

Effect of Ethylene Glycidyl Methacrylate Compatibilizer on the Structure and Mechanical Properties of Clay Nanocomposites Modified with Ethylene Vinyl Acetate Copolymer

B. R. Guduri,^{1,2} A. S. Luyt¹

¹Department of Chemistry, University of the Free State (Qwaqwa Campus), Private Bag X13, Phuthaditjhaba 9866, South Africa

²Materials Science and Manufacturing, Council for Scientific and Industrial Research, P. O. Box 395, Pretoria 0001, South Africa

Received 13 July 2006; accepted 4 September 2006

DOI 10.1002/app.25512

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The structure and mechanical properties of clay modified with ethylene vinyl acetate copolymer in the presence of ethylene glycidyl methacrylate (EGMA) were investigated as a function of compatibilizer and clay contents. The structure and properties were determined by X-ray diffraction, transmission electron microscopy, differential scanning calorimetry, and thermogravimetric analysis (TGA). The presence of EGMA caused strong exfoliation of the clay in the polymer matrix, although at higher clay contents, some clay layers still existed. The more effective exfoliation, however, did not seem to

substantially influence the tensile properties of the nanocomposites because the EGMA itself had a much stronger influence, which overshadowed any possible influence that the EGMA–clay interaction may have had on these properties. The thermal stability of the nanocomposites (as studied by TGA) improved in the presence of EGMA. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 4095–4101, 2007

Key words: composites; mechanical properties; morphology; nanolayers; organoclay

INTRODUCTION

Nanocomposites are a new class of composites derived from ultrafine inorganic particles, with dimensions typically in the range 1–1000 nm, that are homogeneously dispersed in the polymer matrix.¹ Recently, these kinds of materials have received the attention of government, academic, and industrial researchers because of their outstanding properties. These polymer layered silicate nanocomposites can attain a certain degree of stiffness, strength, and barrier properties with a far lower ceramic content than comparable glass or general inorganic-reinforced polymers.² Polymer–clay nanocomposites were first reported in the literature as early as 1961, when Blumstein³ demonstrated the polymerization of vinyl monomers intercalated into montmorillonite clay. Different methods for preparing polymer–clay nanocomposites were developed by several groups.^{4–6} In general, these methods achieve molecular-level

incorporation of the layered silicate (e.g., montmorillonite) into the polymer by the addition of a modified silicate during the polymerization (*in situ* method) to either the solvent-swollen polymer or the polymer melt.^{7–9}

There are four methods for making nanocomposites: exfoliation–adsorption, *in situ* intercalative polymerization, melt intercalation, and template synthesis.¹⁰ Melt intercalation of polymers has proven to be a more efficient and environmentally benign alternative to other methods.¹¹ When polymer–clay nanocomposites are prepared via either *in situ* polymerization or direct intercalation, a very specific temperature is needed in the processing.^{12,13} If the processing temperature is higher than the thermal stability of the organic modifier, decomposition of the organic treatment is meaningful in the process of making polymer–clay nanocomposites.^{14–16}

Direct dispersion of the organoclay in the molten polymer with an extruder is the most appropriate technique for the industrial preparation of polymer layered silicate nanocomposites. Two classes are universally accepted: intercalated nanocomposites, where the polymer chains are intercalated in the galleries, and delaminated or exfoliated nanocomposites, where the delaminated silicate is uniformly dispersed in the matrix. The aspect ratio and dispersion

Correspondence to: A. S. Luyt (luytas@qwa.uovs.ac.za).

Contract grant sponsor: National Research Foundation in South Africa; contract grant number: GUN 2050677.

Contract grant sponsor: University of the Free State.

attain very high values in delaminated nanocomposites. Lamellar aspect ratios ranging from 100 to 1000 result in polymers with high rigidity and heat stability, reduced gas permeability, and good transparency with as little as 5–10% silicate. A number of studies have been performed to investigate the influence of nanosized organoclay on the thermal stability and flammability properties of ethylene vinyl acetate copolymer (EVA) and EVA blends.^{17–23} It has generally been found that the presence of nanoclay improves the thermooxidative stability and flammability behavior of EVA and its blends with other polymers.

There have been a few studies on the morphology and mechanical properties of EVA-based nanocomposites. Chaudhary et al.²⁴ found that a higher vinyl acetate (VA) content in EVA improved the polymer–clay interaction, which gave rise to an increase in the rigid amorphous phase and significantly changed the mechanical properties of the nanocomposites. Gupta et al.²⁵ found predominantly exfoliated morphologies for nanocomposites of EVA with organically modified bentonite clay. Zhang et al.²⁶ investigated nanocomposites containing EVA with different VA contents and different kinds of organophilic and unfunctionalized clays. They proposed a new structure, the wedged structure, where the sheets of clay were partly wedged by the chains of the polymer, in addition to the intercalated and exfoliated structures.

EXPERIMENTAL

Materials

EVA

EVA with 9% VA content was supplied by Plastamid (Elsies River, South Africa). According to the supplier, it had a melting point of 95°C, a density of 0.930 g/cm³, a tensile strength of 19.0 MPa, and an elongation at break of 750%.

Ethylene glycidyl methacrylate (EGMA)

EGMA was also supplied by Plastamid. According to the supplier, it had a melting point of 93°C, a density of 0.94 g/cm³, a tensile strength of 12 MPa, and an elongation at break of 440%.

Modified clay

Cloisite 15A clay (ditallow dimethylammonium salts of bentonite), supplied by Southern Clay Products (Texas), was used as reinforcement. The as received clay particles were disklike stacks of thin silicate layers that were 1 nm thick and ranged in diameter from 100 nm to several micrometers. The specific gravity of the clay particles (stacks) was 1.6–1.8 g/cm³.

According to the supplier, the organic modifier would decompose at temperatures in excess of 200°C.

Preparation of the nanocomposites

EVA and clay were melt-blended at 160°C with a Brabender mixer and extruder (Duisburg, Germany). EVA was first completely melted, and then, the clay was slowly added. The nanocomposites were initially mixed at 60 rpm for 20 min, after which they were extruded as films with thicknesses between 0.4 and 0.5 mm at a screw speed of 30 rpm.

Characterization of the samples

X-ray diffraction (XRD)

The degree of intercalation or exfoliation was evaluated with X-ray diffractometry. XRD patterns of the nanocomposite samples were obtained with a D8 Advance X-ray diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$; Bruker-AXS, Madison, WI). The detector was a Na-I scintillation counter with a monochromator.

Fourier transform infrared spectroscopy

Fourier transform infrared spectra were obtained with a Nicolet Impact 410 spectrometer (Waltham, MA), which operated from 4000 to 400 cm⁻¹ at room temperature.

Transmission electron microscopy (TEM)

The TEM analyses were conducted on a Jeol JEM-100CX II electron microscope (Tokyo, Japan). A MT6000 Sorvall microtome was used to cut thin sections (<100 nm thick) of the samples at room temperature.

Tensile testing

A Hounsfield (H5KS) universal testing machine (Redhill, England) was used to investigate the tensile strength, tensile modulus, and elongation properties of the nanocomposites. Samples measuring 150 × 15 × 0.45 mm were cut for tensile testing. The specimens were analyzed at a crosshead speed of 10 mm/min. A continuous load-deflection curve was obtained. In each case, 10 samples were used, and the average was taken.

Thermogravimetric analysis (TGA)

TGA was performed on a PerkinElmer TGA 7 thermogravimetric analyzer (Wellesley, MA). The experiments were carried out from 30 to 600°C at a heating rate of 10°C/min. The experiments were performed under a nitrogen atmosphere at a flow rate of 20 mL/min.

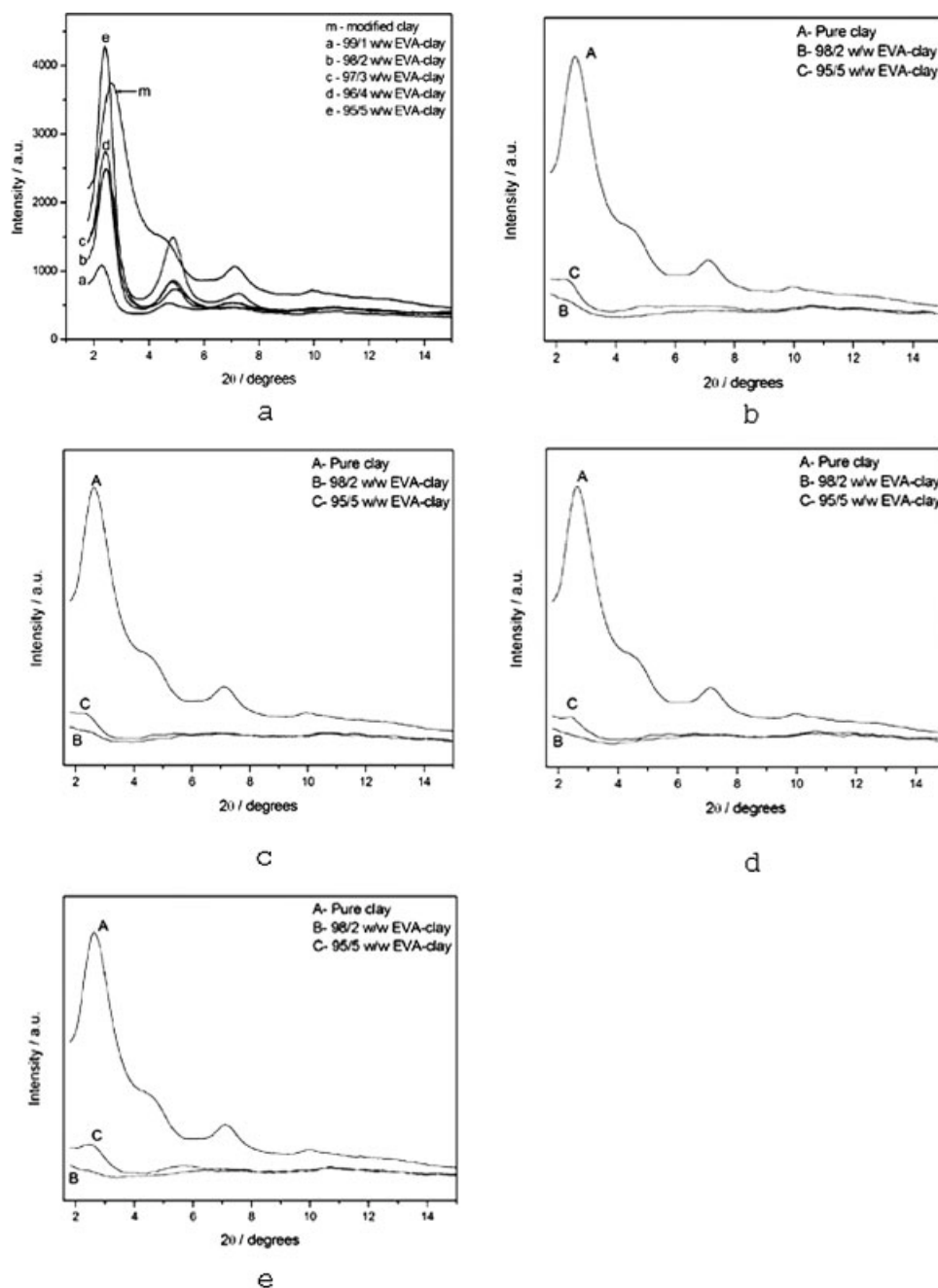


Figure 1 XRD patterns of the modified clay and EVA-clay nanocomposites with (a) 0, (b) 5, (c) 10, (d) 15, and (e) 20% EGMA.

RESULTS AND DISCUSSION

The XRD patterns of the modified clay and the EVA-clay nanocomposites are presented in Figure 1(a). The (001) peak positions in the figure show that the basal spacing of the 99 : 1 w/w EVA-clay nanocomposite was slightly higher than those of the modified clay and the other nanocomposites. All of the nanocomposites had larger basal spacings than the modified clay. Figure 1(a) shows a continuous increase in peak intensity of the $2\theta = 2.3^\circ$ peak with increasing clay content, and there was an almost

linear relationship between the peak intensity and the clay content. From these observations, it seemed as if all of the nanocomposites were (partially) intercalated. Figure 1(b-e) shows that at all EGMA concentrations, there was complete exfoliation of the samples containing 2% clay, whereas the samples containing 5% clay showed a very weak (001) peak at $2\theta = 2.4^\circ$, which corresponded to a basal spacing of 36.78 Å; this indicated the presence of some intercalated layers. For low-clay-content samples, there was complete exfoliation, whereas a mixed interca-

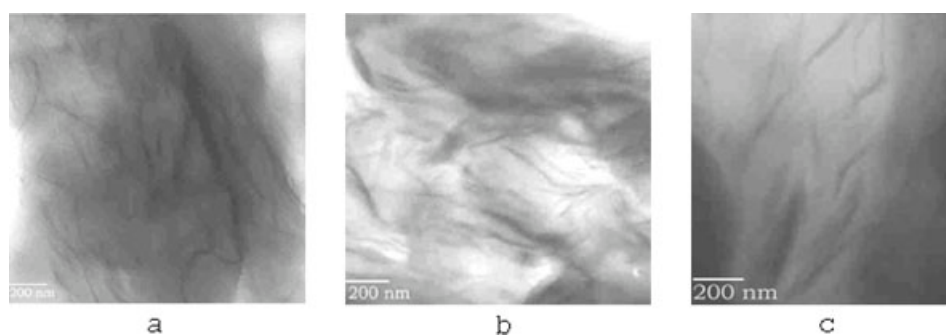


Figure 2 TEM images of (a) 85 : 10 : 5, (b) 80 : 15 : 5, and (c) 75 : 20 : 5 w/w EVA/EGMA/clay.

lated and exfoliated morphology existed at higher clay contents, as shown in the TEM micrographs in Figure 2. The exfoliation was very obvious, but it was also clear that there were stacks where the clay platelets were not completely dispersed, which indicated a mixed morphology at this clay loading. It did not seem as if increased amounts of EGMA improved the exfoliation of the clay in the matrix. As discussed later, the presence of EGMA, however, had a detrimental effect on the tensile properties of the nanocomposites.

Initially, it was thought that EVA may react with EGMA, giving a product that more strongly interacts with the modified clay. Work done by Dikobe and Luyt,²⁷ however, showed that EVA and EGMA do not react with each other. EVA and EGMA are, however, very miscible (according to differential scanning calorimetry curves not presented). Because of the lone electron pair on the epoxy oxygen in

EGMA [Fig. 3(a)], EGMA is attracted by positive or partially positive charges. It will, for example, extract hydrogen from an —OH group. In this system, therefore, the positive charge on the quaternary ammonium of the modified clay [Fig. 3(b)] probably strongly attracted the epoxy oxygen. This caused a much stronger interaction between the EVA/EGMA matrix and the clay.

The tensile modulus of the EVA/EGMA–clay nanocomposites is shown in Figure 4 as a function of the EGMA and clay contents, respectively. Clearly, both EGMA and modified clay caused the modulus to increase. In the absence of EGMA, the tensile modulus increased from 25 MPa for pure EVA to 44 MPa for the 95 : 5 w/w EVA–clay nanocomposite (Table I). In the absence of clay, the presence of EGMA increased the modulus from 25 MPa for pure EVA to 38 MPa for the 80 : 20 EVA/EGMA blend. The sample containing 20% EGMA and 5% clay showed a modulus of 58 MPa. It, therefore, seems that although there was a mixed morphology at higher clay contents even in the presence of higher EGMA

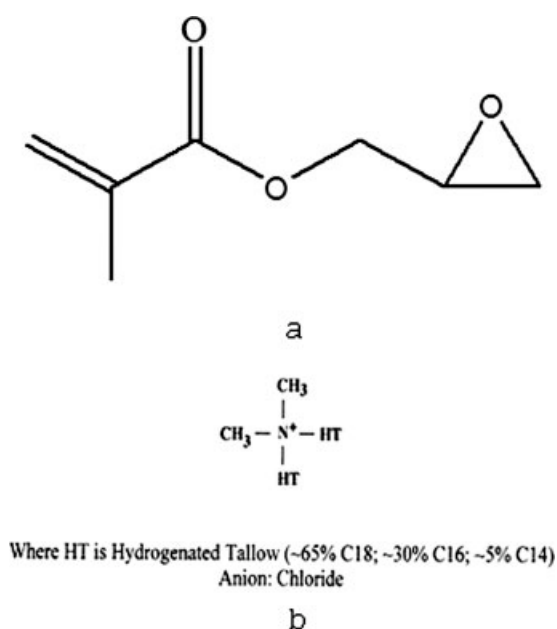


Figure 3 Chemical structure of the (a) EGMA repeat unit and (b) Cloisite 15A organic modifier.

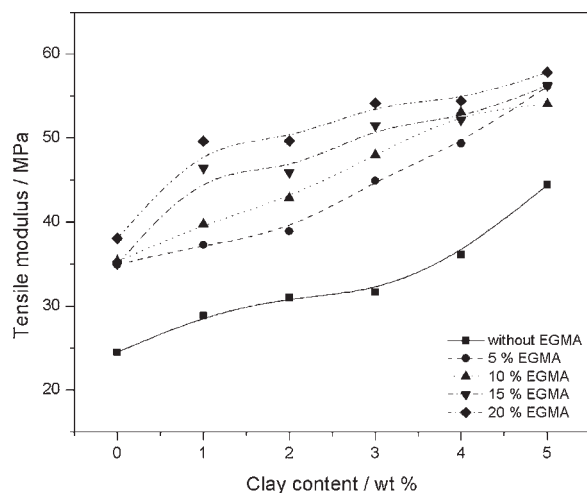


Figure 4 Tensile modulus of the EVA/EGMA–clay nanocomposites as a function of clay content.

TABLE I
Tensile Properties of the EVA/EGMA–Clay Nanocomposites

EVA/EGMA/clay (w/w)	Tensile modulus (MPa)	Tensile strength (MPa)	Tensile elongation (%)
100 : 0 : 0	24.5 ± 1.5	7.8 ± 0.2	552 ± 15
99 : 0 : 1	28.8 ± 1.0	7.5 ± 0.2	585 ± 18
98 : 0 : 2	31.0 ± 1.2	7.1 ± 0.2	552 ± 13
97 : 0 : 3	31.6 ± 1.2	6.9 ± 0.2	553 ± 9
96 : 0 : 4	36.1 ± 1.2	6.6 ± 0.2	540 ± 11
95 : 0 : 5	44.4 ± 1.3	6.4 ± 0.2	518 ± 11
95 : 5 : 0	34.9 ± 1.3	7.3 ± 0.1	520 ± 7
94 : 5 : 1	37.3 ± 1.2	6.7 ± 0.2	515 ± 14
93 : 5 : 2	38.8 ± 1.5	7.2 ± 0.1	480 ± 5
92 : 5 : 3	44.8 ± 1.4	7.1 ± 0.1	485 ± 11
91 : 5 : 4	49.3 ± 1.5	6.7 ± 0.1	479 ± 7
90 : 5 : 5	56.1 ± 0.9	6.9 ± 0.1	468 ± 16
90 : 10 : 0	35.3 ± 0.7	7.1 ± 0.1	489 ± 10
89 : 10 : 1	39.7 ± 2.5	6.6 ± 0.1	480 ± 13
88 : 10 : 2	42.8 ± 1.3	7.1 ± 0.1	468 ± 8
87 : 10 : 3	47.9 ± 1.5	6.8 ± 0.1	462 ± 5
86 : 10 : 4	53.0 ± 1.7	6.4 ± 0.1	470 ± 13
85 : 10 : 5	54.0 ± 1.3	6.5 ± 0.1	460 ± 11
85 : 15 : 0	35.0 ± 1.5	7.2 ± 0.1	456 ± 7
84 : 15 : 1	46.4 ± 0.9	6.7 ± 0.1	460 ± 12
83 : 15 : 2	43.8 ± 1.9	6.8 ± 0.1	445 ± 9
82 : 15 : 3	51.5 ± 1.5	6.5 ± 0.1	438 ± 11
81 : 15 : 4	52.1 ± 2.1	6.3 ± 0.1	430 ± 5
80 : 15 : 5	56.2 ± 1.7	6.7 ± 0.1	428 ± 6
80 : 20 : 0	38.0 ± 2.1	7.5 ± 0.1	438 ± 14
79 : 20 : 1	49.5 ± 2.0	6.7 ± 0.1	418 ± 12
78 : 20 : 2	49.6 ± 1.5	6.8 ± 0.1	402 ± 16
77 : 20 : 3	54.1 ± 1.7	6.6 ± 0.1	378 ± 10
76 : 20 : 4	54.4 ± 2.2	6.2 ± 0.1	381 ± 9
75 : 20 : 5	57.8 ± 1.7	6.7 ± 0.1	375 ± 17

contents, this did not have a substantial effect on the influence of EGMA and clay on the tensile moduli of the nanocomposites. Both of these components increased the modulus, and their coexistence in the EVA matrix had an additive effect on the tensile modulus of the nanocomposite. The reason for the increased modulus in the presence of clay was the demobilizing effect it had on the matrix chains, whereas EGMA itself had a higher modulus than EVA.

Figure 5 and Table I show the influence of the EGMA and clay contents on the tensile strengths of the nanocomposites. Clearly, both the clay and EGMA contents reduced the tensile strength of the nanocomposites, although not substantially. It was, however, interesting to note that the presence of EGMA reduced the negative influence of the clay on the tensile strength of the nanocomposites. In the absence of EGMA, the tensile strength decreased from 7.8 to 6.4 MPa with increasing clay content. However, the presence of EGMA caused the tensile strength of the samples containing 5% clay to be 6.9 MPa, which was slightly better than that for the non-EGMA-containing sample. This was probably the result of the stronger interaction between the matrix and the clay when EGMA was present.

The presence and amount of clay did not seem to have much influence on the elongation at break of the nanocomposites (Fig. 6, Table I). This value decreased slightly from 552% for pure EVA to 518% for the 95 : 5 w/w EVA–clay nanocomposite. This

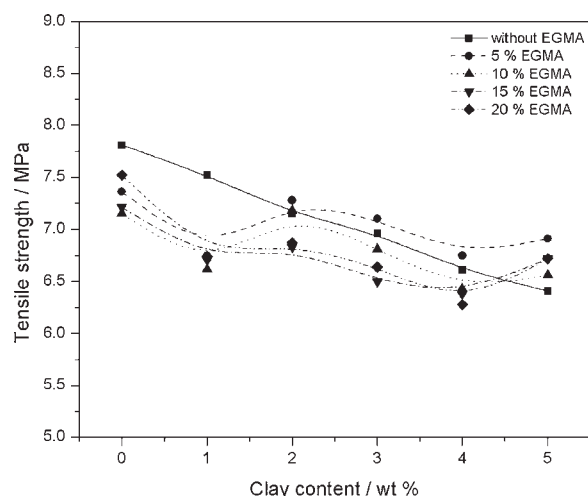


Figure 5 Tensile strength of the EVA/EGMA–clay nanocomposites as a function of clay content.

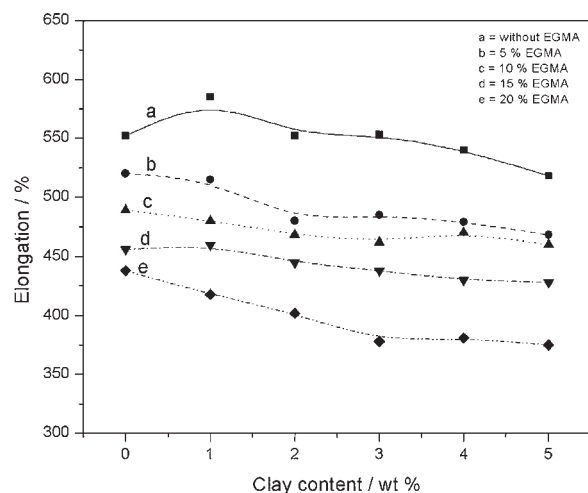


Figure 6 Elongation at break of the EVA/EGMA–clay nanocomposites as a function of clay content.

indicated that although the clay platelets reduced the EVA chain mobility, they had very little influence on the extensibility of the sample, probably because they did not substantially influence the crystallization behavior of EVA. The presence of EGMA, however, substantially reduced the elongation at break, and this value decreases with increasing EGMA content. This was probably the result of the very low elongation at break value of pure EGMA. The influence of clay on the elongation at break of the nanocomposites did not seem to be changed by the presence of EGMA.

The TGA curves of the nanocomposites (Figs. 7 and 8) show that the presence of EGMA gave rise to a higher thermal stability in the EVA–clay nanocomposites. Both figures show that the EVA–clay samples degraded at temperatures lower than pure EVA

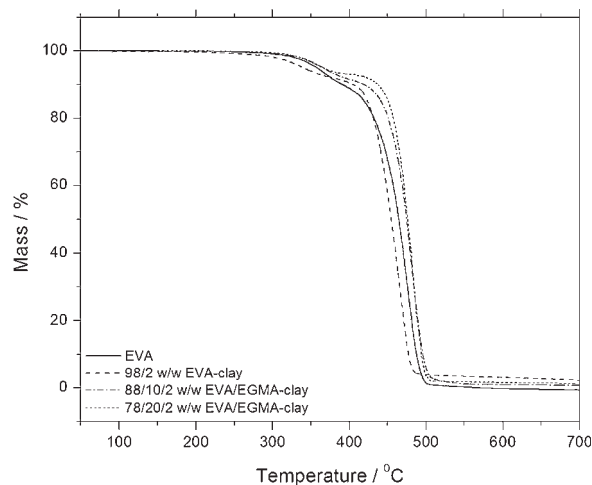


Figure 7 Influence of EGMA on the thermal stability of EVA nanocomposites containing 2% clay.

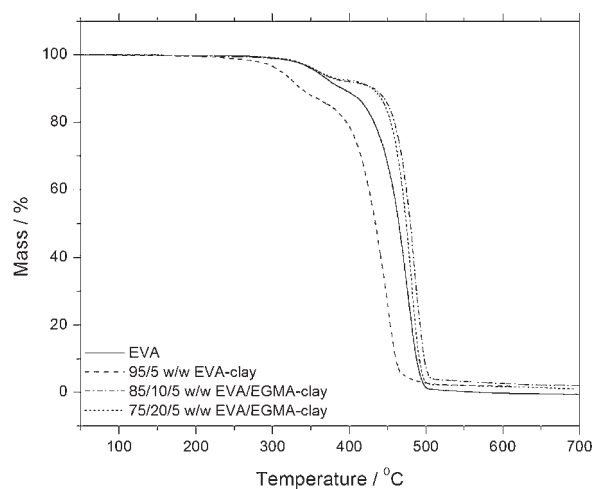


Figure 8 Influence of EGMA on the thermal stability of EVA nanocomposites containing 5% clay.

and that these temperatures decreased with increasing amounts of clay (Fig. 8). From these figures, it is, however, clear that the thermal stability of the composites was improved beyond that of pure EVA in the presence of EGMA. An increase in EGMA content increased the onset temperature of degradation of the composites, although not substantially. Because EGMA has about the same thermal stability as EVA, a probable reason for this improvement in thermal stability was the stronger interaction between EVA/EGMA and modified clay as discussed earlier. This interaction reduced the chain mobility of the matrix chains and gave rise to a reduction in the rate of free-radical transfer.

CONCLUSIONS

We studied the influence of the presence and amount of EGMA copolymer on the morphology and properties of EVA-modified clay nanocomposites. The presence of EGMA caused the strong exfoliation of the clay in the polymer matrix, although at higher clay contents, some clay layers still existed. This was probably the result of interaction between the epoxy oxygen in EGMA and the positive charge on the quaternary ammonium cation. Because EGMA mixed well with EVA, the penetration of the clay layers by the matrix chains was more effective. The more effective exfoliation, however, did not seem to substantially influence the tensile properties of the nanocomposites because the EGMA itself had a much stronger influence, which overshadowed any possible influence that the EGMA–clay interaction may have had on these properties. The thermal stability of the nanocomposites (as studied by TGA) improved in the presence of EGMA.

The authors thank Remy Bucher from iThemba Labs, Somerset-West, South Africa, and Chris van der Merwe, University of Pretoria, South Africa, for assistance with XRD and TEM analyses.

References

1. Komarneni, S. *J Mater Chem* 1992, 2, 1219.
2. Hwu, J. M.; Jiang, G. J.; Gao, Z. M.; Xie, W.; Pan, W. P. *Appl Polym Sci* 2002, 83, 1702.
3. Blumstein, A. *Bull Chim Soc* 1961, 899.
4. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. *J Mater Res* 1993, 8, 1185.
5. Lan, T.; Pinnavaia, T. J. *Chem Mater* 1994, 6, 2216.
6. Usuki, A.; Kato, M.; Okada, A.; Kurauchi, T. *J Appl Polym Sci* 1997, 63, 137.
7. Giannelis, E. *Adv Mater* 1996, 8, 29.
8. Lee, J.; Giannelis, E. *Polym Prepr* 1997, 38, 688.
9. Fisher, H.; Gielgens, L.; Koster, T. *Nanocomposites from Polymer and Layered Minerals; TNO-TPD report; 1998.*
10. Alexandre, M.; Dubois, P. *Mater Sci Eng* 2000, 28, 1.
11. Dahman, S. J. Presented at New Plastics Asia 2000, Singapore, March 2000.
12. Dong, C. L.; Lee, W. J. *J Appl Polym Sci* 1996, 61, 1117.
13. Hirata, T.; Kashivagi, T.; Brown, J. E. *Macromolecules* 1995, 18, 1410.
14. Hu, Y.; Song, L.; Xu, J.; Yang, L.; Chen, Z.; Fan, W. *Colloid Polym Sci* 2001, 279, 819.
15. Gilman, J. W. *Appl Clay Sci* 1999, 15, 31.
16. Yu, H.; Song, L. Presented at the International Fire Safety Conference (Fire Retardant Chemicals Association), March 2001.
17. Ergungor, Z.; Cakmak, M.; Batur, C. *Macromol Symp* 2002, 185, 259.
18. Dennis, H. R.; Hunter, D. L.; Chang, D.; Kim, S.; White, J. L.; Cho, J. W.; Paul, D. R. *Polymer* 2001, 42, 9513.
19. Zilg, C.; Reichert, P.; Dietsche, F.; Engelhardt, T.; Mulhaupt, R. *Kunststoffe* 1998, 88, 1812.
20. Gilman, J. W.; Kashivagi, T.; Nyden, M.; Brown, J. E. T.; Jackson, C. L.; Lomakin, S.; Giannelis, E. P.; Manias, E. In *Chemistry and Technology of Polymer Additives*; Al-Malaika, S.; Golovoy, S.; Wilkie, C. A., Eds.; Blackwell Science: Oxford, 1999.
21. Gilman, J. W.; Kashivagi, T. C. L.; Giannelis, E. P.; Manias, E.; Lomakin, S.; Lichtenhan, J. D.; Jones, P. In *Fire Retardancy of Polymers*; Le Bras, M.; Camino, G.; Bourbigot, S.; Delobel, R., Eds.; The Royal Society of Chemistry: Cambridge, England, 1998.
22. Fornes, T. D.; Paul, D. R. *Polymer* 2003, 44, 4993.
23. Yoon, P. J.; Fornes, T. D.; Paul, D. R. *Polymer* 2002, 43, 6727.
24. Chaudhary, D. S.; Prasad, R.; Gupta, R. K.; Bhattacharya, S. N. *Thermochim Acta* 2005, 433, 187.
25. Gupta, R. K.; Prasad, R.; Bhattacharya, S. N. *Proceedings of the Polymer Processing Society, 20th Annual Meeting, Ohio, 2004, paper 256.*
26. Zhang, W.; Chen, D.; Zhao, Q.; Fang, Y. *Polymer* 2003, 44, 7953.
27. Dikobe, D. G.; Luyt, A. S. *J Appl Polym Sci*, to appear.