

Effect of Poly(oxyalkylene)amines on Structure and Properties of Epoxide Nanocomposites

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ABSTRACT: A shortcoming of most polymer nanocomposites is relatively low toughness. An effective method to eliminate this is the use of a suitable combination of polymeric impact modifiers with organoclay, which may impart synergistic effects on the mechanical behavior of both thermoplastic and thermoset matrix nanocomposites. This work focuses on the effect of various combinations of amine-terminated (APOP) and hydroxyl-terminated poly(oxypropylene) (POP) and layered silicates on the structure and mechanical behavior of epoxy nanocomposites. The combination of APOP and POP with 0.5–5% wt % of organoclay leads to some compositions that produce well balanced mechanical behavior of the epoxy nanocomposite. The higher toughening effectiveness of APOP/montmorillonite (MMT) compared with that of POP/MMT is a consequence of formation of blended domains consisting of clay tactoids and fine APOP inclusions. An increase in the dispersed particle size with clay content

was observed to be a consequence of more significant clay-induced nucleation of phase separation at the expense of clay-induced accelerated curing. The best mechanical behavior was observed for materials using an adduct of APOP and MMT, which was obtained using the ion exchange of sodium ions of MMT by protonated APOP. The enhanced mechanical behavior was due to the formation of nanosized planar arrays by self-pilling of elastomer-modified clay and the corresponding increase in the T_g of the epoxy. The structure/property relationships of these systems indicate that this type of clay polymer combination provides an effective way of modifying the mechanical behavior of epoxy nanocomposites. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2755–2763, 2012

Key words: epoxy nanocomposites; mechanical properties; microstructure

INTRODUCTION

The degree of intercalation and/or delamination of layered silicates in melt-mixed thermoplastic and epoxy matrix nanocomposites depends critically on polymer structure and the type of clay organophilization.^{1–3} The increased hydrophobicity of clay and thus its interaction with the matrix can be achieved mostly by ionic exchange with various compounds. The use of various oligomers and polymers is also advantageous.^{4–8} Lin et al.^{9,10} have shown the promising potential of polymer/clay adducts, such as poly(oxypropylene)amine (APOP) and analogous polyamine/montmorillonite (MMT), for exfoliation in an epoxy matrix accompanied by the formation of ordered nanosheet-like structures. These adducts can also self-assemble on solid surfa-

ces into microscale fibrous bundles.^{11,12} In various applications using these adducts in epoxy systems with different curing agents, in general, only the hardness and the coefficient of thermal expansion have been tested.^{10,13} More detailed characterization of mechanical properties has been done in systems cured with Jeffamine D 2000,¹⁴ i.e., in an epoxy with a low- T_g elastic network possessing very poor mechanical properties. Sallahuddin¹⁵ has observed enhanced hardness and toughness of an epoxy with an Jeffamine T5000/MMT adduct cured with Jeffamine D 230. This result, among others, indicates that clay modification with a higher-molecular-weight poly(oxypropylene) (POP) di(tri)amine, itself producing a toughening effect in epoxies,¹⁶ represents a type of nanofiller/toughener combination, which in many cases leads to favorable mechanical behavior.^{17–21} This is also demonstrated in our study of the polyamide 6/ethylene propylene rubber/MMT system,^{22–24} in which clay combined with a dispersed polymer may not affect, for example, the particle size or phase inversion only and may allow the formation of complex structures to occur. For example, a core-shell structure consisting of an elastomer core with a shell formed by clay platelets

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enhances the toughening efficiency²⁴ and leads to the improvement of all basic mechanical parameters. A similar synergy has been observed in analogously toughened epoxy nanocomposites.^{17–19}

This work is focused on the application of APOP/MMT adducts in epoxy systems with high crosslink density (high T_g). Namely, the effect of the degree of MMT modification with APOP, and its chain length on the structure and properties of the resulting nanocomposites were taken into account. The effect of an adduct on the structure and properties of epoxy systems with both hydroxyl-terminated POP and APOP was evaluated. A comparison of the adduct with a single combination of clay and POP was made.

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 acquired from Southern Clay Products, TX. POP with molecular weight (mw) of 4000 g/mol was obtained from Sigma Aldrich. APOP, monoamines Jeffamines M600 (mw 600 g/mol), M2005 (mw 2000 g/mol), and M2070 (mw 2000 g/mol); and diamines Jeffamines D230 (mw 230 g/mol), D400 (mw 400 g/mol), D2000 (mw 2000 g/mol), and D4000 (mw 4000 g/mol) were supplied by Huntsman Inc. (TX). Diglycidyl ether of bisphenol A-based epoxy resin Epilox A19-02 and the cycloaliphatic amine hardener Laromin C260 were obtained from Leuna-Harze GmbH, Germany and BASF SE, Germany, respectively.

Preparation of APOP-MMT adduct

A suspension of 5 g of Cloisite Na⁺ in 500 ml of water was stirred for 90 min at 70°C. An appropriate amount of APOP, e.g., 23 g in the case of APOP 4000, was dissolved in 100 ml of deionized water. A half-equivalent amount of HCl was added and stirred for 90 min at room temperature. This solution of protonized APOP was then poured into the suspension of Cloisite Na⁺ and stirred for 300 min at 70°C. The precipitated adduct was then filtered and washed with deionized water. The adduct was then dried at 60°C for 24 h.

Preparation of epoxy samples

Epoxy samples were prepared using a rotary mixer with an evacuated chamber. All samples were mixed at 70°C. Clay was added first to the epoxy resin and mixed for 60 min, and then POP/APOP was added

and mixed for 10 min. A curing agent was added and mixed after cooling to ambient temperature. Adduct APOP/MMT was first dissolved in ethyl acetate. The ethyl acetate solution was added to epoxy resin and mixed for 60 min at 70°C. The solvent was removed using an evacuating mixer for 100 min. The prepared nanocomposite was cast to prepare a test specimen (dog-bone) in a silicone mold, whereas Charpy bars were prepared in a steel mold. The curing regimen was 24 h at room temperature, then 2 h at 70°C and finally 6 h at 120°C.

Testing

Tensile tests were carried out at 22°C using an Instron 5800 apparatus at a crosshead speed of 1 mm/min. At least eight dog-bone specimens (working part: cross section $4 \times 1.5 \text{ mm}^2$, length 40 mm) were tested for each sample. The stress at break, σ_b (variation coefficient < 2%), elongation at break, ε_b (variation coefficient < 5%), and Young's modulus, E (variation coefficient < 6%), were evaluated. Impact strength was measured using a Zwick hammer (Charpy, specimens $4 \times 10 \times 80 \text{ mm}^3$) with energy of 4 J. The reported values are the averages of 10 measurements (variation coefficient 10–12%).

Dynamic mechanical analysis (DMA) was carried out with an ARES apparatus (Rheometric Scientific, Piscataway, NJ). Chemorheological experiments, which were conducted to characterize the evolution of the dynamic viscosity and complex shear modulus during curing at 70°C (the observation at 20°C was omitted due to slow curing rate) were performed in a parallel-plate geometry using an oscillatory shear deformation at a frequency of 6.28 rad/s (1 Hz) using the same equipment. Cloud point (CP) evaluation (effect of clay on the onset of phase separation) at 20°C and 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. The elastomer phases were etched with acetone for 1 h. The size of the dispersed particles was evaluated from the micrographs using a Mini Mop image analyzer (Kontron, Germany). For transmission electron microscopy (TEM), ultrathin (60 nm) sections were cut using an Ultracut UCT (Leica) ultramicrotome. Wide-angle X-ray diffraction patterns were obtained with a powder diffractometer HZG/4A (Freiberger Präzisionsmechanik GmbH, Germany) and monochromatic CuK α radiation. The CP was evaluated by light transmission measurements.

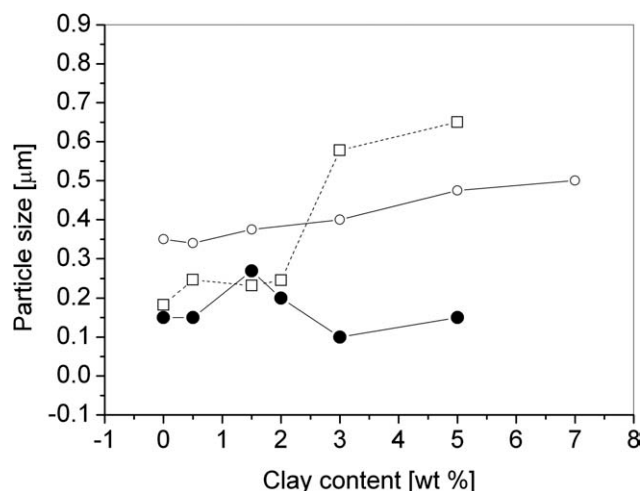


Figure 1 Effect of clay on particle size of dispersed phase in epoxy containing 5 % of APOP ● and POP □ cured at 20°C and APOP ○ at 70°C.

RESULTS AND DISCUSSION

Effect of clay on morphology of epoxy/POP

The dependence of particle size on clay content (Fig. 1) shows a clear increase in the dimensions of reaction-induced phase separation-formed²⁵ POP inclusions with clay content. At the same time, the particle size (and most probably its dependence on the clay content) is also significantly influenced by the curing temperature and functionality of POP. The effect of temperature on the particle size is documented namely by different course of this dependence (Fig. 1) for APOP at ambient temperature and at 70°C and also by larger sizes of particles formed at higher temperature. With respect to the low content of POPs, which is apparently below the critical volume fraction, the phase separation that gives rise to the structure of POP particles in epoxy matrix proceeds by nucleation and a growth mechanism.^{26,27}

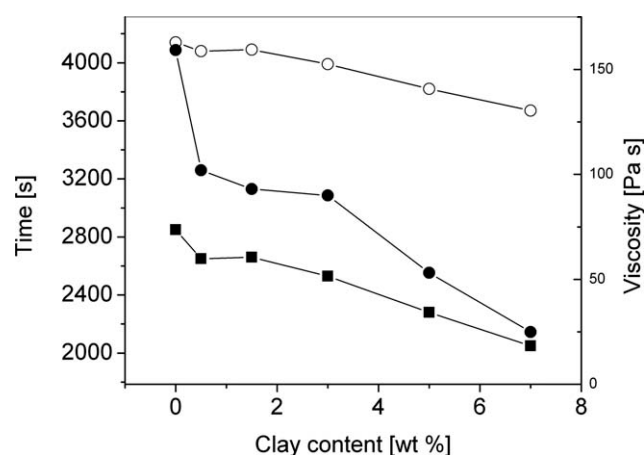


Figure 2 Effect of clay on gelation time ○ and time to CP ■ and related viscosity ● at 70°C.

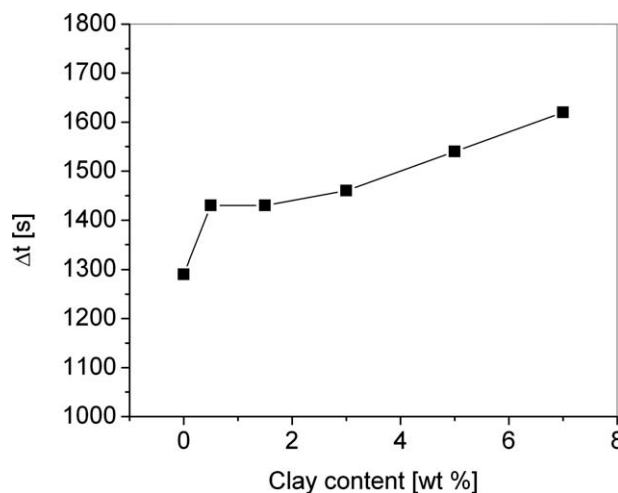


Figure 3 Dependence of time available for particle growth (interval between CP and gelation) on clay content.

Figure 1 shows further evidence of a significant increase in particle size with clay content found for nonreactive POP compared with APOP.

To explain this behavior, the effect of clay on the most significant factors affecting reaction-induced phase separation, i.e., gelation time (curing rate) at 70°C,²⁸ time to CP at 20°C and 70°C and related viscosity at CP,²⁹ were evaluated. The time to CP is influenced by the nucleation effect induced by the clay³⁰ and possibly by the changed miscibility.¹⁹ The results in Figure 2 show a nearly parallel decrease of all parameters with clay content, slightly more significant in the case of time to CP and related viscosity (Figs. 2 and 3). Due to the contradictory effect of faster crosslinking and earlier nucleation on particle size, the increase in particle size in spite of accelerated gelation indicates a stronger influence of the nucleation effect induced by clay, which causes phase separation at lower conversion and thus lower viscosity (Fig. 2) and easier diffusion of dissolved POP. The earlier onset of phase separation also prolongs the time available for particle growth²⁶ (till vitrification/gelation) (Fig. 3). The importance of lower viscosity at CP (Fig. 2) is also confirmed by the fact that particle size increases despite the expected hindrance of APOP diffusion by interaction with clay and the expected presence of an in situ-formed epoxy/APOP compound.¹⁶ These factors are undoubtedly the reason larger particle sizes are found at 70°C than at 20°C (due to lower viscosity at 70°C²⁹ and expected lower clay/APOP interactions). The more significant increase in particle size with clay content for POP (Fig. 1) corresponds to the increased degree of exfoliation (Fig. 5) of the clay in the epoxy/POP4000 matrix compared with epoxy/APOP, which leads to a more significant nucleation effect. The expected reduced interaction of POP with clay

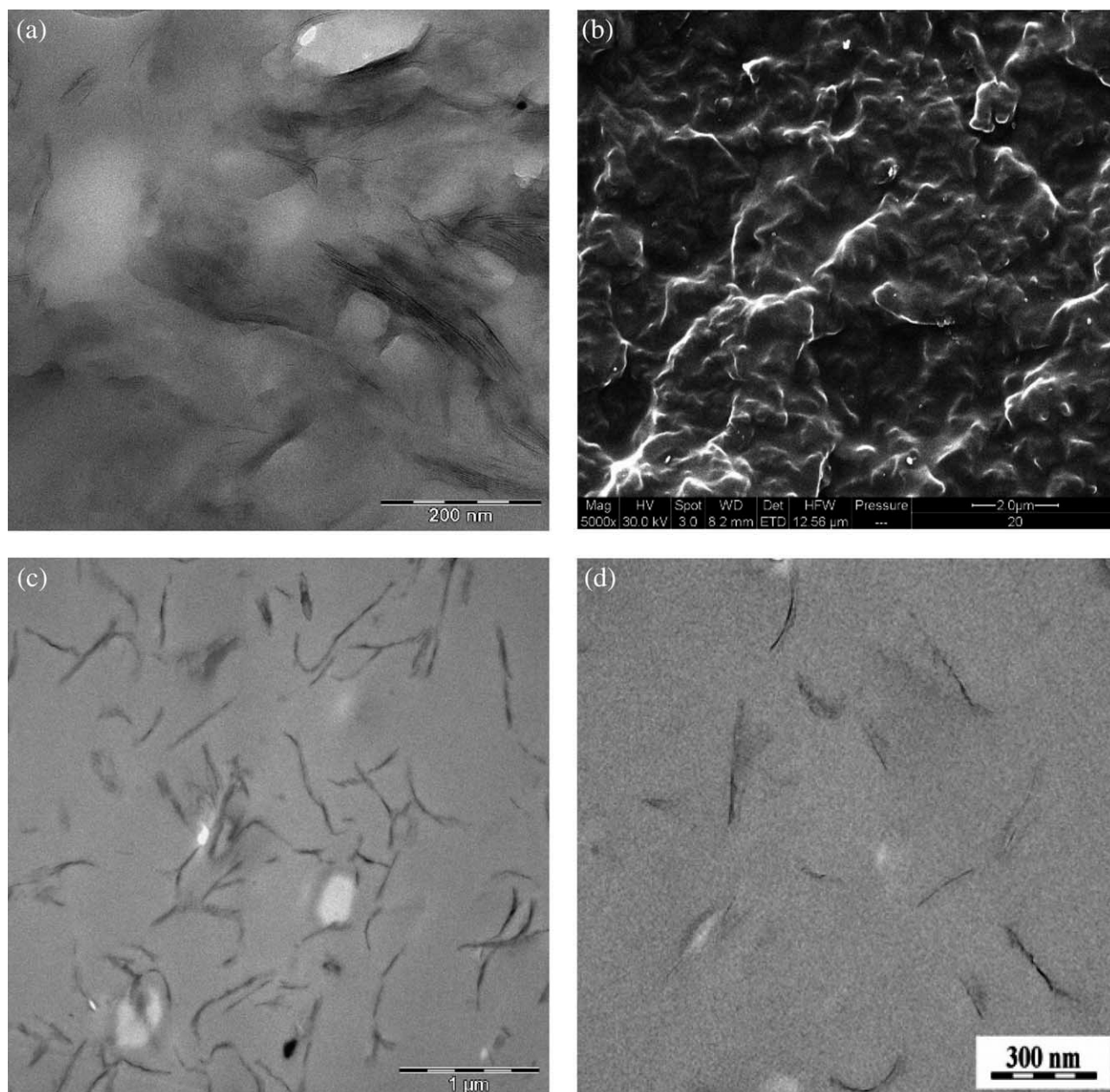


Figure 4 a) TEM image of epoxy containing APOP/Cloisite 30B combination. b) SEM image of liquid-nitrogen-fractured surface of epoxy containing 6.8% of APOP 4000/MMT adduct. c, d) TEM images of the same system as in b).

(easier diffusion, expected lower viscosity at “zero shear rate”) together with the limited presence of epoxy/POP compound in comparison with APOP is also important. A similar increase in particle size with a higher clay content was found for epoxy/carboxyl-terminated butadiene – acrylonitrile rubber.³¹ Finally, TEM observation did not show any presence of clay in the interfacial area in all of the above systems; however, Figure 4(a) indicates the existence of blended inclusions formed in the APOP system, confirming the expected clay/APOP interactions.

The above results indicate that the structure-forming effect of clays is determined predominantly by

the balance between clay-induced acceleration of curing and the nucleation of phase separation.

Morphology of an epoxy with APOP/MMT: adduct

From Figure 4(b), it is clear that in the epoxy containing APOP4000/MMT adduct, no etched phase-separated inclusions are observed. TEM observation [Fig. 4(c,d)] indicates that this adduct forms nanosized planar arrays, probably by the self-pilling mechanism proposed by Lin et al.¹⁰ It is currently not clear whether these structures are formed by self-assembling in an uncured epoxy or in the course of crosslinking. From Table I, it is clear that the

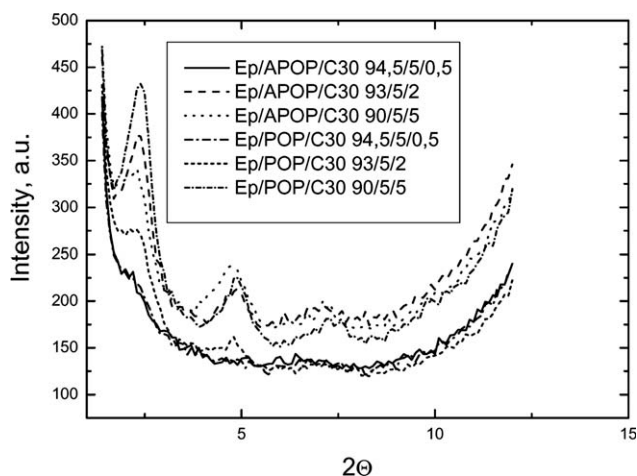


Figure 5 XRD patterns of epoxy (Ep) containing 5% of POP 4000 and APOP 4000 with different nanoclay contents (Cloisite 30 B).

interlamellar distance evaluated by XRD for a single APOP 4000/clay adduct does not correspond to an analogous dimension found in the epoxy nanocomposite in the arrays formed, where the existence of small clay domains with significantly shorter distances is indicated. This closer arrangement also agrees with TEM observations [Fig. 4(c,d)] and may be a consequence of the reaction and/or interaction of the remaining amino groups of APOP with the epoxy matrix. This seems to be confirmed by the fact that a sample in which the remaining amino groups were blocked by the formation of ammonium salt showed two orders of reflections and also a “broader” lamellar structure (not shown). Unfortunately, all of these measurements are close to the resolution limit of the XRD applied. Evaluation of the effect of the molecular weight of APOP (in the adduct) on the structures indicates that these planar arrays were present in APOP2000 and 4000. The reason why they are not formed in adducts of lower-MW APOP may be partly caused by their poor dispersion in an epoxy.

In the case of the combination of adduct (instead of C30B) with neat APOP4000 and POP 4000, it follows from Figure 6 that the presence of both added polymers interfered with the nanoarray formation. Figure 6(c) further shows that in the case of APOP4000, a kind of blended inclusion was also formed. At the same time, the particle size of APOP inclusions is comparable with the inclusions found in the system containing C30B (Fig. 1). From Figure 6(d), it can be observed that in the case of POP, there is a visible presence of clay at the interface. At the same time, the particle size [Fig. 6(b)] increased to an extent similar to that of the epoxy/POP/C30B nanocomposite containing more than 3% C30B (Fig. 1). Taking into account the low clay content in

the adduct (21%, corresponding to 1.5% of clay in epoxy), this effect occurs at a lower clay content than that of C30B. The “falling out” of POP particles from the microtomed layer [Fig. 6(d)] also confirms that the adhesion of particles in the epoxy matrix was relatively weak. These results confirm that the “copolymer-like” APOP/MMT adduct affects phase separation in a manner similar to that of a conventionally modified clay.

Mechanical properties

The dependence of the properties of an epoxy containing 5% of POP4000 and APOP4000 on the clay content is shown in Figure 7(a–c). In the case of POP4000, the addition of a small amount of clay slightly enhances the strength, indicating some synergistic influence of the dispersed phases; the subsequent decrease is less marked compared to that observed for APOP4000, where only a decrease in the originally higher value occurs. This is most likely due to the higher degree of exfoliation observed for MMT in the epoxy/POP4000 matrix (Fig. 5). At the same time, the effect of clay on strength is relatively insignificant in both cases, though the MMT/POP4000 combination leads to a higher strength in comparison with the neat nanocomposite [Fig. 7(a)]. The addition of clay also leads to the expected enhancement in the tensile modulus (E).^{1–3} The higher level found for APOP4000 is comparable to that of the single nanocomposite, whereas the lower E for POP4000 is in contradiction to the aforementioned slightly higher degree of exfoliation (Fig. 5). Therefore, the modulus seems to be more significantly influenced by network parameters, as indicated by the differences in T_g . [Fig. 7(d)], and especially by the interaction between amino groups and MMT, which leads to physical crosslinking.³² The enhancement in toughness with the addition of clay [Fig. 7(c)] indicates a certain synergy between the added polymer and clay, as has been observed by

TABLE I
Interlamellar Distance of (A) Single APOP-MMT Adduct and (B) Epoxy Nanocomposite-Containing Adduct

Adduct composition	d -spacing (Å)	
	A	B
APOP 230/MMT (17/83)	14	NA
APOP 400/MMT (25/75)	18	NA
APOP 2000/MMT (63/37)	52	13.4
APOP 4000/MMT (68/32)	37	19.6
APOP 4000/MMT (79/21)	88	13.4
APOP 600/MMT (30/70) ^a	18	NA
APOP 2005/MMT (63/37) ^a	17	19.6
APOP 2070/MMT (63/37) ^a	18	NA

^a POP monoamine.

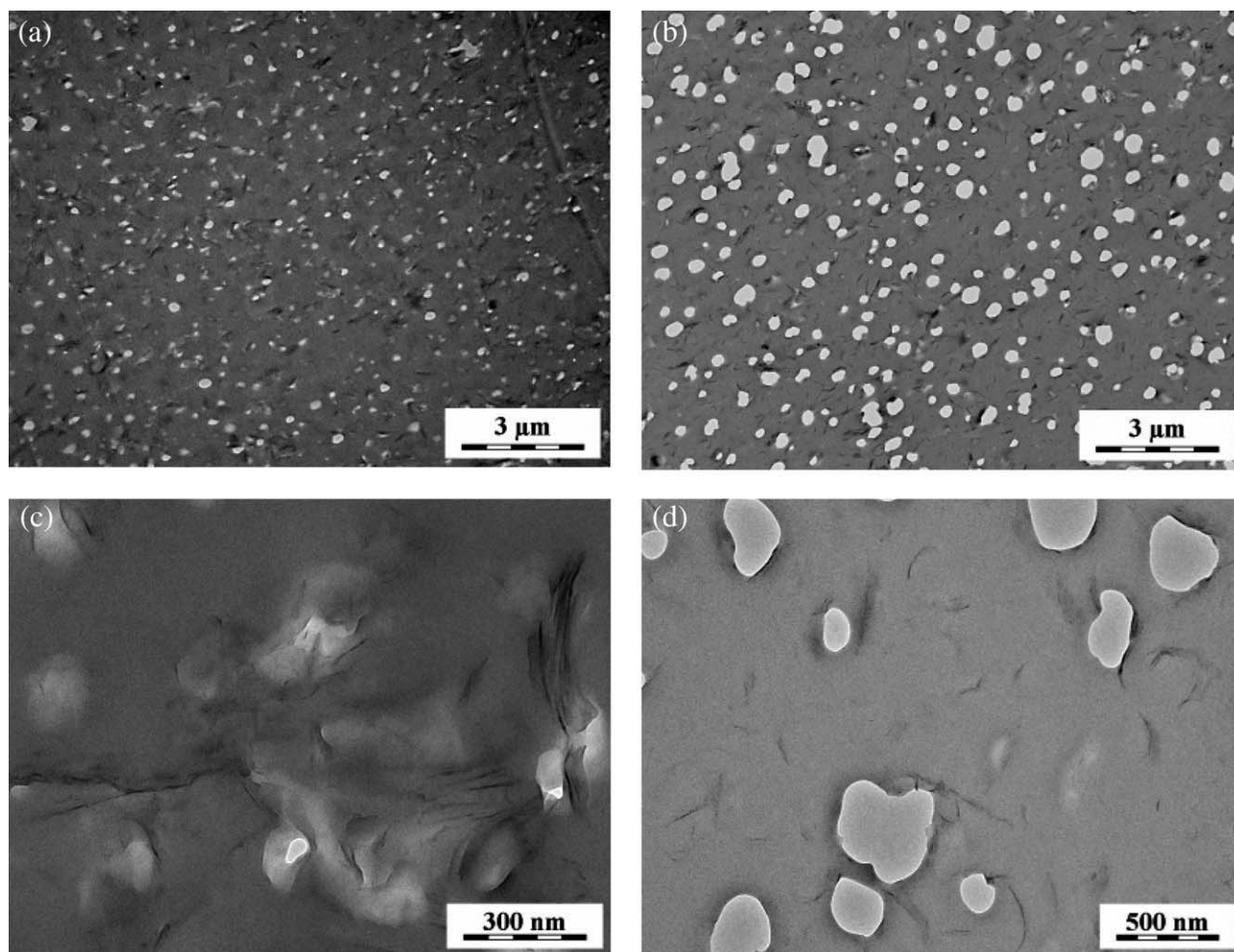


Figure 6 TEM image of APOP/MMT adduct/APOP a), c) and POP b), d) combination c) APOP-based complex inclusions d) POP particles with clay at the interface.

other authors.¹⁷⁻¹⁹ This phenomenon is more remarkable for APOP4000, which shows a significant enhancement at a clay content between 0.5–3% in comparison with the increase only at a 0.5% clay content for POP4000. This effect seems to be unaffected by particle size because toughness is enhanced at similar particle sizes (Fig. 1).

The increased toughness of the epoxy/APOP4000 system may be due to a more favorable blended structure [Fig. 4(a)], which also produces a higher efficiency for the ATBN/clay system.³³ At the same time, larger POP particles at higher clay contents are apparently within an interval of “effective size”. This is confirmed by similar dependencies of strength and toughness on clay concentration for both POP4000 and APOP4000 at higher clay contents, in spite of significant differences in particle sizes (Fig. 1). Thus, the decrease in both parameters is caused predominantly by the negative effect of the high clay content.

In the case of a similar use of the APOP4000/MMT adduct (the added amount corresponds to

1.5% of neat MMT) instead of C30B in the epoxy/POP4000, worse mechanical behavior was observed (Table II). The reason for this unexpected result seems to be the less favorable structure of weakly bonded particles larger than 500 nm [Fig. 4(c)], with part of the clay located at the interface, leading to a lower content of nanoarrays (see later). At the same time, enhanced toughness and satisfactory properties for the application of the APOP4000/MMT adduct in an epoxy/APOP4000 system (Table II), despite the suppression of nanoarray formation, is most probably caused by smaller particles (<200 nm) and the formation of a complex blended structure [Fig. 6(c)] analogous to that found in APOP4000/C30B (Fig. 4).

The results in Table III indicate that the epoxy containing an APOP 4000/MMT adduct represents the most effective method of combining clay and APOP. Simultaneous enhancement of all mechanical parameters in comparison with neat epoxy was found at a relatively low 6.8% content of adduct containing 79% of APOP (corresponding to 1.5% of neat

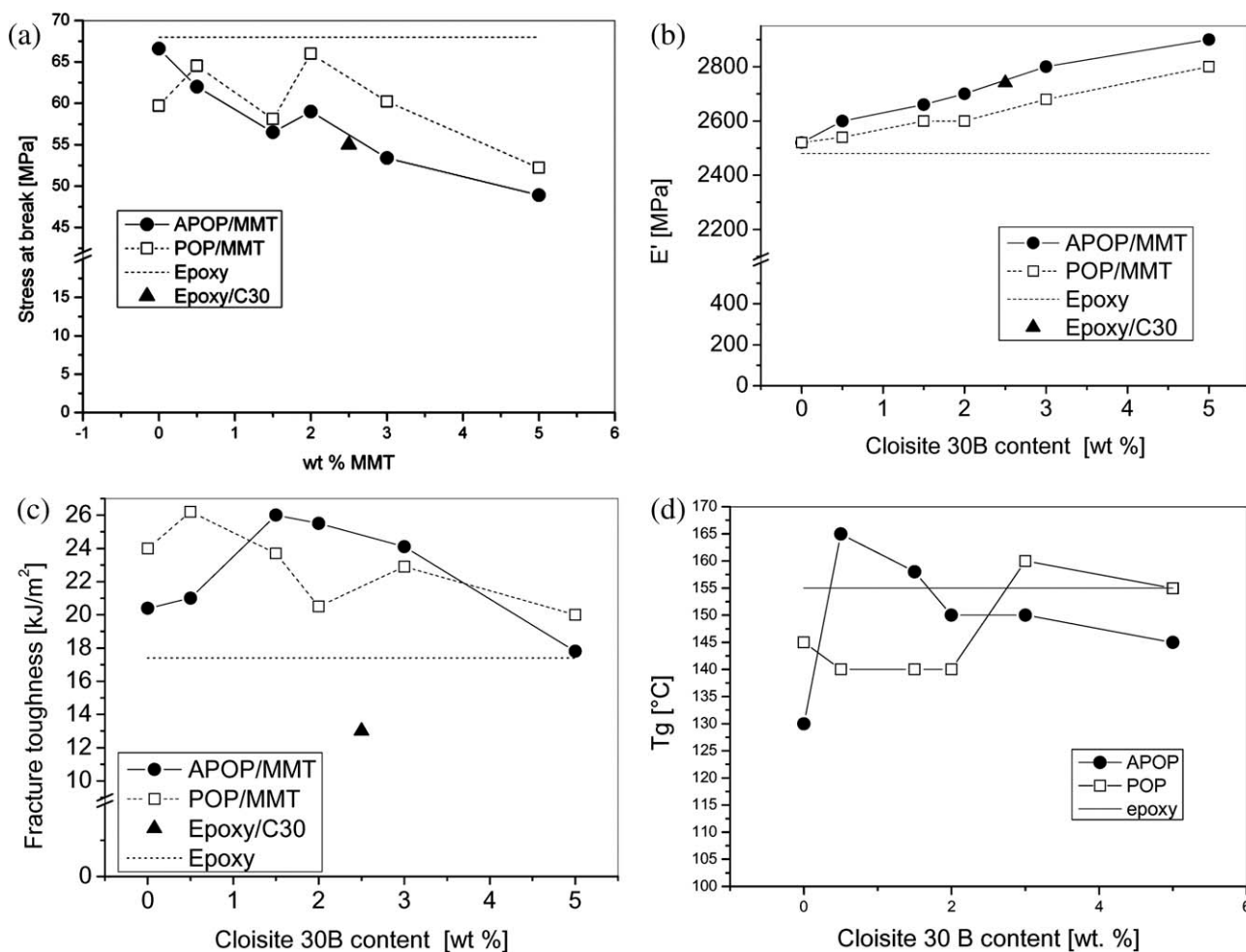


Figure 7 Dependence of properties of epoxy containing 5% of POP 4000 and APOP 4000 on clay content: a) stress at break, b) tensile modulus, c) toughness and d) glass transition temperature (T_g).

MMT), whereas the adduct with a lower APOP content (65%) was less effective. These results indicate that the adduct is effective not only in rubber-like epoxy systems¹⁰ but also in networks with high crosslinking density (high T_g). Moreover, DMA indicates that the APOP4000/MMT adduct does not interfere with network formation and even improves its density, as confirmed by both a higher T_g especially in comparison with APOP2000/MMT adduct containing system and a narrower T_g peak³² (Fig. 8). This was probably due to reactions that produced a

TABLE II
Mechanical Behavior of Epoxy with POP/(APOP/MMT) Combinations

Composition	σ (MPa)	ε (%)	E (MPa)	a ($\text{kJ}\cdot\text{m}^{-2}$)
Epoxy	68	5.3	2480	17.4
Epoxy/cloisite 30B 97.5/2.5	55	3.9	2740	13.0
Epoxy/APOP 4000-MMT (79/21) adduct/POP 4000 88.2/6.8/5	43	2.5	2440	8.6
Epoxy/APOP 4000-MMT (79/21) adduct/APOP 4000 88.2/6.8/5	57	3.4	2280	31.6

more dense network due to amino-group adducts of APOP chains. The increase in toughness and decrease in strength (Table III) at lower adduct contents (4.5% corresponding to 1% clay) and the contrasting increase in strength (still lower than the matrix) accompanied by a significant drop of toughness at 2.25% of adduct (corresponding to 0.5% of clay) are of particular interest. These results differ from the effect of a low content of both single MMT and APOP4000 on epoxy and suggest a new way of affecting mechanical behavior with the APOP/MMT adduct.

This is further confirmed by the above-mentioned significant difference in the properties of the epoxy/POP/C30B and analogous epoxy/POP/(APOP/MMT adduct) systems (Table II). From Table III, it is clear that, despite the relatively fair mechanical behavior of most binary epoxy/APOP systems, a significantly higher effectiveness of the adduct was found for the epoxy/APOP 4000/MMT system only. This suggests that the nanolayered structure [Fig. 4(c,d)] is most effective in the case of its "elastic" embedding and/or linking to the matrix. This

TABLE III
Mechanical Parameters of Epoxy/APOP and Epoxy/(APOP/MMT) Systems

Composition of epoxy systems	σ_b (MPa)	ϵ_b (%)	E(MPa)	a (kJ.m ⁻²)
Epoxy	68	5.3	2480	17.5
APOP 600 95/5	62	3.8	2680	24
APOP 2070 95/5	73	4.4	2800	17
APOP 2000 95/5	73	6.4	2410	13.5
APOP 4000 95/5	67	4.8	2600	20.5
APOP 230-MMT (17/83) adduct, 1.8% ^a	37	1.6	2710	7.5
APOP 400-MMT (25/75) adduct, 2% ^a	28	1.3	2670	5
APOP 600-MMT (30/70) adduct, 2.1% ^a	43	2.0	2810	6
APOP 2005-MMT (63/37) adduct, 4.1% ^a	40	1.7	2910	9
APOP 2000-MMT (63/37) adduct, 4.1% ^a	48	2.2	2810	18
APOP 4000-MMT (68/32) adduct, 5% ^b	57	3.0	2707	13
APOP 4000-MMT (79/21) adduct, 2.3% ^c	62	2.7	2948	9
APOP 4000-MMT (79/21) adduct, 4.5% ^d	39	1.8	2846	40
APOP 4000-MMT (79/21) adduct, 6.8% ^a	72	5.2	2790	26

^a 1.5% of MMT.

^b 1.6% of MMT.

^c 0.5% of MMT.

^d 1% of MMT.

conclusion is valid when comparing the mechanical behavior of the epoxy with that of the APOP 2000/MMT adduct and APOP4000/MMT adduct, because adducts of MMT with APOP 600, 400, and 230 were not soluble in epoxy monomer. As a result, the formation of layered structures was less significant. The aforementioned results show that the effectiveness of the adducts is strongly dependent on the MW of APOP, the content of ion-exchanged APOP and the adduct content.

CONCLUSIONS

The combination of clay and low-molecular-weight hydroxyl- and amine-terminated POP is a useful method for improving the balance in mechanical behavior of epoxy nanocomposites. Improved tough-

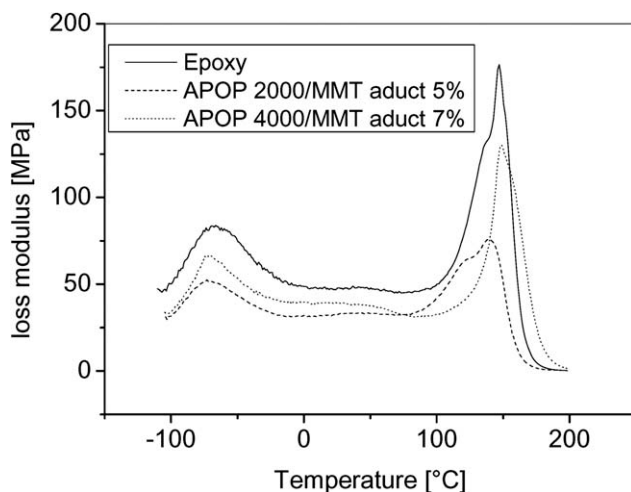


Figure 8 DMA of epoxy containing APOP/MMT adducts.

ness was found for APOP combined with 0.5–3% wt % of organoclay due to the formation of blended domains consisting of clay tactoids and fine APOP inclusions. Under the curing conditions applied, a minor increase in APOP particle size with clay content was found, whereas at a clay content >2%, the POP particle size increased significantly. This is a consequence of shifting the equilibrium between clay-induced accelerated curing and the nucleation of phase separation. The best mechanical behavior was observed when using an adduct of APOP4000 and MMT obtained by the ion exchange of sodium ions of MMT for protonated APOP. This is caused by the formation of nanosized planar arrays of elastomer-modified clay and an increase in the T_g of the epoxy network. The mechanical behavior of this system is strongly influenced by the molecular weight of APOP and the adduct composition and content. The particularly different influences of the adduct on the epoxy compared to that of its components, including the deterioration of mechanical properties at low adduct contents, reveal the special effects of elastically embedded nanoplatelet arrays on the mechanical behavior of epoxies. This is also confirmed by a significant reduction in toughness when the adduct is combined with POP.

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