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Synthesis and characterization of polyurethane/epoxy interpenetrating network nanocomposites with organoclays

Q. M. Jia, M. Zheng (✉), H. X. Chen, R. J. Shen

School of Material Science & Engineering, Xi'an Jiaotong University, Xi'an 710049, China
E-mail: mszheng@mail.xjtu.edu.cn, Fax:+86-29-82663453

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Summary

Novel nanocomposites with varying contents of organophilic montmorillonite (oMMT) were prepared by intercalating oMMT to interpenetrating polymer networks (IPNs) of polyurethane and epoxy resin (PU/EP). The PU/EP networks and the oMMT modified PU/EP IPNs nanocomposites were studied with Fourier transform infrared spectrometry, scanning electronic microscopy, transmission electronic microscopy, wide-angle X-ray diffraction, water absorption and tensile test. The results show that oMMT and the IPNs of polyurethane and epoxy resin exhibit synergistic effect on the phase structure and morphology of the IPNs nanocomposites. The addition of oMMT to the PU/EP IPNs matrix provides two fold benefits to the properties of the IPNs nanocomposites. oMMT has not a distinct effect on chemical structure of PU/EP IPNs but promotes the compatibility and phase structure of the IPNs, and the 'forced compatibility' of PU and EP in interpenetrating process improves the dispersion degree of oMMT. Both the mechanical properties and water resistance of the PU/EP IPNs nanocomposites are superior to those of the pure PU/EP IPNs.

Introduction

Polyurethane (PU) is one of the most versatile polymers today. It is widely used in coatings, adhesives, leather, thermoplastic elastomers and composites. PU properties can be adjusted by two approaches. The first is to change the molecule structure of PU by modification of its three basic building blocks: polyether or polyester, diisocyanate, and chain extender, or change the phase structure of PU by blending it and other one or two polymers. Interpenetrating polymeric method is one of the best blending methods. IPNs allow mutual enhancement of the properties of component polymers, which is promising to many application fields. IPNs are polymer alloys consisting of at least two polymers in the networks, which is held together by permanent entanglements with only occasional covalent bonds between the chains of the two different types of polymers. Owing to the simplicity of its synthesis and the versatility of the properties, PU is one of the most widely used polymeric components in the synthesis of IPNs. Many investigators studied the polyurethane IPNs as one of the constituent polymers to improve the properties [1-5].

Alternative method is to introduce inorganic fillers into the polyurethane. Inorganic particles are introduced into the polymer to improve the mechanical performance of polyurethane and reduce the production cost. However, such approach has some disadvantages, such as the reduction of ductility, decrease of water resistance, etc. Recently, much effort has been conducted to find new approaches for preparing PU/oMMT. Wang[6] reported an intercalated PU/oMMT by *in situ* polymerization of TDI and a mixture of polyol and MMT. Zilg *et al*[7] succeeded in a similar method. Chen *et al* [8] proposed a solution intercalation method, PU prepolymer was inserted into a MMT intergallery in solution condition followed by a curing procedure with 1,4-butanediol (BD). Han *et al*[9] studied the effect of organophilic montmorillonite with different polarity on properties of PU/MMT nanocomposites.

However, study in clay modified IPNs nanocomposites is comparatively limited. In this paper, organophilic montmorillonite was prepared and intercalated to the IPNs of castor oil-based PU/EP by *in situ* polymerization method so as to obtain oMMT modified PU/EP IPNs nanocomposites with excellent mechanical properties and water resistance. FTIR, WAXD, SEM and TEM techniques were employed to characterize the structure and properties of the PU/EP IPNs and the PU/EP IPNs nanocomposites.

Experimental

Materials

The commercial 2,4-toluene diisocyanate(TDI) and Octadecylammonium were made in Shanghai Chemical Reagent Co(China). Commercial castor oil, diglycidyl ether of biphenol A (DGEBA) and 2,4,6-tri(dimethylaminomethyl) phenol(DMP-30) were made in Tianjin Chemical Co(China). The MMT was obtained by purification of natural sodium bentonite, provided by South Clay Co(China). Castor oil and DGEBA were dried under a vacuum prior to use. The equivalent weight per hydroxyl group of castor oil is 370.8 g and that of TDI per NCO group is 87.0 g. These two values were used to calculate the NCO/OH ratio for the synthesis of the phase.

Preparation of oMMT

The method for preparing oMMT was similar to Kawasumi et al [10]. 15 g of the clay was dispersed into 1200 mL distilled water at the temperature of 80 ℃. Octadecylammonium chloride [$CH_3(CH_2)_{17}NH_3Cl$] was prepared by mixing 5.7 g octadecylamine [$CH_3(CH_2)_{17}$ NH_2] with 2.1 mL HCl solution (10*N*) in 350 mL distilled water. It was poured into the hot clay-water mixture at a temperature of 80 ℃ and stirred vigorously for 2 h. The mixture was then filtered and washed with water in EtOH (50/50 vol %) until chloride cannot be detectable in the mother liquor. The octadecylamine-exchanged clay was then dried at a temperature of 75 ℃ for 3~4 days in a vacuum oven. Thereafter, the organoclay was stored in a dessicator.

Synthesis of PU/EP IPNs

A weighed amount of castor oil was placed in a round-bottomed flask, heated until 60 ℃, and thoroughly mixed with a predetermined amount of TDI, the reaction system was stirred vigorously with a Teflon-coated magnetic stir bar, under a dry nitrogen atmosphere, for about 45 min to form a urethane prepolymer. Then, a predetermined amount of the epoxy precursor (DGEBA, PU/EP=80:20) was added to the system which was stirred for a while before adding 1.5%, by weight, of DMP-30 (based on the amount of DGEBA).The mixture was degassed under a vacuum for some minutes and then poured and pressed into the preheated Teflon molds. The filled molds were heated until 120 ℃ and then the IPNs samples were cured at that temperature for some hours to perform the completion of the polymerization in both phases.[11]

Synthesis of PU/EP IPNs nanocomposites

A weighted amount of oMMT and castor oil were placed in a round-bottomed flask, heated and stirred vigorously with a Teflon-coated magnetic stir bar, for about 4 hours, then the temperature of the mixed system was reduced to room temperature, quantitative TDI was added to the system. Then, the following steps were the same as synthesis of PU/EP IPNs.

Characterization

Fourier transform infrared spectra(FTIR) of the pristine, organophilic MMT, PU/EP IPNs and PU/EP nanocomposites were conducted on an IRrestige-21 spectrometer in the wave number range 4000-400 cm^{-1}.

Wide-angle X-ray diffraction(WAXD) was used to determine d-spacings of the MMT before and after treatment in the nanocomposites, and the test was performed at room temperature with a Rigaku X-Ray diffractometer with a CuK_α radiation source (λ=0.154 nm), which was operated at 40 kV and 30 mA.

Samples were frozen under liquid nitrogen, then fractured and mounted on a stub. They were coated with gold (100A) using a Edwards S 150A sputter coater. The phase microstructure of the nanocomposites was observed by a JEOL JSM-6400 Scanning electron microscope operated at 20 kV.

Samples were prepared by a LKB Bromma 2088 Ultrotome at –50 ℃, giving sections of nearly 100 nm in thickness. No further staining was used to improve contrast. Subsequently, one layer of carbon of about 10 nm in thickness was deposited on these slices on mesh 300 copper nets for TEM observations on a Hitachi H-600 electron microscope with an acceleration voltage of 120 kV.

Tensile tests were done using a PDL series instron tensile strength tester at a crosshead speed of 450 mm/min at 20 ℃, The measurements were performed according to the Chinese standard GB/T 528-1998. The result reflected an average of five specimens.

The water absorption test was carried out referring to the specifications of ASTM D570, and the test specimens were cut in the shape of $12.5\times4.0\times0.145$ mm^3. The totally dried specimens were weighed to the nearest 0.0001 g to get the initial weight, W_0. The conditioned specimens were entirely immersed in a container of deionized water maintained at 25±0.2 ℃ for a definite interval. Then the specimens were removed from the water, one at a time, surface water on specimens was removed with a dry cloth, and the specimens were weighed immediately to get the weight, W_1. The percentage of increase in weight of the samples was calculated to the nearest 0.1% by using the formula $(W_1-W_0)/W_0$.[12]

Results and discussion

IR analysis

The FTIR spectra of the pristine and treated MMT are depicted in Figure 1a. In the spectra, the peaks at 2918 cm^{-1} and 2856 cm^{-1} contribute to the absorbance of methylene's asymmetric and symmetric stretching vibrations, which shows that Octadecylammonium cations have been inserted into the interlayer of pristine MMT. This is also proved by the following WAXD patterns.

Figure 1b shows the FTIR spectra of the PU/EP nanocomposite with 3% oMMT and the PU/EP IPNs. It can be seen, both the PU/EP IPNs and the PU/EP nanocomposite with 3% oMMT have the characteristic peaks at 3300,1720,1600,1537 and 1107 cm^{-1}. Besides these peaks, the PU/EP nanocomposite with 3% oMMT also has the characteristic peaks of oMMT: 462, 524 and 1038 cm^{-1}, which correspond to the bending vibration of Si-O , the stretching vibration of Al-O and the Si-O-Si stretching vibration of oMMT respectively. It indicates that oMMT has been incorporated in PU/EP IPNs, but the chemical structures of PU/EP IPNs are not altered by the presence of the silicate layers.

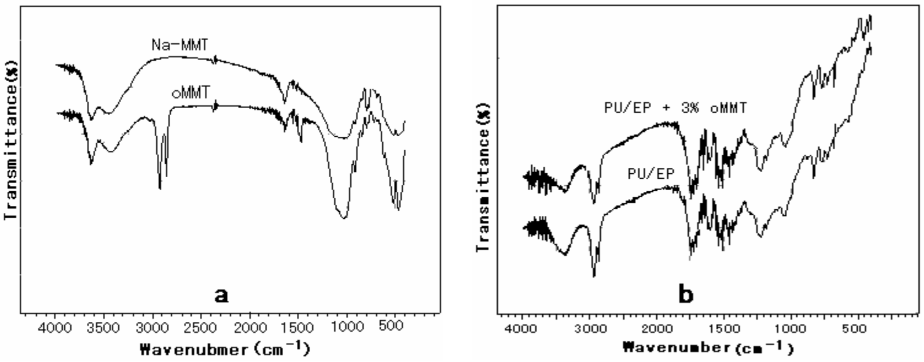

Figure 1. FTIR spectra of a) the pristine MMT and oMMT ; b) PU/EP nanocomposite with 3% oMMT and PU/EP IPNs

WAXD analysis

The d-spacings of the MMT before and after treatment and PU nanocomposites are calculated using Bragg's relation according to the angle of the 001 diffraction peak in the WAXD pattern. $2d \sin\theta = n\lambda$, where λ corresponds to the wave length of the X-ray radiation used in the diffraction experiment, d is the spacing between diffraction lattice planes, and θ is the measured half diffraction angle or glancing angle.[13] The results are shown in Figure 2. It can be seen from Figure 2 that after treatment, the d-spacings have increased from 1.26 nm of pristine MMT to 1.96 nm, which means an ordered intercalation structure was obtained. When 3% oMMT was added to the pure PU, The relatively small diffraction peak displays at $2\theta = 2.1^\circ$ in the WAXD pattern of the PU/EP nanocomposite, corresponded to a d-spacing of 4.20 nm. This indicates PU is intercalated into the oMMT platelets , the d-spacing of the oMMT is expanded more. While the PU/EP nanocomposite with 3% oMMT shows no diffraction peak from 1.5 to 15°, which means an exfoliated structure was derived. Therefore, becoming PU/EP IPNs benefits to obtain exfoliated structure of oMMT, compared with the pure PU nanocomposites.

From the WAXD of Figure 2, it can also be seen that, all the nanocomposites show a diffraction peak at about 20.2°, especially the PU/EP nanocomposite with 3% oMMT, which means that the introduction of clay layers induces the crystallization of PU hard segments. This change of crystallization may lead to some change of mechanical properties.[14]

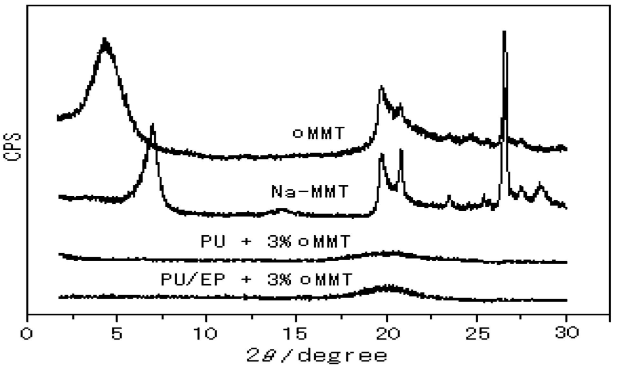

Figure 2. WAXD patterns for the different materials

SEM analysis

It has been shown that the morphology of IPNs systems, at a given composition, is controlled by the chemical miscibility of the two components, interfacial tension, and crosslink densities. This last factor is, in turn, ultimately related to the percent of crosslinker used as well as the method of synthesis. Usually, IPNs have a two-phase morphology where the size of the phase domains decreases with increasing crosslink density. In the case of the studied castor oil-based PU/EP IPNs, it was experimentally observed that mixtures of uncured epoxy resin with castor oil in the low concentration range of the former are completely miscible, at the working temperature, forming clear solution. This miscibility may be attributed to strong intermolecular interactions

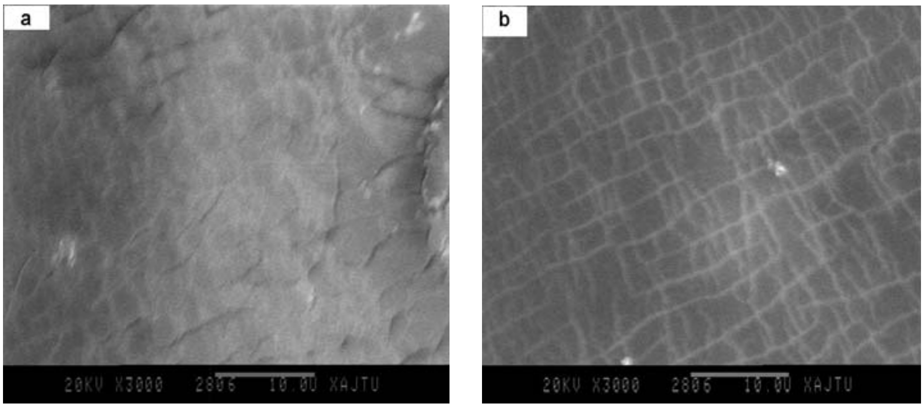

Figure 3. SEM patterns of a) PU/EP IPNs; b) PU/EP nanocomposite with 3% oMMT

established between molecules of the two uncured components via their hydroxyl groups or the epoxide groups of the epoxy[6].

Figure 3 presents the morphology of the cross-sectional surface of the frozen fractured surfaces of PU/EP IPNs and PU/EP nanocomposite with 3% oMMT, as observed by the SEM. From Figure 3, it indicates that one continuous phase morphology without manifest dispersed microdomains in the PU/EP IPNs. Moreover, when 3% oMMT was added to PU/EP IPNs, the PU/EP IPNs nanocomposite has a distinct 'net' fracture structure, which means proper amount of oMMT can improve phase morphology of PU/EP IPNs. There are two reasons to explain the above phenomenon. one is that the polymer chains of PU and EP are tied on the surface of the oMMT through hydrogen bonds, which improves the phase morphology of PU/EP IPNs. The other may be that the catalytic effect of oMMT accelerates the cure rate of the EP[15] and slowers the cure rate of the PU which form intact PU/EP interpenetrating networks, but this needs to be proved further by curing kinetics. The epoxy resin of the PU/EP nanocomposite with 3% oMMT displays the white 'net' structure which acts as a net framework to bear tensile stress so as to enhance tensile properties of the PU/EP nanocomposite with 3%. The IPNs nanocomposite has better tensile properties than the pure PU/EP IPNs, which is also seen from Figure 6.

TEM analysis

From Figure 4, the intercalated structure of the PU nanocomposite with 5% oMMT and the exfoliated structure of the PU/EP nanocomposite with 5% oMMT are visualized by TEM. From Figure 4a, it can be shown, The interlayer spacing of oMMT is expanded and keeps a fairly ordered structure, but some oMMT still aggregates. It can be also seen from Figure 4b, oMMT in the PU/EP nanocomposite with 5% oMMT disperses more uniformly, the ratio of exfoliation and intercalation of oMMT in the PU/EP nanocomposite is higher than that of the pure PU nanocomposite. It may be because the 'forced compatibility' of PU and EP in interpenetrating process improves the dispersion degree of oMMT.

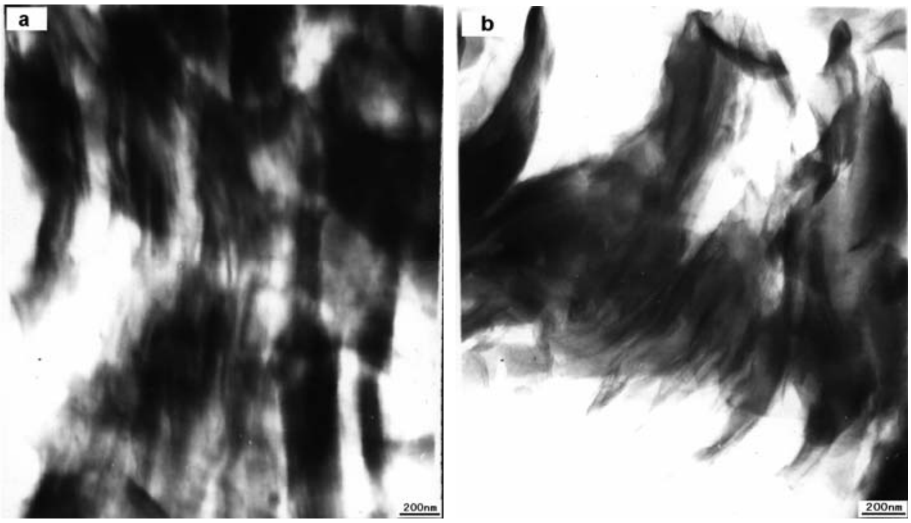

Figure 4. TEM patterns of a)PU with 5% oMMT and b) PU/EP nanocomposite with 5% oMMT

Water absorption

Properties of many materials change with the difference in water absorption. The actual application of PU is confined because its excellent properties will be greatly affected by water absorption. Its properties, mainly mechanical properties, decrease greatly with the increase of water absorption. So it is important to study the change of moisture adsorption before and after modification. The number of hydrophilic groups, free volume and morphology induced by phase separation of PU are more significant in determining ultimate water absorption. In this paper, due to the limits of specimen preparation, water absorption measurement is carried out according to the corresponding ASTM specifications, and the results only display some qualitative trend. The results are shown in Figure 5. It can be seen that, at the first stage, pure PU and the PU/EP IPNs show a much higher water absorption rate, and pure PU attains the balance of water absorption much quicker relative to the PU/EP IPNs. Pure PU has higher water absorption because of the existence of many hydrophilic groups. Lower water absorption of the PU/EP IPNs results from increasing crosslinking density of pure PU and decreasing free volume in pure PU. The nanocomposites from PU and PU/EP IPNs show a much lower water absorption rate and attain the balance of water absorption much more slowly relative to the PU matrix and the PU/EP IPNs. The introduction of oMMT layers increases the path for water molecules to penetrate the nanocomposites film and then delays the time to attain balance. On the other hand, the existence of oMMT improves phase morphology of pure PU and PU/EP IPNs, which also causes the decrease of the total water absorption accordingly. The PU/EP IPNs nanocomposites have the minimum water absorption and take the longest time to attain the balance. The results indicate that PU/EP IPNs and oMMT have synergistic effect on the water resistance of PU/EP IPNs nanocomposites. Decrease of water absorption means that the material has more stable properties, which is interesting for practical applications.

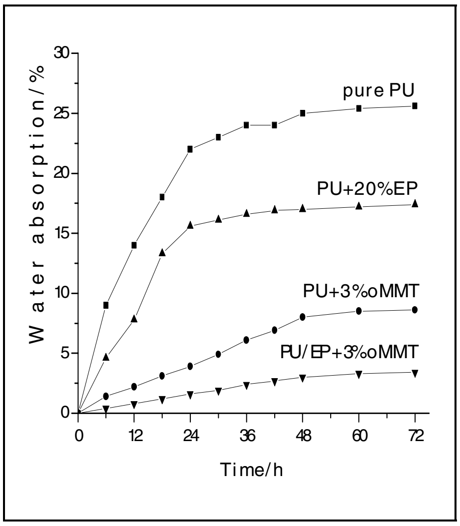

Figure 5. Water absorption curves of different PU materials

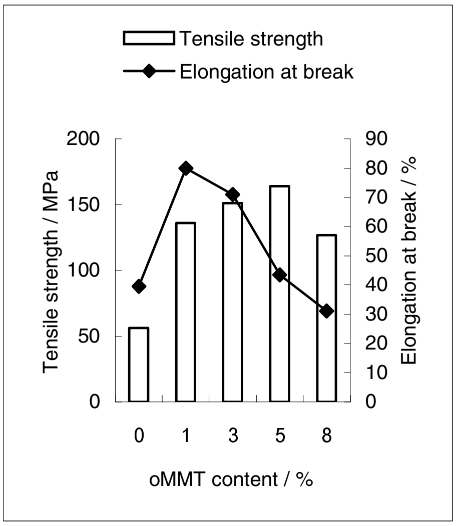

Figure 6. Tensile properties of PU/EP IPNs with different oMMT contents

Tensile test

The tensile strength and the elongation at break of PU/EP IPNs with various oMMT contents are shown in Figure 6. As we are known, an increase of material tensile strength results in the decrease of its tensile elongation at break for most polymers or polymer composites. However, both the tensile strength and elongation at break of PU/EP IPNs nanocomposites are improved to a certain degree with the addition of the oMMT. With an increase in the oMMT content, both tensile strength and elongation at break increased, but they can't reach maximum at the same time. The tensile strength of PU/EP IPNs nanocomposites reaches maximum when oMMT content is 5%, but the elongation at break of these nanocomposites improves rapidly with increase of oMMT content and reaches maximum when oMMT content is 1%. As the oMMT continued to increase, the tensile strength and elongation decreased. Two possible mechanisms are as follows. When a low oMMT content is added, the crosslinking density of PU/EP IPNs increases and the phase morphology of PU/EP IPNs is improved, which is favorable for enhancing the mechanical propertied of the polymer. Another mechanism is that there are interactions between oMMT and PU/EP through hydrogen bonds, which may also be responsible for the increase in the mechanical properties. However, when a relatively high oMMT content is used, more and more oMMT aggregates instead of being intercalated, which results in a deterioration of the mechanical properties.

Conclusions

It is concluded from this study that by intercalating oMMT to interpenetrating polymer networks of polyurethane and epoxy resin by *in situ* polymerization, the PU/EP IPNs nanocomposites were prepared. The novel nanocomposites exhibit excellent mechanical properties and water resistance. PU/EP IPNs and oMMT have some synergistic effect on the properties of PU. Introducing oMMT into PU/EP IPNs can dramatically improve the phase morphology of PU/EP IPNs and the 'forced compatibility' of PU and EP in interpenetrating process can enhance the dispersion degree of oMMT.

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References

1. Suthar B (1993) Ind J Technol. 31:419.
2. Hourston DJ, Song M, Schafer FU, Pollock HM, Hammiche A (1998) Thermochim Acta 324:109.
3. Athawale VD, Kolekar S (2000) J Appl Polym Sci 75:825.
4. Siddarammiah, Mallu P, Somashekar R (1998) J Appl Polym Sci 68:1793.
5. Athawale VD, Kolekar S (1998) Polymer J 30:813.
6. Wang Z, Pinnavaia TJ (1998) Chem Mater 10:3769.
7. Zilg C, Dietsche F, Hoffmann B, Dietrich C, Mulhaupt R (2001) Macromol Symp 169:63.
8. Chen TK, Tien YI, Wei KH (1999) J Polym Sci Polym Chem Ed 37:2225.
9. Han B, Cheng AM, Ji GD, Wu SS, Shen J (2004) J Appl Polym Sci 91:2536.
10. Kawasumi M, Hasegawa N, Kato M, Usuki A, Okada A (1997) Macromolecules 30:6333.
11. Raymond MP, Bui VT (1998) J Appl Polym Sci 70:1649.

12. Chen TK, Tien YI, Wei KH (2000) Polymer 41:1345.
13. Vaia KH, Giannelis EP (1997) Macromolecules 30:8000.
14. Tien YI, Wei KH (2001) Polymer 42:3213.
15. Lan T, Kaviratna PD, Pinnavaia TJ (1996) J Phys Chem Solids 57:1005.