

High Mechanical Properties of Polychloroprene/Montmorillonite Nanocomposites

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The principal objective of this study is to improve the mechanical properties of polychloroprene through the addition of montmorillonite. Three modifying cations are tested. The polychloroprene-MMT composite is characterized by FTIR, SEM, EDX, XRD, ICP-MS and TEM. The tensile and tear strength of polychloroprene was increased significantly after the modification of montmorillonite.
[doi:10.2320/matertrans.47.2753]

(Received July 10, 2006; Accepted September 13, 2006; Published November 15, 2006)

Keywords: nanocomposite, montmorillonite, polychloroprene, mechanical properties

1. Introduction

There is tremendous current excitement in the study of montmorillonite with respect to their fundamental properties, organization to form superstructures, and applications.¹⁻³⁾ It has been reported that polymer-MMT composites have excellent mechanical,³⁻⁵⁾ barrier^{6,7)} and thermal^{8,9)} properties. Especially, researches on the subject of rubber nanocomposite have been attracted much interest.¹⁰⁻¹²⁾

Polychloroprene or chloroprene rubber, introduced by DuPont in 1931, was the first synthetic rubber developed that exhibited the elastomeric properties of natural rubber. It remains one of the most important speciality elastomers with an annual consumption of 300,000 tons worldwide.¹³⁻¹⁵⁾ Key roles in changing the properties of polychloroprene are played by the tensile stress and its modulus, hardness, tear strength, and elongation-at-breakage. However, enhancing the tear strength of this synthetic material is challenging. Furthermore, MMT addition suppresses chloroprene pop foaming. Consequently, although various polymer-MMT composites have been prepared, the polychloroprene-MMT composite has less to be investigated.¹⁶⁾ The present study attempts to increase the tear strength of polychloroprene through the addition of modified MMT.

2. Experimental Procedure

2.1 Materials

The unmodified clay (C0) used in this study was purchased from Pai Kong Technology Co. Ltd, Taiwan. The d-spacing of the (001) plane was 1.28 nm and the cationic exchange capacity (CEC) was 114 milli-equivalent/100 g clay. The clay had a pH of 2 and an average particle diameter of 0.63 μm . HCl was used to separate the Na^+ and MMT, thus facilitating the introduction of surfactants.

Three surfactants were used in the present study. The first surfactant (S1) was octadecylamine ($\text{C}_{18}\text{H}_{37}\text{NH}_2$), the second surfactant (S2) was polyoxyethylene octadecylamine ($\text{C}_{18}\text{H}_{37}(\text{C}_2\text{H}_4\text{O})_{12}\text{NH}_2$), and the third surfactant (S3) was dioctadecyl-dimethylammonium chloride ($(\text{C}_{18}\text{H}_{38})_2(\text{CH}_3)_2\text{NCl}$).

Conventional additives for polychloroprene include ZnO, MgO, carbon black and Diphenyl guanidine (DPG). ZnO serves as a vulcanizing agent, *i.e.* the reaction of ZnO and chlorine forms ZnCl_2 , which is an active catalyst

of vulcanization. The function of MgO is to neutralize any trace hydrogen chloride which may be liberated by the polychloroprene during processing, vulcanization, heat aging, or service. As with all elastomers, polychloroprene requires the addition of appropriate reinforcing fillers to achieve the required balance of processability, hardness, tensile strength, and tear strength. The most commonly used reinforcing material is carbon black. Finally, the adding of DPG can increase the maximum resistance of polychloroprene to heat.

2.2 Modification of clay

The quantity of the intercalating agent to be used for the cation-exchange reaction is given by:

$$114/100 \times 50 \times 1.3 \times \text{Mw}/1000 = X \quad (1)$$

where X is the weight in grams of the intercalating agent when 50 g of MMT clay is used, 114/100 is the cation exchange capacity per 100 g of MMT, 1.3 is the excess amount of intercalating agent used, Mw is the molecular weight of the intercalating agent, and 1000 is used to balance the units.⁶⁾

To modify the MMT, MMT-surfactant-HCl solutions were dispersed in high resistivity water in the three-necked flask. Nitrogen gas was bubbled into the flask throughout the reaction processes. While being stirred continuously at 500 rpm, the solutions were maintained at a temperature of 80°C for 3 hours. The resulting suspensions were then filtered, and the solid residues rinsed with water to remove all traces of chloride, as determined by a silver nitrate test. The products were then dried at 80°C for 24 hours in a convection oven, milled with a ball end mill, and finally sintered with a 325 mesh net to yield the final modified clay samples (S1, S2, and S3).

2.3 Mixing process

Mixing was carried out at 75°C by using a mixer (XK-160, JiangSu, China) in accordance with ASTM method D3184-80. The modified MMT powder was mixed directly with ZnO in a ratio of 1 to 1. After mixing, the powder was cured at 80°C for 2 hr. Polychloroprene was mixed alone in the tank for 20 sec and then DPG, carbon black, MgO, CaCO_3 and foaming agent (azodicarbonamide) were added and mixed for 40 sec. The MMT-ZnO powder was then added and mixed for a further 40 sec. The composite samples were then passed

through the two-roll mill several times until the thickness of the uncured rubber is 3 mm. Following this, the rubber was foaming at 90°C for 2 hrs.

2.4 Characterization

The bonding of the modified and unmodified MMT was examined with a Fourier transform infrared spectroscopy (FTIR, FTS-7, Bio-Rad, Hercules, USA). Meanwhile, an inductively coupled plasma-mass spectroscopy (ICP-MS, Hewlett Packard 4500, Japan) was employed to analyze the displaced percentage of surfactants to Na^+ . A X-ray diffractometer (XRD, NanoStar, Bruker AXS, USA) was employed to measure the d-spacing of the MMT and the polychloroprene/MMT samples at a scanning rate of $0.5^\circ/\text{min}$. After this, the morphology of the composite samples were investigated using a Hitachi S4200 Field Emission SEM. Finally, the composite samples were cut by Cryostat Microtome (CM 1900, Leica, Germany) at temperature down to -40°C and then characterized by a high-resolution transmission electron microscopy (HR-TEM, JEM-2100F, JEOL Co., Japan).

Polychloroprene/MMT composite specimens for the tensile and tear tests were punched out from the vulcanized sheets. The tensile testing procedure was carried out in accordance with Test Method A prescribed by ASTM D412. A Monsanto tensometer (Tensometer T10, Alpha Technologies, USA) was used to determine the tensile properties of the various rubber blends. Readings of the tensile strength, tensile modulus at 60% elongation, tensile modulus at 120% elongation, and percentage elongation at breakage were recorded directly from the digital displays at the conclusion of each test. The tear strength of each specimen was measured using an unnotched 90° -angled test specimen according to ASTM D624. The tensile tests and tear tests were all performed at a stretching rate of 50 cm/min. The hardness tests were conducted using a Shore type durometer according to ASTM 2240. All tests were conducted at room temperature (25°C).

3. Results and Discussion

3.1 Bonding of surfactant and MMT

An FTIR spectrometer was employed to analyze the bonding. Figure 1 presents the infrared spectrographs of the unmodified (C0) and modified (S1-S3) MMT samples. The unmodified and modified MMT bond at 1040 and 1090 cm^{-1} (Si-O), 3429 and 1635 cm^{-1} (H-O), 600 (Al-O), and 420 cm^{-1} (Mg-O).¹⁷ Meanwhile, the modified samples bond at 850 and 2920 cm^{-1} for CH_2 . The modifier in the S2 powder bonds with polyoxyethylene by C-O bonding, creating the broad peak evident between 1050 and 1150 cm^{-1} . These results imply that polyoxyethylene bonds with the amide, which then bonds with the MMT.

3.2 D-Spacing and displaced percentage

Figure 2 presents the XRD results for the modified and unmodified MMT samples. As shown, the (001) d-spacing of the SiO_2 sheets in MMT-C0 is 1.31 nm . In MMT-S1, the d-spacing increases to 2.01 nm . Further, in MMT-S2, the d-spacing of the silicate increases to 3.74 nm due to the

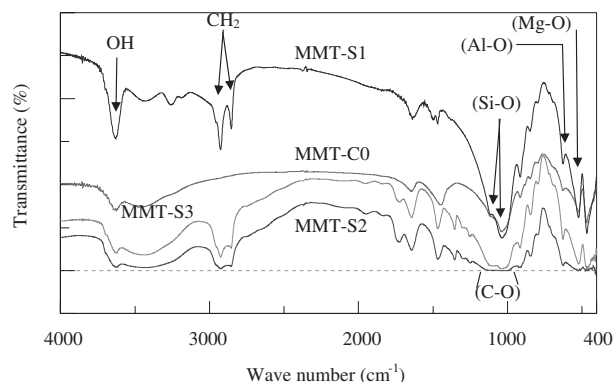


Fig. 1 FTIR analysis of modified montmorillonite.

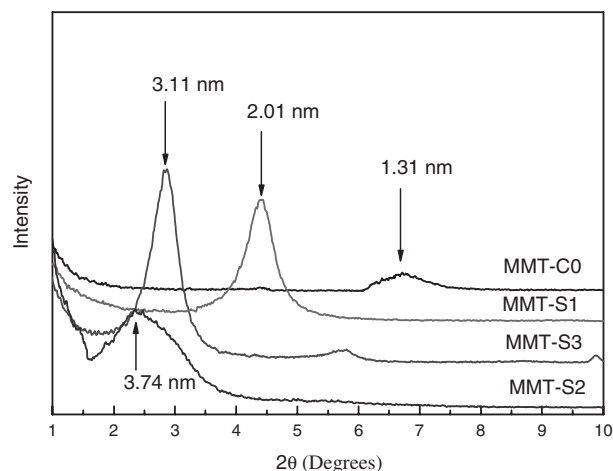


Fig. 2 XRD pattern of modified montmorillonite.

Table 1 The displaced percentage of surfactant on Na^+ at 85°C .

| | Displaced Na^+ ($\mu\text{mole/g}$ clay) | Displaced percentage (%) | d-spacing |
|--------|---|-----------------------------|-------------------|
| MMT-C0 | 1140.0 | — | 13.1 \AA |
| MMT-S1 | 941.6 | 82.6 | 20.1 \AA |
| MMT-S2 | 719.3 | 63.1 | 37.4 \AA |
| MMT-S3 | 803.7 | 70.5 | 31.1 \AA |

presence of more hydrocarbon tails. Finally, in MMT-S3, the d-spacing increases to 3.11 nm . These results indicate that the modified MMT efficiently displaces sodium ions and reduces the attraction between the Na^+ ions and the silicate.

Table 1 shows the residual percentage of Na^+ in MMT was inspected by ICP-MS after the modification of surfactants S1-S3. The highest displaced percentage was 82.6% when S1 displaced Na^+ . The displaced percentage decreased from 82.6 to 63.1% when S2 displaced Na^+ . This is because when the process temperature is close to 90°C , which is the cloud point of S2. The displaced percentage of MMT-S3 increased to 70.5%. The d-spacing of MMT-S3 is 32.3 \AA . Although the d-spacings of MMT-S2 and MMT-S3 are larger than MMT-S1, the displaced percentage of MMT-S2 and MMT-S3 are both smaller than MMT-S1. This implies that the displaced percentage is not correlated with the d-spacing.

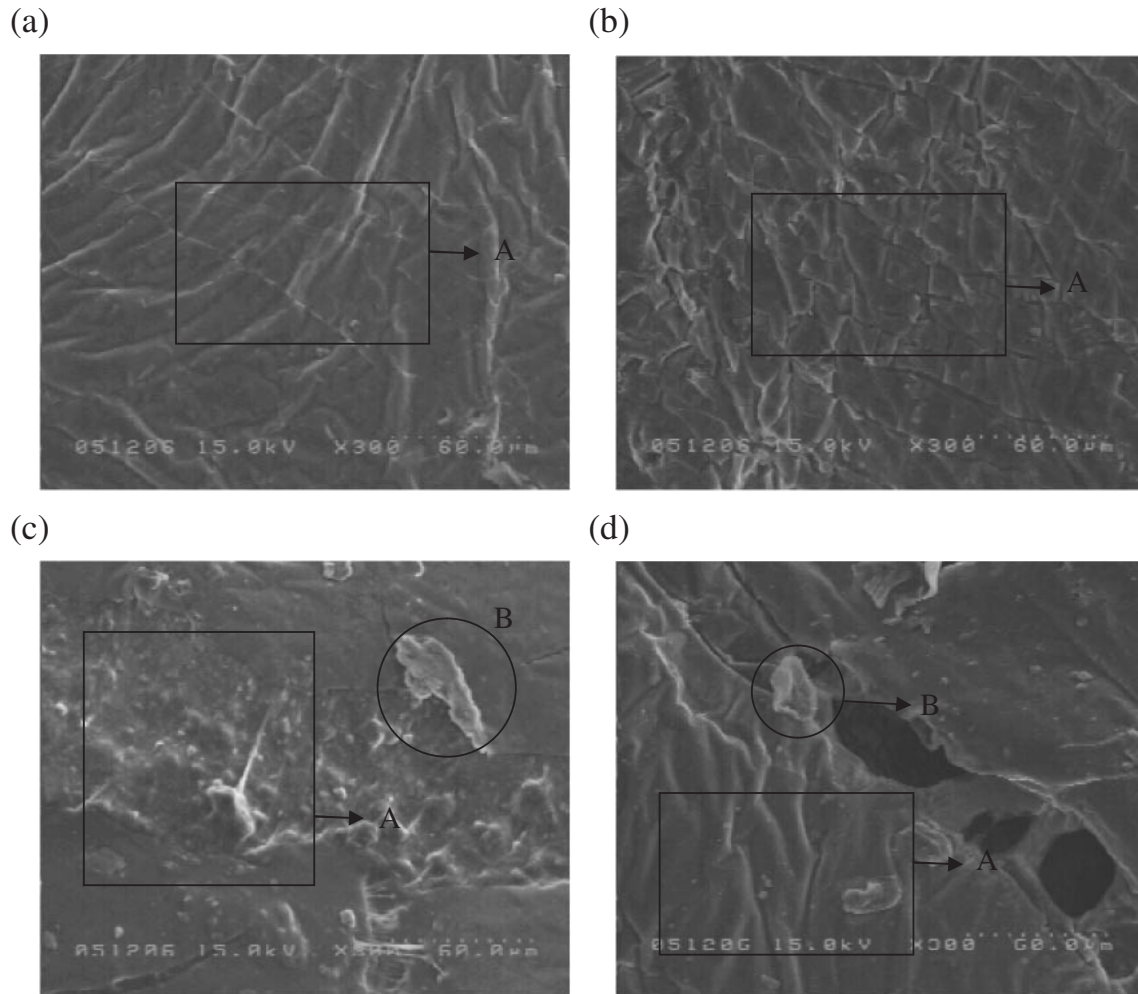


Fig. 3 SEM morphologies of polychloroprene before foaming. Polychloroprene doped (a) without montmorillonite (NE) (b) with MMT-S1 powders (c) with MMT-S2 powders and (d) with MMT-S3 powders.

Table 2 The elemental analysis of Fig. 3.

| Polychloroprene | Blank | MMT-S1 | MMT-S 2 | MMT-S3 |
|-----------------|-------|--------|-----------|-----------|
| Elements (%) | A | A | A B | A B |
| Zn | 4 | 4.9 | 6.0 0.2 | 4.0 1.3 |
| Si | 0 | 8.2 | 5.1 45.8 | 6.6 40.2 |
| Al | 0 | 3.0 | 2.1 24.2 | 2.9 12.3 |
| Ca | 2.2 | 3.8 | 3.2 2.2 | 3.9 3.2 |
| Cl | 90.2 | 75.1 | 80.6 22.3 | 80.4 45.5 |
| Mg | 3.6 | 5.0 | 3.0 5.3 | 2.2 3.5 |

3.3 Morphology of polychloroprene

Figure 3 presents the morphologies before pop foaming of polychloroprene. The elemental compositions of the samples presented in Fig. 3, as analyzed by the Energy-Dispersive X-ray, are shown in Table 2. As discussed previously, MMT is composed primarily of silica and aluminum hydroxide. Therefore, the identification of Si and Al in the polychloroprene samples was taken as an indication of the presence of MMT. Figure 3(a) shows the morphology of the unmodified polychloroprene (NE). In area A, no Si or Al can be identified, whereas Cl is 90%. Figure 3(b) shows the morphology of S1-doped polychloroprene.

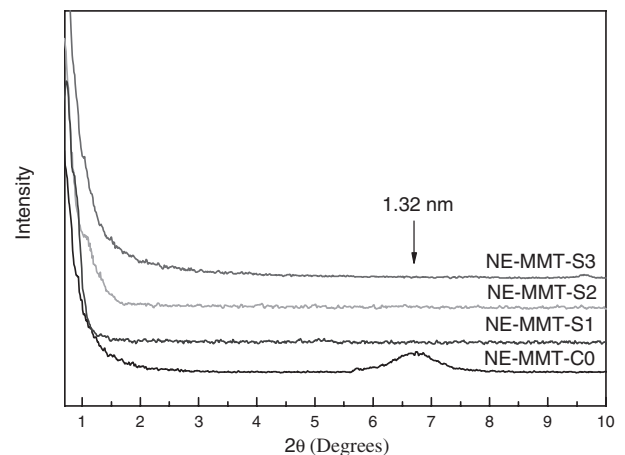


Fig. 4 XRD pattern of polychloroprene with different modified montmorillonite.

oprene. The surface is less smooth than the unmodified polychloroprene. This is because the MMT blocks the absorption of the processing oil into the polychloroprene.¹⁶⁾ In area A, 8.2% Si and 3.0% Al was identified because of the adding of MMT. Figure 3(c) presents the morphology of

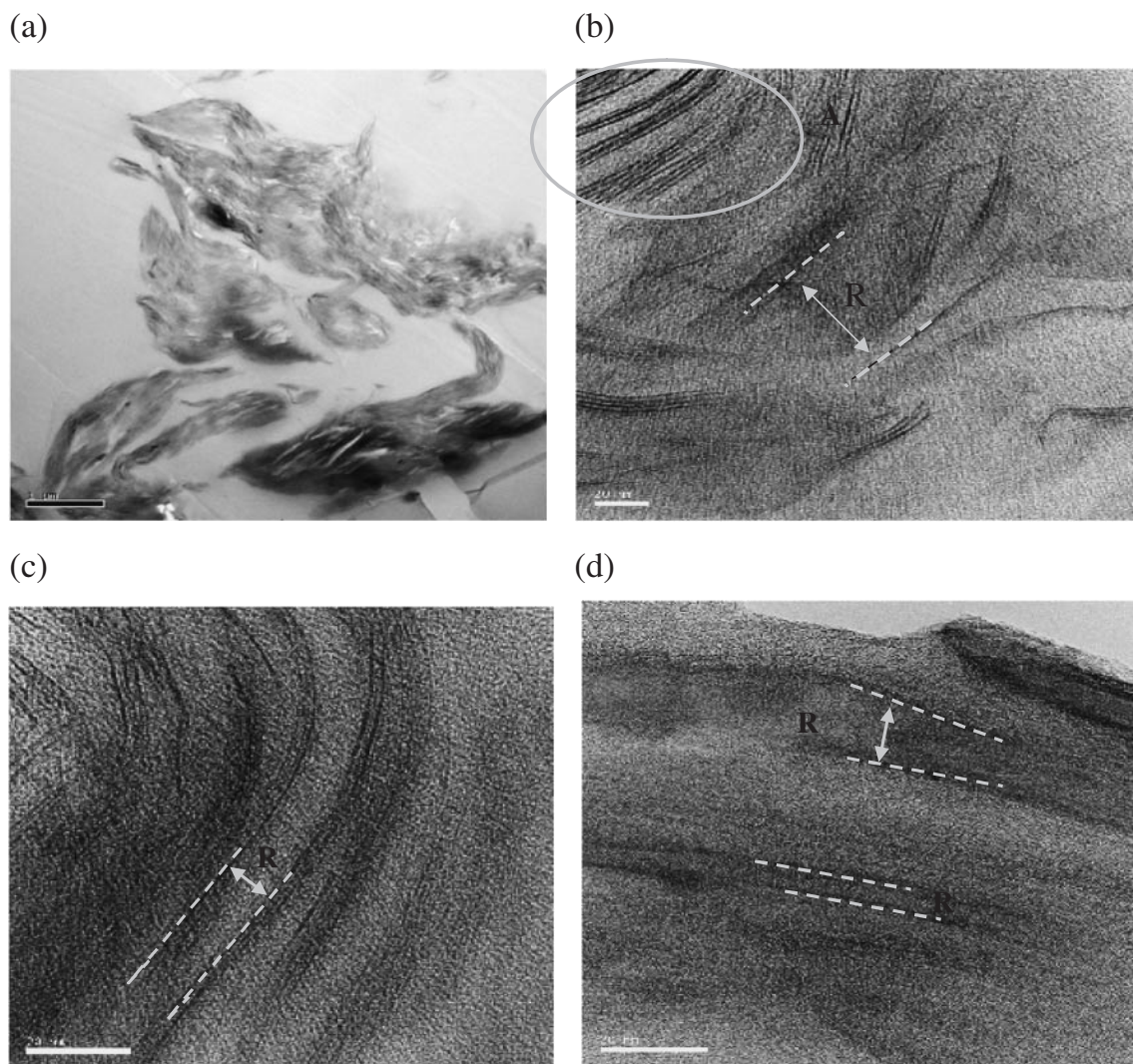


Fig. 5 TEM analysis of polychloroprene doped with (a) MMT-C0(b) MMT-S1 (c) MMT-S2 and (d) MMT-S3.

S2-doped polychloroprene. In area A, the percentage of Si and Al decreased to 5.1 and 3.1%, respectively. Furthermore, particle B is evidenced as MMT owing to the fact that 45% Si and 24% Al was identified. Figure 3(d) presents the morphology of S3-doped polychloroprene. The percentage of Si and Al in area A increased to 6.6 and 2.9%, respectively. MMT can also clearly visible in this SEM image.

Figure 4 presents the XRD results for the unmodified polychloroprene sample and the MMT-doped polychloroprene samples formed. It can be seen that no diffraction peaks are evident in the composite samples mixed, which implies that the clay is exfoliated. The XRD results are confirmed by the TEM images presented in Fig. 5, which indicate that the montmorillonite are all exfoliated. Figure 5(a) presents the MMT-C0 doped polychloroprene. As can be seen, MMT-C0 aggregate together. Figures 5(b), (c) and (d) show the polychloroprene doped with MMT-S1, MMT-S2 and MMT-S3, respective. Although in area A the montmorillonite is intercalated, most parts of these figures present that the d-spacing of montmorillonite is larger than 5 nm, *i.e.* montmorillonite is exfoliated.

3.4 Mechanical properties of polychloroprene/montmorillonite nanocomposite

The tensile strengths, tensile modulus at 60% elongation, and tensile modulus at 120% elongation of the four MMT-doped polychloroprene samples are presented in Figs. 6(a), 6(b) and 6(c), respectively. Compared to the unmodified MMT doped polychloroprene, the addition of the S1 powder causes the tensile strength of the polychloroprene composite to increase substantially from 100 to 136% on the surface and to 166% on the center. Comparatively, the addition of the S2 and S3 powders has little effect on the tensile strength. Furthermore, tensile strength variation of S2-polychloroprene is bigger than C0-polychloroprene. There is highest tensile modulus in S1-polychloroprene for tensile modulus at 60% elongation. The modulus is increased from 100 to 234% on the center and 286% on the center. As consider modulus at 120% elongation, the addition of the S1, S2 or S3 powders leads to a significant increase in the tensile modulus of the polychloroprene composite. The highest modulus is observed in S1-polychloroprene which is increased to 202 and 282% on the surface and center, respectively.

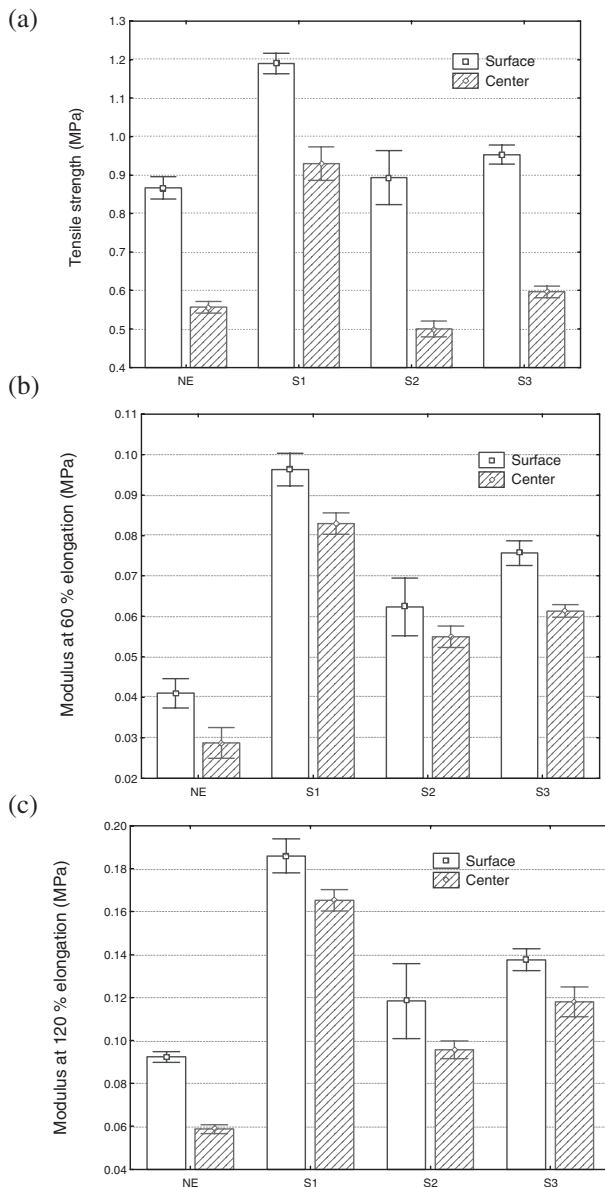


Fig. 6 Tensile properties of different MMT in foam polychloroprene. (a) Tensile strength (b) Modulus at 60% elongation (c) Modulus at 120% elongation.

Figures 7(a), 7(b), and 7(c) present the tear strength, hardness, and elongation-at-breakage of the polychloroprene composite samples. It is noted that the S2-doped composite has the greatest percentage of elongation at the surface, whereas the S3-doped sample has the highest percentage of elongation at the center. Figure 7(a) shows that the addition of modified MMT, and particularly the addition of the S1 powder, increases the tear strength of the polychloroprene considerably from 100% to 148% and 158% on the surface and center, respectively. As shown previously in Figs. 4 and 5, the MMT separates uniformly and become exfoliated in S1-doped polychloroprene. Figure 7(a) suggests that the exfoliated MMT leads to a significant increase in the tear strength. Meanwhile, Fig. 7(b) indicates that the addition of modified MMT leads to an increase in the hardness of the polychloroprene composite. It is apparent that the S1-doped polychloroprene has the greatest hardness, both at the surface and at the center. This result suggests that S1 powder addition enhances the crosslinking of polychloroprene. Finally,

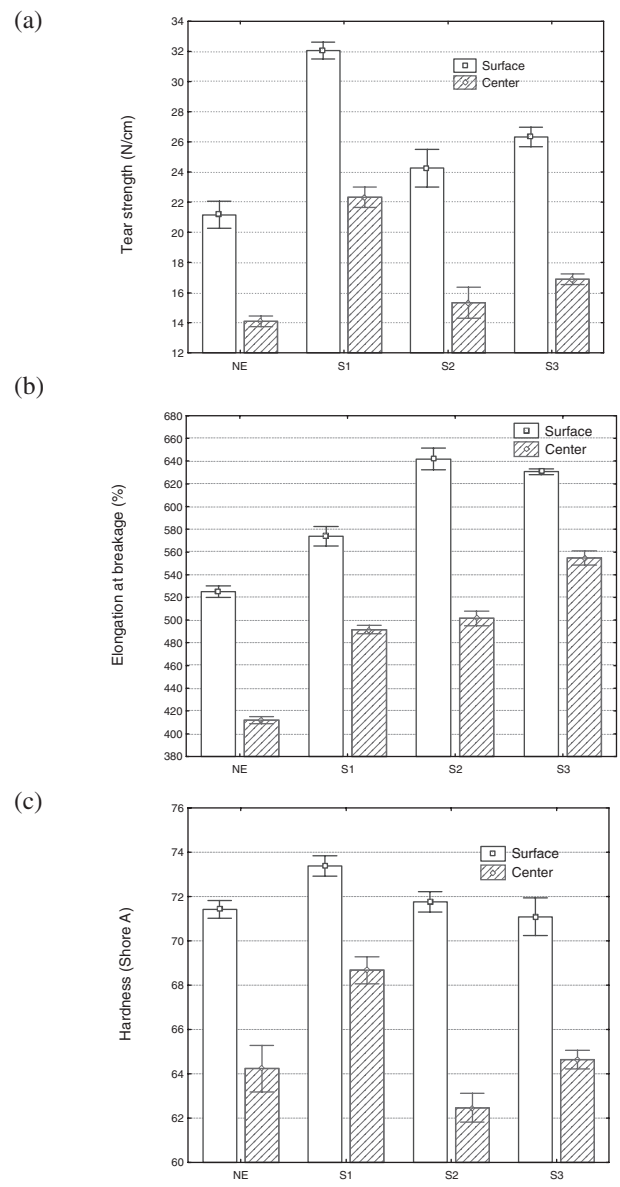


Fig. 7 Mechanical properties of different MMT in foam polychloroprene. (a) Tear strength (b) Hardness (c) Elongation at break.

Fig. 7(c) confirms that the addition of modified MMT is beneficial in promoting the elongation-at-breakage of the polychloroprene composite samples. It is noted that the S2-doped composite has the greatest percentage of elongation at the surface, whereas the S3-doped sample has the highest percentage of elongation at the center.

The results of Figs. 6 and 7 show that the addition of modified MMT enhances the mechanical properties of the polychloroprene-MMT composite. The results suggest that exfoliated MMT enhances the crosslinking of polychloroprene and improves its mechanical properties. Other than the elongation-at-breakage property, the S1-modified polychloroprene sample demonstrates the optimum mechanical properties.

4. Conclusions

In this study, modified and unmodified MMT has been

added to polychloroprene to enhance the mechanical properties. The results have shown that the mixing process causes the modified MMT to become exfoliated, which leads to an enhancement in the mechanical properties of the resulting polychloroprene-MMT composites. Octadecylamine(S1)-MMT modified polychloroprene shows the lowest d-spacing but the highest displaced percentage and best mechanical properties. The addition of the S1 powder causes the tensile strength of the polychloroprene composite to increase substantially from 100 to 136% on the surface and to 166% on the center. Furthermore, the tensile modulus increase from 100% to more than 200%. Particularly the addition of the S1 powder, increases the tear strength of the polychloroprene considerably from 100 to 148% and 158% on the surface and center, respectively.

REFERENCES

- 1) B. Morgan and J. W. Gilman: J. Appl. Polym. Sci. **87** (2003) 1329.
- 2) A. Okada, M. Kawasumi and T. Kurauchi: Polym. Prepr. **28** (1987) 447.
- 3) Y. P. Wu, L. Q. Zhang, Y. Q. Wang, Y. Liang and D. S. Yu: J. Appl. Polym. Sci. **82** (2001) 2842.
- 4) Z. Zhang, L. Zhang, Y. Li and H. Xu: Polymer **46** (2005) 129.
- 5) J. W. Lim, A. Hassan, A. R. Rahma and M. U. Wahit: J. Appl. Polym. Sci. **99** (2006) 3441.
- 6) J. S. Shelley, P. T. Mather and K. L. DeVries: Polymer **42** (2001) 5849.
- 7) J. Yeh, S. Liou, C. Lin, C. Cheng and Y. Chang: Chem. Mater. **14** (2002) 154.
- 8) M. Kawasumi, N. Hasegawa, M. Kato, A. Usuki and A. Okada: Macromolecules **30** (1997) 6333.
- 9) K. Varlot, E. Reynaud, M. H. Kloppfer, G. Vigier and J. Varlet: J. Polym. Sci. B **39** (2001) 1360.
- 10) V. P. Privalko, S. M. Ponomarenko, E. G. Privalko, F. Schön and W. Gronski: Eur. Polym. J. **41** (2005) 3042.
- 11) V. P. Privalko, S. M. Ponomarenko, E. G. Privalko, F. Schön, W. Gronski, R. Staneva and B. Stühn, Macromol: Chem. Phys. **204** (2003) 1480.
- 12) Y. Xu, J. Zhou and M. A. Hanna: Cereal Chem. **82** (2005) 105.
- 13) D. D. Jiang, G. F. Levchik, S. V. Levchik, C. Dick, J. J. Liggat and C. E. Snape: Polym. Degrad. Stabil. **68** (2000) 75.
- 14) K. N. Pandey, D. K. Setua and G. N. Mathur: Polym. Test. **22** (2003) 353.
- 15) J. Hao, C. A. Wilkie and J. Wang: Polym. Degrad. Stabil **71** (2001) 305.
- 16) M. H. Yeh, W. S. Hwang and Y. C. Chang: Jpn. J. Appl. Phys. **44** (2005) 6847.
- 17) T. N. Chi and W. Y. Shang: *PLS Nano Composite Materials*, eds. R. T. Yang (Wu-nan, Taipei, 2004, 1st ed.)