cPa s
5 wt% 2MBHT MMT	36,300 cPa s

elastic solid behaviour. This is the exact opposite of other 5 wt% MMT mixtures and suggests the 2MBHT cation has significantly more affinity with the cyanate ester monomer than the others evaluated. The dramatic viscosity increases observed with this cyanate ester/MMT system suggests a significant degree of MMT exfoliation. The rheology of these systems is now described in more detail.

Figs. 3 and 4 reflect the effect of 2MBHT MMT content on mixture rheology. The classical power law increase in viscosity with additive content can be seen in Fig. 3(A). Mixtures with contents of 4 and 5 wt% have significantly higher viscosity than the lower contents, indicating that the mixtures are reaching a percolation threshold [34]. In Fig. 3(B), the frequency dependence of the complex viscosity is presented. At low contents (0–2 wt%) the viscosity is frequency independent, as would be expected of a suspension [32,33,38–41,48,49]. However, at high contents (3–5 wt%) mixture viscosity decreases with frequency, particularly the 4 and 5 wt% mixtures. A decrease in viscosity with frequency is indicative of shear thinning and is well documented with polymer/layered silicate mixtures [32–34,36,48,49]. This behaviour has generally been interpreted as destruction of the percolated silicate network by alignment of the silicate sheets [32–34, 48,49].

Fig. 4(A) presents the effect of 2MBHT content on the loss and storage modulus of these mixtures as a function of frequency, whilst Fig. 4(B) presents them as a function of concentration at 0.2 rad s^{-1}. At low MMT contents, $G' < G''$ indicating that the viscoelastic behaviour is dominated by viscous liquid behaviour. However, the difference between G' and G'' decreases dramatically with 2MBHT MMT content and at 4 wt% $G' > G''$, indicating that the mixture has switched from viscous liquid to elastic solid behaviour (the percolation limit). At this content there is sufficient montmorillonite dispersion to facilitate the formation of a continuous structural network.

The percolation limit is approached at around 4 wt%, which is much lower than has been reported for intercalated systems [50] and one of the lowest presently reported [32–34,48,49]. Ren et al. [42] have developed a model to approximate the size of montmorillonite stacks (number of montmorillonite layers per tactoid, η_{per}). The model is based on a simple volume filling calculation and assumes a uniform distribution of identically sized tactoids (Eq. (3)).

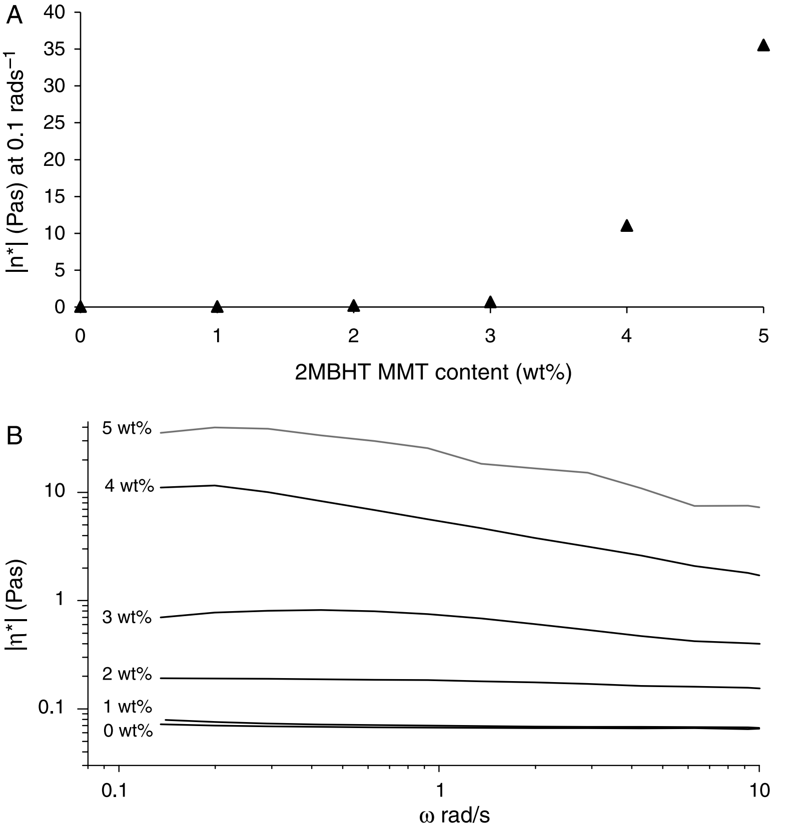


Fig. 3. Effect of 2MBHT MMT content on bisphenol E dicyanate ester monomer complex viscosity.

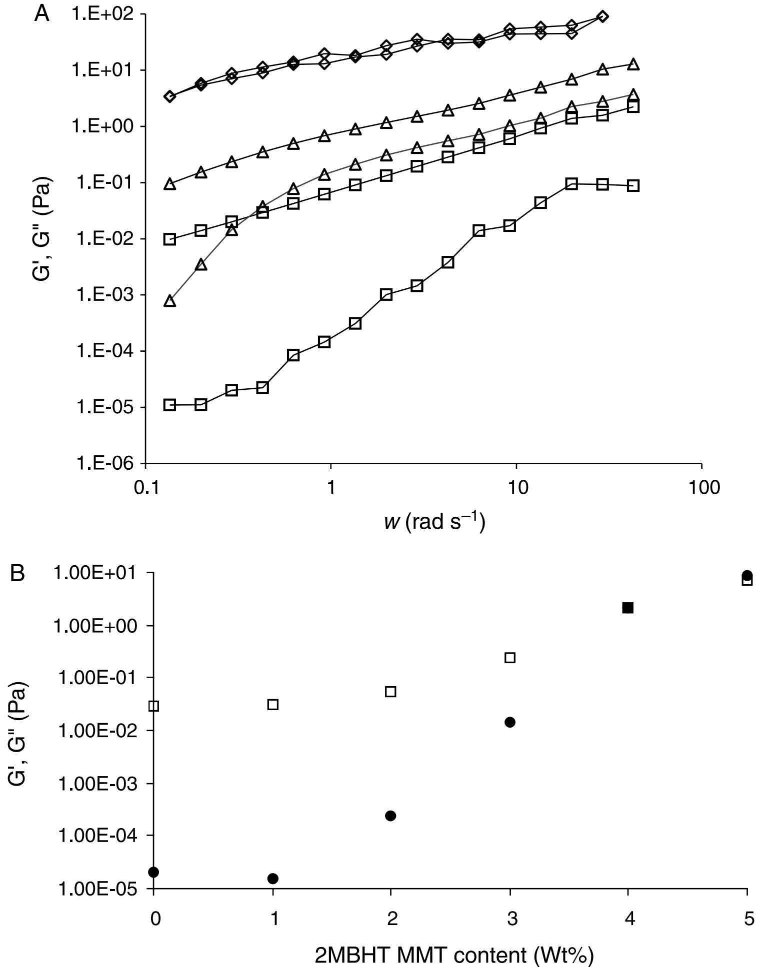


Fig. 4. Effect of 2MBHT MMT content on the dynamic storage (G') and loss (G'') moduli of bisphenol E dicyanate ester MMT mixtures. (A) The effect of MMT concentration on the loss (G', solid line) and storage (G'', dashed line) moduli of (I) bisphenol E dicyanate ester monomer, with (II) 1 wt% 2MBHT MMT, (III) 2 wt% 2MBHT MMT, (IV) 3 wt% 2MBHT MMT (V) 4 wt% 2MBHT MMT (VI) 5 wt% 2MBHT MMT. (B) G' (closed circle) and G'' (open square) as a function of concentration at 0.2 rad s^{-1}.

$$\eta_{\text{per}} = \frac{4}{3\phi_{\text{per}}}\left[\frac{w_{\text{sil.per}}\rho_{\text{org}}}{w_{\text{sil.per}}\rho_{\text{org}} + (1 - w_{\text{sil.per}})\rho_{\text{sil}}}\right]\frac{R_{\text{h}}}{h_{\text{sil}}} \tag{3}$$

where η_{per}, number of montmorillonite layers per tactoid; ϕ_{per}, percolation limit for random spheres in three dimensions, 0.30 [51]; $w_{\text{sil.per}}$, weight fraction at percolation; ρ_{org}, ρ_{sil}, density of the polymer and silicate, respectively; h_{sil}, thickness of each montmorillonite sheet; R_{h}, radius of the hydrodynamic volume (radius of the silicate (approximated as 0.25 μm)).

When studying a polystyrene/polyisoprene MMT mixture, Ren et al. [42] obtained a percolation limit of 6.7 wt%, which corresponded to tactoids consisting of 30 layers. The present system has a percolation limit of ~4 wt%, which corresponds to tactoids consisting of approximately 20 layers, suggesting greater dispersion. However, it also indicates that percolation can occur without total exfoliation, mainly due to the high aspect ratio of the montmorillonite.

The insertion of a phenolic unit onto the cation dramatically increases the compatibility between the MMT and the cyanate ester monomer. The compatibility is such that monomer not only permeates into the gallery but also causes significant delamination of the layers. XRD analysis of this mixture permitted only the conclusion that the layer structure was intercalated, the same as the MT2EtOH MMT system [27–29,52]. However, rheological analysis has enabled differentiation of the structure of the two systems. The MT2EtOH MMT cyanate ester mixture resides at the intercalated end of the spectrum, whereas the 2MBHT MMT cyanate ester mixture contains a significant amount of delaminated layers, suggesting that it resides more towards the exfoliated end of the spectrum.

The melt rheology studies of these mixtures suggest that maximal montmorillonite dispersion is achieved when bisphenol E dicyanate ester is mixed with 2MBHT treated montmorillonite. Thus, this montmorillonite was used to demonstrate the effect of montmorillonite on cyanate ester mechanical properties. The properties studied were crack resistance (Fig. 5), strength and modulus (Fig. 6).

The most dramatic increase in bisphenol E dicyanate ester mechanical properties occurs in the crack resistance (Fig. 5). It can be seen that crack resistance increases with montmorillonite content, as expected. However, there is a decrease after the percolation limit (as determined from Fig. 4) from 4 to 5 wt%. This decrease reflects difficulties in dispersion above the percolation limit (the 5 wt% sample).

At the maximum (4 wt% montmorillonite), there is an 80% increase in crack resistance. This increase is much more than would be expected with similar silica filler content [22,53]. However, it is comparable to other montmorillonite systems [54,55]. The large increase is explained by the large surface area (~760 $m^2 g^{-1}$ for MMT [25] as opposed to ~0.8 $m^2 g^{-2}$ for silica filler [56]) available for interaction with the progressing crack front.

A SEM micrograph of the fractured surface of the 4 wt% sample is presented in Fig. 7. The distinct platelet pattern of the montmorillonite is readily observed. The rough surface of the crack arises from the montmorillonite platelets causing the crack to deflect, tilt and twist as it reaches and passes them. The toughening mechanisms here, crack pinning, blunting and deflection, are similar in nature to other particulate reinforcements.

The flexural properties of the cyanate ester montmorillonite nanocomposites were also examined (Fig. 6). The addition of montmorillonite caused a systematic increase in flexural modulus, however, a decrease was observed from 4 to 5 wt%. Again this inflection reflects lower montmorillonite dispersion in the 5 wt% sample. At best, a 33% increase in modulus was observed, similar in magnitude to those obtained in epoxy networks [54,55]. Montmorillonite addition also caused a moderate decrease in strength. At worst, a decrease of only 23% was observed. This indicates that there is high interfacial adhesion between the montmorillonite platelets and the cyanate ester resin. The source of the high adhesion is likely to be similar to that occurring with silica and alumina fillers [57–60]. Cyanate ester triazine rings have been shown to participate in charge transfer interactions with both Al and Si atoms in inorganic filler particles [57–60], and as montmorillonite is an aluminosilicate it is predicted that these interactions will also occur in montmorillonite systems.

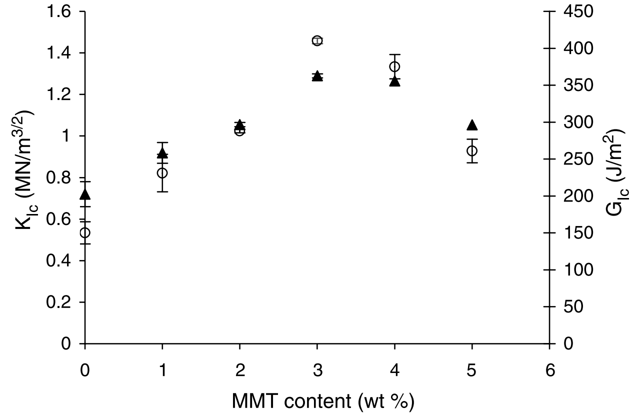


Fig. 5. Crack resistance of bisphenol E dicyanate ester containing 2MBHT treated montmorillonite, fracture toughness (closed triangle), fracture energy (open circle).

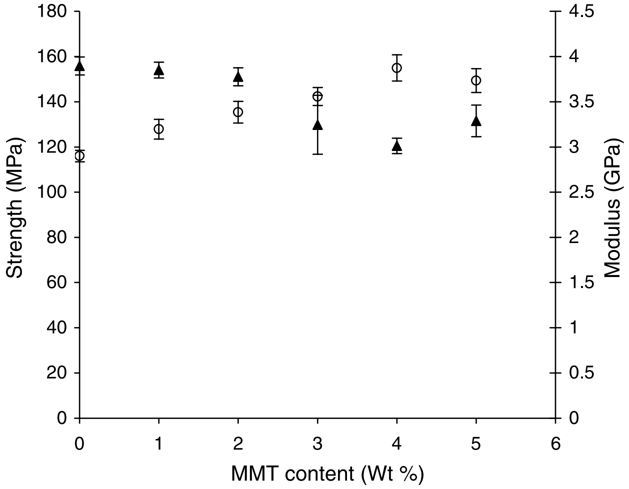


Fig. 6. Flexural mechanical properties of bisphenol E dicyanate ester containing 2MBHT treated montmorillonite.

4. Conclusions

The addition of montmorillonite smectic clays to cyanate esters has been found to alter rheological and mechanical properties. It was found that the dispersion state was the critical factor that determined the change in rheology and mechanical properties. Dynamic rheological measurements enabled greater understanding of montmorillonite dispersion throughout the cyanate ester. These measurements found that montmorillonite dispersion was greatest when the MMT cation had high chemical affinity with the cyanate ester monomer. This enabled the selection of a gallery

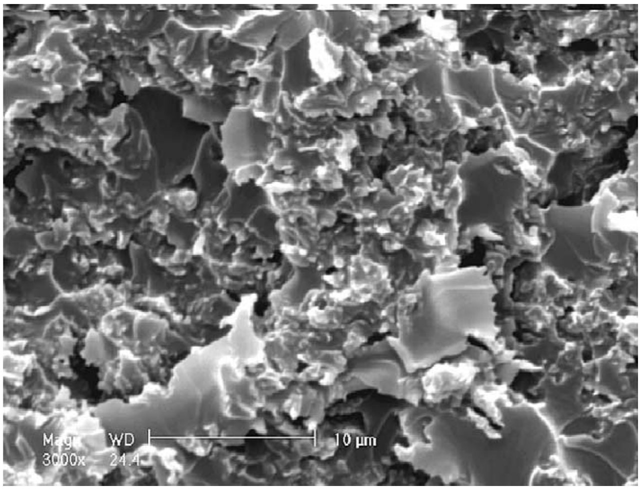


Fig. 7. SEM image of fracture surface of 4 wt% 2MBHT MMT in cure bisphenol E dicyanate ester.

cation (2MBHT, a phenylated hydrogen tallow) that affected significant clay dispersion, leading to an intercalated system with significant exfoliation. Subsequent assessment of cyanate ester MMT composite mechanical properties revealed a dramatic increase in crack resistance without sacrifice of strength.

Acknowledgements

The authors wish to thank Robert BOSCH Australia for financial support of this research. We would like to thank Sajal Das of Lonza USA for generous donation of cyanate ester monomers and Jim Chambers (Australian representative of Southern Clay Products) for generous donation of Cloisite montmorillonite products and technical discussions. Finally we would like to thank Fosters for technical assistance.

References

[1] Hamerton I, Hay JN. High Perform Polym 1998;10:163–74.
[2] Lin S-C, Pearce EM. High-performance thermosets, chemistry, properties, applications. Munich: Hanser; 1993 [chapter 3].
[3] Mackenzie PD, Malhotra V. In: Hamerton I, editor. Chemistry and technology of cyanate ester resins. London: Chapman and Hall; 1994.
[4] Hamerton I. In: Hamerton I, editor. Chemistry and technology of cyanate ester resins. Suffolk: Chapman and Hall; 1994. p. 193–229.
[5] Shimp DA. In: Hamerton I, editor. Chemistry and technology of cyanate ester resins. London: Chapman and Hall; 1994. p. 282–328.
[6] Hamerton I, Hay JN. Polym Int 1998;47:465–73.
[7] Reghunadhan Nair CP, Mathew D, Ninan KN. Adv Polym Sci 2001;155:1–99.
[8] Hamerton I. In: Hamerton I, editor. Chemistry and technology of cyanate ester resins. London: Chapman and Hall; 1994.
[9] Borrajo J, Riccardi CC, Williams RJJ, Cao ZQ, Pascault JP. Polymer 1995;36:3541–7.
[10] Hillermeier RW, Seferis JC. J Appl Polym Sci 2000;77:556–67.
[11] Cao Z, Mechin F, Pascault J-P. Adv Chem Ser 1996;252:177–94.
[12] Cao Z, Mechin F, Pascault J-P. Polym Int 1994;34:41–8.
[13] Hayes BS, Seferis JC, Parker GA. Polym Eng Sci 2000;40:1344–9.
[14] Uhlig C, Bauer J, Bauer M. Macromol Symp 1995;93:69–79.
[15] Hwang JW, Cho K, Park CE, Huh W. J Appl Polym Sci 1999;74:33–45.
[16] Hwang JW, Park SD, Cho K, Kim JK, Park CE, Oh TS. Polymer 1997;38:1835–43.
[17] Harismendy I, Del Rio M, Eceiza A, Gavalda J, Gomez CM, Mondragon I. J Appl Polym Sci 2000;76:1037–47.
[18] Kim Y-S, Kim S-C. Macromolecules 1999;32:2334–41.
[19] Harismendy I, Del Rio M, Marieta C, Gavalda J, Mondragon I. J Appl Polym Sci 2001;80:2759–67.
[20] Kinloch AJ, Taylor AC. J Mater Sci 2003;38:65–79.
[21] Srinivasan SA, Mcgrath JE. SAMPE Q 1993;24:25–9.
[22] Kinloch AJ, Taylor AC. J Mater Sci 2002;37:433–60.
[23] Giannelis EP, Krishnamoorti R, Manias E. Adv Polym Sci 1999;138:107–47.
[24] Alexandre M, Dubois P. Mater Sci Eng R 2000;28:1–63.
[25] Lebaron PC, Wang Z, Pinnavaia TJ. Appl Clay Sci 1999;15:11–29.
[26] Ray SS, Okamoto M. Prog Polym Sci 2003;28:1539–641.
[27] Ganguli S, Dean D, Jordan K, Price G, Vaia R. Polymer 2003;44:1315–9.
[28] Ganguli S, Dean D, Jordan K, Price G, Vaia R. Polymer 2003;44:6901–11.
[29] Dean D, Abdalla MO, Ganguli S, Jose M, Campbell S, Gillman J, et al. Int SAMPE Symp Exhibition 2003;48:2572–84.
[30] Kim DS, Lee KM. J Appl Polym Sci 2003;90:2629–33.
[31] Morgan AB, Gilman JW. J Appl Polym Sci 2003;87:1329–38.
[32] Krishnamoorthi R, Yurekli K. Curr Opin Colloid Interface Sci 2001;6:464–70.
[33] Krishnamoorthi R, Giannelis EP. Macromolecules 1997;30:4097–102.
[34] Galgali G, Ramesh C, Lele A. Macromolecules 2001;34:852–8.
[35] Solomon MJ, Almusallam AS, Seefeldt K, Somwangthanaroj A, Varadan P. Macromolecules 2001;34:1864–72.
[36] Incarnato L, Scarfato P, Acierno D. Polymer 2004;45:3487–96.
[37] Rhoney I, Brown S, Hudson NE, Pethrick RA. J Appl Polym Sci 2004;91:1335–43.
[38] Shenoy AV. Rheology of filled polymer systems. Dordrecht, Netherlands: Kluwer; 1999.
[39] Gupta RK. Polymer and composite rheology. 2nd ed. New York: Marcel Dekker; 2000.
[40] Callister WD. Materials science and engineering and introduction. 4th ed. New York: Wiley; 1997.
[41] Larson RG. The structure and rheology of complex fluids. New York: Oxford University Press; 1999.
[42] Ren J, Silva AS, Krishnamoorthi R. Macromolecules 2000;33:3739–46.
[43] Ray SS, Okamoto M. Prog Polym Sci 2003;28:1539–641.
[44] In Standard Test Designation D790; 1992.
[45] Indrani DJ, Cook WD, Televantos F, Tyas MJ, Harcourt JK. Dent Mater 1995;11:201–7.
[46] Spanoudakis J, Young RJ. J Mater Sci 1984;19:473–86.
[47] Wooster TJ, Abrol S, Hey JM, Macfarlane DR. Macromol Mater Eng 2004;289:872–9.
[48] Larson RG. New York: Oxford University Press; 1977. p. 663.
[49] Krishnamoorti R, Vaia RA, Giannelis EP. Chem Mater 1996;8:1728–34.
[50] Zhang L-M, Jahns C, Hsiao BS, Chu B. J Colloid Interface Sci 2003;266:339–45.
[51] Isichenko MB. Rev Mod Phys 1992;64:961.
[52] Wooster TJ, Abrol S, Macfarlane DR. Polymer 2004;45:7845–52.
[53] Wooster TJ, Abrol S, Hey J, Macfarlane DM. Compos Part A: Appl Sci Manuf 2004;35A:75–82.
[54] Becker O, Varley RJ, Simon GP. Polymer 2002;43:4365–73.
[55] Zilg C, Mulhaupt R, Finter J. Macromol Chem Phys 1999;200:661–70.
[56] Deferm P. Technical bulletin Millisil M4–M6–M6.1–M10 silicas. Sibleco; 2004.
[57] Possart W, Dieckhoff S. Int J Adhes Adhes 1999;19:425–34.
[58] Possart W, Dieckhoff S, Fanter D, Gesang T, Hartwig A, Hoper R, et al. Proceedings of the annual meeting of the adhesion society. vol. 18 1995 p. 15–7.
[59] Possart W, Fanter D, Bauer M. J Adhes 1995;54:261–75.
[60] Possart W, Fanter D, Dieckhoff S, Gesang T, Hartwig A, Hoeper R, et al. J Adhes 1996;57:227–44.