Effect of Amine-Terminated Butadiene-Acrylonitrile/Clay Combinations on the Structure and Properties of Epoxy Nanocomposites

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ABSTRACT: The effect of the clay content and the method of its combination with amine-terminated butadiene-acrylonitrile (ATBN) on the structure and behavior of epoxy was studied. In the case of the simultaneous addition of both components, the increasing clay content had a very small effect on the size of the reaction-induced phase separation-formed particles at 5% rubber content due to predominant elimination of two major clay effects, i.e., the nucleation due to phase separation and the kinetics. As a result, both the time window between the onset of phase separation and vitrification and the viscosity at the cloud point did not change significantly. The minor change in the particle size/clay content dependences with different curing temperatures indicates that the balance between the two clay effects shifted. The corresponding study of the mechanical behavior indicated that the best balanced mechanical properties were obtained at certain clay/ATBN ratios, and thus, there was synergy between the components. Similar mechanical parameters were obtained for the application of both components in the form of ATBN/montmorillonite intercalate. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: epoxy nanocomposites; mechanical properties; microstructure

INTRODUCTION

It is well known that the low toughness of epoxy resins is typically enhanced by polymeric modifiers with various characteristics. These modifiers are initially dissolved in the uncured resin, forming a two-phase structure with varying morphology during the course of crosslinking. The application of liquid rubbers is the traditional method[1]; amine-, carboxyl-, and hydroxyl-terminated butadiene/acrylonitrile copolymers are the most often applied modifiers. The disadvantages of this method are the considerable reductions in the strength and the modulus, but the substitution of these copolymers with traditional high-modulus inorganic fillers leads to other undesirable characteristics.[2,3] Much more effective is the use of nanofillers, mostly organophilized clays.[4–8] In this case, the toughening effect is combined with advances in the nanocomposite concept, especially the high reinforcement ability already low clay contents, and thus, there is a much less adverse effect on the toughness. Lee et al.[4] observed an increase in the impact strength of epoxy/carboxyl-terminated butadiene-acrylonitrile (CTBN) upon addition of small amount of clay. Analysis of the effect of mixing order indicated the mixing order affected the clay localization and had a slight effect on the mechanical behavior. Pugh and coworkers[5] observed increases in toughness, strength, and modulus with increasing clay content (up to 6%) for epoxy containing 20% CTBN cured with boron trifluoride monoethylamine, but the strength and modulus were reduced significantly in comparison with neat resin (also containing clay). An increase in the CTBN particle size due to the presence of the clay was observed.

An increasing number of studies indicate that the increased hydrophobicity of clay and thus its interaction with the matrix can be achieved by modification of the montmorillonite (MMT) using various aminated polymer-based polycations[9–15] including aminated liquid rubbers, especially polybutadiene[16]; aminated nitrile rubbers such as ATBN[17,18]; and aminated polyoxypropylene (APOP) and polyoxyethylene.[19–22] Most previous studies were devoted to the effect of the polymer-modification of MMT on its degree of dispersion (exfoliation); the successful application of APOP-modified MMT in epoxies[10,23–26] indicates that polymer-intercalated clay may represent an effective type of toughener. Lin and coworkers[23] observed the self-pinning formation of lamellar arrays and enhanced behavior in the case of low-T_g network. A study by Salahuddin[24] and our

TABLE I
Mechanical Behavior of Epoxy/(ATBN/MMT Intercalate) Systems

Composition	σ (MPa)	ε (%)	E (MPa)	a (kJ/m^2)
Epoxy	2783.0	75.2	4.03	25.9
/C30 98.5/1.5	2656.0	48.7	2.4	27.3
/ATBNX16/MMT (77/23) intercalate 93.8/6.2 *	2870.0	62.6	3.2	20.2
/ATBNX21/MMT (82/18) intercalate 92.3/7.7 *	2708.0	57.2	3.1	18.3
/ATBNX35/MMT (72/28) intercalate 94.8/5.2 *	2713.0	58.6	3.0	23.4
/ATBNX35/MMT (80/20) intercalate 93/7 *	2892.0	55.1	2.6	13.0
/ATB/MMT (78/22) intercalate 97.5/6.5 *	2630.0	43.3	2.1	21.4
/ATBNX45/MMT (88/12) intercalate **	2600.0	57.9	3.2	32.3
/ATBNX45/MMT (88/12) intercalate 89.2/10.8 *	2527.0	63.9	12.8	36.6
/ATBNX45/MMT (88/12) intercalate ***	2290.0	54.6	4.1	32.6

Content of intercalate corresponding to * 1.5% of MMT, **1% and ***2%.

recent study[26] have demonstrated the effectiveness (simultaneous improvement in all basic mechanical properties) of these structures in high-T_g epoxy. In the case of an ATBN/MMT intercalate, Baer and co-workers successfully prepared even highly MMT-filled ATBN by ionic exchange.[17,18] Because of the significant effectiveness of ATBN as an impact modifier of epoxy even at low contents,[27] the objective of this work is to study various ATBN/clay combinations including the application of protonated ATBN-intercalated MMT. The goal is to evaluate the reinforcing and toughening effects together with potential to influence the reaction-induced phase separation-formed structure.

EXPERIMENTAL

Materials

Cloisite Na$^+$-layered silicates with a cation exchange capacity of 92.6 meq/100 g and Cloisite C30 B (MMT modified with methyl tallow bis(2-hydroxyethyl) quaternary ammonium chloride) were obtained from Southern Clay Products, Inc. (Texas, USA). Amine-terminated butadiene-acrylonitrile (ATBN) copolymers with amine equivalent weights of 1200 (ATBN 1300X21), 900 (ATBN 1300X16), 700 (ATBN 1300X35), and 1850 (ATBN 1300X45) were obtained from Nanoresins AG, Germany. Diglycidyl ether of bisphenol A (DGEBA)-based epoxy resin Epilox A19-02 (Leuna-Harze GmbH, Germany) and cycloaliphatic amine hardener Laromin C260 (BASF SE, Germany).

Preparation of ATBN-MMT intercalate

A suspension of 5 g of Cloisite Na$^+$ in 500 mL of water was stirred for 90 min at 70°C. An appropriate amount (see composition in Table I) of amine-terminated butadiene-acrylonitrile copolymer, e.g., 34 g in the case of ATBN 1300X45, was dissolved in 100 mL of tetrahydrofuran. A half-equivalent of HCl was

added to the solution and stirred for 90 min at room temperature. This solution of protonated ATBN was then poured into the suspension of Cloisite Na$^+$ and stirred for 300 min at 70°C. The precipitated adduct was then collected by filtration. The adduct was then dried at 60°C for 24 h.

Preparation of epoxy samples

The epoxy nanocomposites were prepared using a rotary mixer with an evacuated chamber. Clay and ATBN were mixed with epoxy resin at 70°C for 60 min. A curing agent was added, and the mixing continued for 5 min at the same temperature. The ATBN/MMT intercalate was first dissolved in ethyl acetate. This solution was added to the epoxy resin, which was then mixed for 60 min at 70°C. The solvent was removed by simultaneous evacuation of the mixer. Obtained mixtures were cast to prepare a test specimen (dog-bone) in a silicone mold, and Charpy bars were prepared in a steel mold. The curing regime was 2 h at 70°C (in the mold) and then 6 h at 120°C after removing the specimen from the mold.

Testing

Tensile strength tests were carried out at 22°C using an Instron 5800 apparatus at a crosshead speed of 1 mm/min according to ISO 527. At least, eight specimens were tested for each sample. The stress at break, σ_b (variation coefficient <2%), and Young's modulus, E (variation coefficient <5%), were evaluated. The impact strength was measured using a Zwick hammer (Charpy, ISO 179) with an energy of 4 J (variation coefficient <11%). The reported values are the averages of 12 measurements.

Dynamic mechanical analysis (DMA) was carried out with an ARES apparatus (Rheometric Scientific, Piscataway, NJ). Chemorheological experiments to characterize the evolution of the dynamic viscosity and the complex shear modulus during curing at 70°C (the observation at 20°C was omitted due to
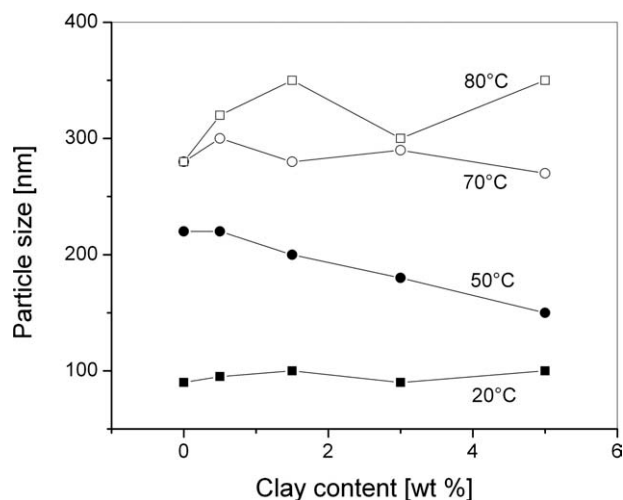
Figure 1 Effect of clay on the particle size of the dispersed phase in epoxy containing 5% ATBN cured at 20°C ■, 50°C ●, 70°C ○, or 80°C □.

the slow curing rate) were conducted in the parallel-plate geometry using an oscillatory shear deformation at a frequency of 6.28 rad/s (1 Hz) using the same equipment (estimated variation coefficient of viscosity at gel point is 5%). Cloud point (CP) evaluation (variation coefficient <2%) at 70°C was based on light transmission measurements using an in-house-developed apparatus.

Morphological observations

The phase structure of cryofractured samples was observed using scanning electron microscopy (SEM). The elastomer phases were etched with acetone for 1 h. The size of the dispersed particles was evaluated from the micrographs (from 5 representative pictures containing ∼ 100 particles) using a Mini Mop image analyzer (Kontron Co., Germany).

For transmission electron microscopy (TEM), ultra-thin (60 nm) sections were cut using an Ultracut UCT (Leica) ultramicrotome. Wide-angle X-ray diffraction (WAXS) patterns were obtained with an HZG/4A powder diffractometer (Freiberger Präzisionsmechanik GmbH, Germany) and monochromatic CuKα radiation. The CP was determined from light transmission measurements.

RESULTS AND DISCUSSION

Effect of clay on the particle size of ATBN

As shown in Figure 1, the particle size at various curing temperatures did not depend significantly on the clay content. The predominant trend was a slight decrease in particle size with increasing clay content which was most remarkable at 50°C. In contrast, there was a significant dependence of the particle

size on the curing temperature, with an increase in size from ∼ 100 nm at 20°C to ∼ 300 nm at 80°C. This increase undoubtedly corresponds to phase separation via nucleation and growth mechanism expected for the low concentrations of the second phase polymer[28–30] that we used. A similar increase in the particle size with increasing temperature has been reported for analogous epoxy systems by others.[28,31,32] The increase of particle size with increasing temperature indicates that the lower viscosity at the CP[31] at elevated temperature is the primary contributor to particle growth. To explain the effect of clay on the particle size, chemorheological measurement was performed at 70°C. From Figure 2, which shows the effect of clay on the course of curing as expressed by the gelation time, it is obvious that the presence of clay induced a slight acceleration of curing[33] and a shortening of the time to reach the CP due to the nucleation effect of the clay,[34] with nearly parallel course of both dependences. Our results show that the two main factors influencing the particle size, the time window (Fig. 3) between the onset of phase separation and the gelation[28] and the viscosity at the CP[31] (Fig. 2), are not significantly influenced by the clay content. This result corresponds with the observed negligible influence of clay on the particle size at 70°C (Fig. 1). The importance of this parameter was documented in a previous study[26] in which the viscosity of an epoxy/APOP/clay system at the CP changed significantly with varying clay content (5x lower in the range from 0 to 5% of clay), with the particle size ranging from 200 to 600 nm.

The different dependences of particle size on clay content at 50°C and 80°C indicate a shift in the equilibrium between the above-mentioned clay-induced effects resulting in change in time available for particle growth caused by temperature. Because of the fact that the chemorheological measurements were
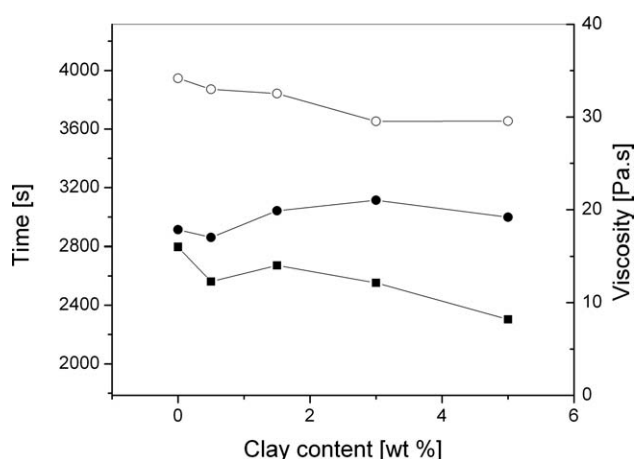

Figure 2 Effect of clay on the gelation time ○, the time to reach the cloud point ■ and the related viscosity ● at 70°C.
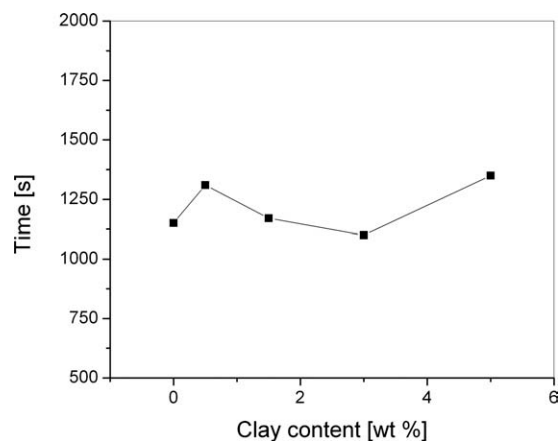
Figure 3 Dependence of the time available for particle growth (interval between the cloud point and gelation) on the clay content.

performed at 1 Hz, which does not allow the capture of the conditions of the quiescent state under which the phase separation takes place, and taking into account the possible shear thinning of the nanocomposites, the corresponding viscosity at the lowest possible shear rate at 20°C and 70°C was measured (Fig. 4). The results show that, in contrast to our expectation, there was no marked difference in the viscosity at low frequency for the systems containing 5% ATBN with and without added clay. In addition, the clay had an insignificant effect on the particle size (Fig. 1) and confirms the relevancy of the data obtained at the higher frequency.

Effect of clay on mechanical properties

The dependence of the mechanical properties of an epoxy containing 5% ATBN on the clay content is shown in Figure 5(a,b). The addition of a small amount of clay simultaneously enhanced the strength and the toughness, with a maximum enhancement at 1.5% clay content, whereas the modulus increased
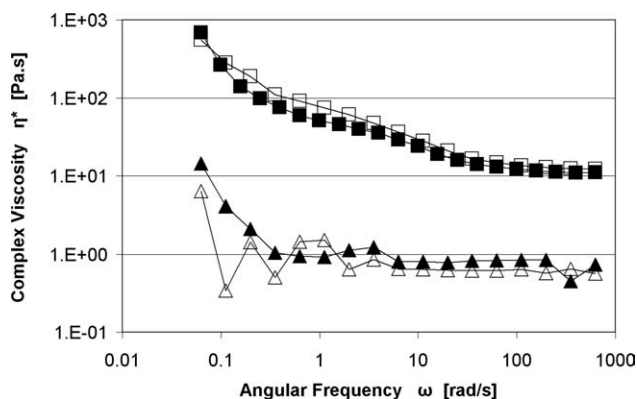

Figure 4 Viscosity of the epoxy ATBN/C260 system at 20°C with ■ and without □ clay and at 70°C with ▲ and without △ clay at a low shear rate.
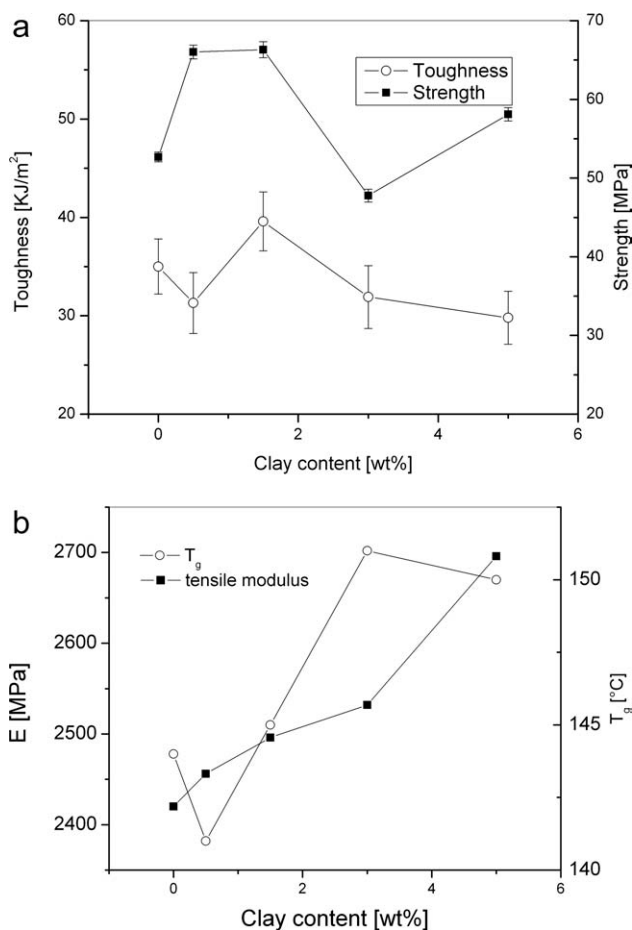
Figure 5 Dependence of the properties of epoxy containing 5% ATBN on the clay content: (a) stress at break and toughness, (b) tensile modulus and glass transition temperature (T_g).

with increasing clay content as expected. In this case, the contribution of the clay is not only reinforcement; the increase in the T_g [Fig. 5(b)] induced by the clay, indicating increased density of network formed, should also be taken into account. The simultaneous
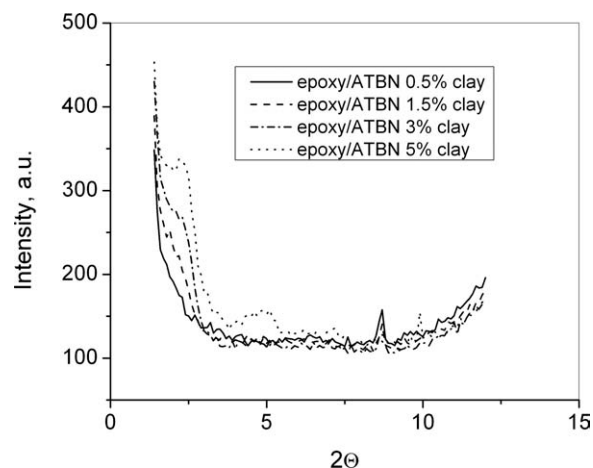

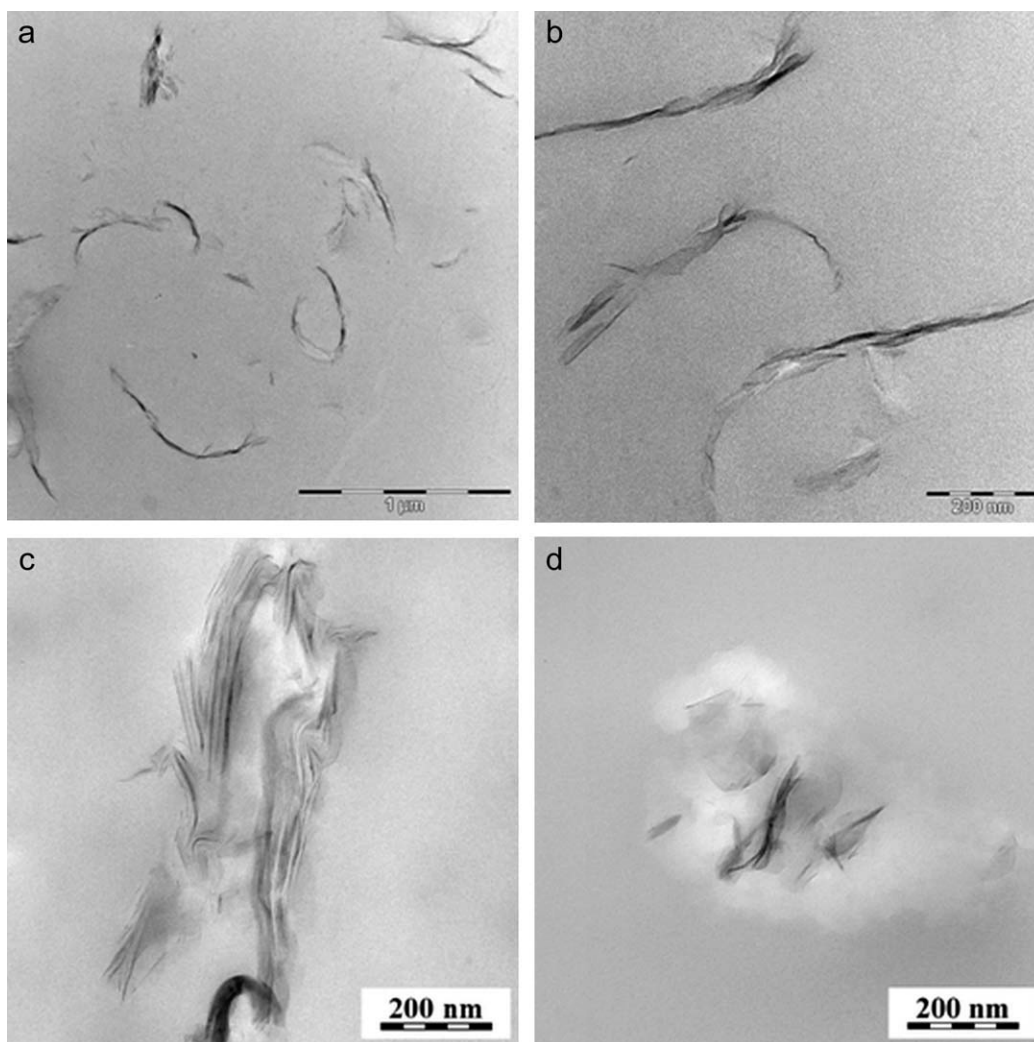**Figure 6** WAXS patterns of epoxy containing 5% ATBN and 0–5% MMT.

Figure 7 TEM of (a) epoxy/(ATBNX16/MMT intercalate), (b), and (c) ATBNX45/MMT intercalate.

increase in the magnitudes of all basic mechanical properties at 1.5% clay content indicates a synergy between the clay and the dispersed phase found
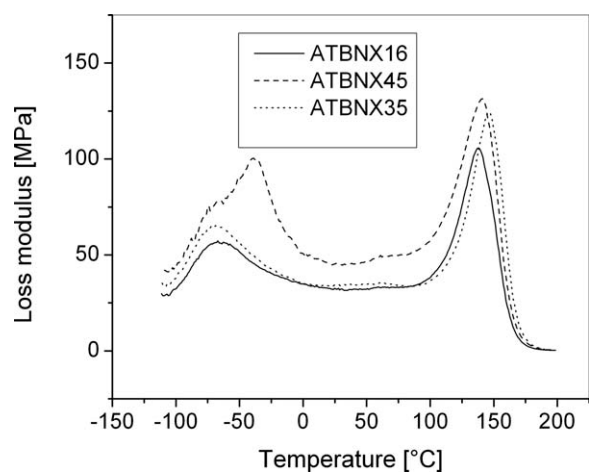

Figure 8 DMA of epoxy containing ATBN/MMT intercalates.

both in analogous epoxy[4,6,35] and thermoplastic-based nanocomposites.[36,37]

Tentatively, we expect that this synergy is caused by almost undetectable changes in network parameters.[38] In the WAXS patterns (Fig. 6), there are obvious negligible differences in the degree of clay dispergation, and the difference in the peak intensity corresponds only with growing clay content. The TEM observations did not reveal any observable difference in the structure (not shown) including

TABLE II
Interlamellar Distance of (A) a Single ATBN-MMT Adduct and (B) an Epoxy Nanocomposite-Containing Adduct

	d-spacing (Å)	
Adduct composition	A	B
ATBNx16/MMT (77/23)	14.7	14.1
ATBNx35/MMT (72/28)	14.2	14.1
ATBNx45/MMT (88/12)	15.2	14.4

TABLE III
Effect of the ATBN/Clay Intercalate on the Properties of Epoxy/ATBN

Composition	σ (MPa)	ε (%)	E(MPa)	a (kJ/m^2)
Protonated ATBNx16 93.5/5/1.5	2560.0	52.1	2.7	30.9
ATBN/(ATBNx45/MMT (88/12) intercalate) 84.2/5/10.8 (1.5% MMT)	1480.0	48.6	7.0	34.0
ATBNx16/C30 /5/1.5	2496.0	66.3	4.3	39.6

particle size (Fig. 1). Moreover, the particle size seems to be in the interval of practical independence of toughness.[38] In addition, the temperature dependence of the loss modulus indicates negligible differences in the dumping characteristic, whereas the increase in T_g with increasing clay content was almost linear [Fig. 5(d)]. From the results presented in Table III, it is obvious that the increase in the affinity of ATBN for the clay via protonation did not lead to better properties or to a change in the structure (not shown).

Effect of ATBN-modified clay on structure and behavior

Based on the results presented in Table I showing effect of clay modified with different types of ATBN on epoxy behavior, it is obvious that for every type of ATBN, the best overall properties were observed for the composition of the intercalate prepared using stoichiometric ratio of clay and the half protonated ATBN. The most favorable properties were observed for the intercalate of clay with ATBNX45, which when added to epoxy at a concentration corresponding to 1.5% of neat clay caused an increase in the toughness over that of the neat epoxy and an increase in the strength over that of the nanocomposite with C30 with a comparable value for the tensile modulus. From the data presented in Figure 8 showing the temperature dependence of the loss modulus, it is obvious that greatest toughness of the ATBNX45 intercalate seems to be a consequence of a more intensive dumping peak in comparison with other intercalates. Based on the DMA, it is also obvious that the small increase in the T_g over that of the unmodified epoxy/clay nanocomposite (+1°C) and 5°C over the neat epoxy occurs for the ATBNX45 intercalate. Overall, the effect of ATBN clay intercalates on the mechanical properties was comparable with analogous system with simple combination of components [Fig. 5(a–c)] (Table I). This result is different than that for an analogous APOP system[26] for which the best properties were recorded for the intercalate.

TEM observations of the epoxy ATBNX16 clay intercalate (Fig. 7) revealed a lamellar structure formation similar to that of the analogous APOP system.[23,26] The fact that the best properties were found for epoxy/ATBNX45-modified clay (Fig. 7), which

has a less organized blended structure, represents a further difference between the APOP- and ATBN-intercalated clays. Another difference between the APOP and ATBN intercalates is obvious from the WAXS patterns, which indicated that all ATBN-modified clays had relatively low interlamellar distances (d-spacing) of 15 Å (Table II), whereas in case of APOP with the analogous chain length much greater d-spacing of 90 Å was found.[20,26] This narrow spacing is in agreement with that found by Akelah et al.,[18] which suggests that there is horizontal packing of the ATBN chains in this type of modified clay. Because of the fact that the main difference between ATBNX16 and ATBNX45 is the lower functionality of the latter, the reason for the different arrangements of the intercalates in epoxy (Fig. 7) is hypothesized to be the different structures of the intercalates and possibly the lower content of amino groups in ATBNX45.

From the data presented in Table III, it is obvious that the combination of 5% liquid rubber and the ATBN clay intercalate resulted in worse mechanical properties. This result is another difference from the analogous APOP systems.[26]

CONCLUSIONS

The addition of clay to epoxy containing 5% ATBN led to synergistic effects on the mechanical behavior at 1.5% clay, similar to analogous systems published. At the same time, the influence of the clay on particle size was negligible because of the mutual elimination of the two main factors influencing the phase separation, that is, the time to reach the CP and the acceleration of curing. As a result, both the viscosity at the CP and the time window available for particle growth between the onset of phase separation and gelation were nearly unchanged. Both the simple combination of ATBN and clay and the application of corresponding intercalate of ATBN with clay led to an enhanced balance of the mechanical properties of the epoxy nanocomposite. The effect of mentioned methods of clay/ATBN combination was comparable.

References

1. Riew, C. K.; Kinloch, A. J. Adv Chem 1996, Ser 252, 1.
2. Bandyopadhyay, S.; Silva, V. M.; Low, I. M.; Mai, W. M. Plast Rubber Proc Appl 1988, 10, 193.

3. Kinloch, A. J.; Maxwell, D. L.; Young, R. J. J Mater Sci 1983, 18, 208.
4. Lee, H.-B.; Kim, H.-G.; Yoon, K.-B.; Lee, D.-H.; Min, K.-E. J Appl Polym Sci 2009, 113, 685.
5. Liu, W.; Hoa, S. V.; Pugh, M. Polym Eng Sci 2004, 44, 1178.
6. Bakar, M.; Kostrzewa, M.; Hausnerova, B.; Sar, K. Adv Polym Tech 2010, 29, 237.
7. Lee, K. Y.; Kim, K. Y.; Huang, I. R.; Cho, Y. S.; Hong, C. H. Polym Test 2010, 29, 139.
8. Fröhlich, J.; Thomann, R.; Mühlhaupt, R. Macromolecules 2003, 36, 7205.
9. Zhang, J.; Manias, E.; Wilkie, C. A. J Nanosci Nanotechnol 2008, 8, 1597.
10. Zilg, C.; Mühlhaupt, R.; Finter, J. Macromol Chem Phys 1999, 200, 661.
11. Zaman, I.; Le, Q. H.; Kuan, H. Ch.; Kawashima, N.; Luong, L.; Gerson, A.; Ma, J. Polymer 2011, 52, 497.
12. Ha, Y. H.; Kwon, Y.; Breiner, T.; Chan, E. P.; Tzianetopoulou, T.; Cohen, R. E.; Boyce, M. C.; Thomas, E. L. Macromolecules 2005, 38, 5170.
13. Hoffmann, B.; Dietrich, C.; Thomann, R.; Friedrich, C.; Mühlhaupt, R. Macromol Rapid Commun 2000, 21, 57.
14. Zhang, J.; Wilkie, C. A. Polymer 2006, 47, 5736.
15. Seo, W. J.; Sung, Y. T.; Han, S. J.; Kim, Y. H.; Ryu, O. H.; Lee, H. S.; Kim, W. N. J Appl Polym Sci 2006, 101, 2879.
16. Su, S.; Jiang, D. D.; Wilkie, C. A. Polym Degrad Stab 2004, 84, 279.
17. Akelah, A.; Salahuddin, N.; Hiltner, A.; Baer, E.; Moet, A. NanoStruct Mater 1994, 4, 965.
18. Akelah, A.; Salah El-Deen, N.; Hiltner, A.; Baer, E.; Moet, A. Mater Lett 1995, 22, 97.
19. Jan, I. N.; Lee, T. M.; Chiou, K. C.; Lin, J. J. Ind Eng Chem Res 2005, 44, 2086.
20. Lin, J. J.; Chou, C. C.; Shieu, F. S. Macromolecules 2003, 36, 2187.
21. Lin, J. J.; Chou, C. C.; Lin, J. L. Macromol Rapid Commun 2004, 25, 1109.
22. Lin, J. J.; Cheng, I. J.; Chu, C. C. Polym J 2003, 35, 411.
23. Chu, C. C.; Lin, J. J.; Shiu, C. R.; Kwan, C. C. Polym J 2005, 37, 239.
24. Salahuddin, N. A. Polym Adv Technol 2004, 15, 251.
25. Malucelli, G.; Bongiovanni, R.; Sangermano, M.; Ronchetti, S.; Priola, A. Polymer 2007, 48, 7000.
26. Kelnar, I.; Rotrekl, J.; Kaprálková, L.; Hromádková J. J Appl Polym Sci, submitted.
27. Chikki, N.; Fellahi, S.; Bakar, M. Eur Polym J 2002, 38, 252.
28. Chen, J. L.; Chang, F. C. Polymer 2001, 42, 2193.
29. Li, J.; Du, Z.; Li, H.; Zhang, C. J Polym Sci B 2010, 48, 2140.
30. Nunes, P. N.; Inoue, T. J Membr Sci 1996, 111, 93.
31. Verchere, D.; Pascault, J. P.; Sautereau, H.; Moschiar, S. M.; Riccardi, C. C.; Williams, R. J. J. J Appl Polym Sci 1991, 42, 701.
32. Olmos, D.; Loayza, A.; González-Benito, J. J Appl Polym Sci 2010, 117, 2695.
33. Bao, S.; Shen, S.; Liang, G.; Zhai, H.; Xu, W.; He, P. J Appl Polym Sci 2004, 92, 3822.
34. Lee, M.; Lee, K.; Min, B. H.; Kim, J. H. J Appl Polym Sci 2010, 117, 49.
35. Mirmohseni, A.; Zavareh, S. J Polym Res 2010, 17, 191.
37. Alyamac, E.; Yilmazer, U. Polym Compos 2007, 28, 251.
38. Bagheri, R.; Marouf, B. T.; Pearson, R. A. J Macromol Sci C 2009, 49, 201.