EPDM 고무/유기 벤토나이트 복합체의 제조: 개질된 벤토나이트와 최종 생성물의 특성에 대한 염산의 영향

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Fabrication of EPDM Rubber/Organo-bentonite Composites: Influence of Hydrochloric Acid on the Characteristics of Modified Bentonite and Final Products

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초록: 고무 매트릭스와 벤토나이트의 상용성을 향상시키기 위하여 유기개질 벤토나이트는 벤토나이트 현탁액에서 실란커플링제인 [3-(2-aminoethylamino)propyl]trimethoxysilane(AEAPTMS)]를 사용하여 합성되었다. 유기개질 벤토나이트의 구조와 특성을 FTIR-spectroscopy, thermogravimetric analysis(TGA) and X-ray diffraction(XRD) 등을 사용하여 분석하였다. Ethylene-propylene-diene monomer(EPDM) 고무와 유기 벤토나이트를 two-roll mill에서 배합하였으며 가황을 하고 물성을 측정하였다. 벤토나이트 개질에 대하여 염산과 물의 농도가 복합체의 물성에 중요한 영향을 미치는 것으로 확인되었다. 벤토나이트의 함량이 20 phr 포함된 복합체의 경우 가장 좋은 물성을 나타내었고 인장강도는 1.95에서 4.8 MPa로 증가되었으며 신장률은 300에서 500%로 증가하는 경향을 보였다.

Abstract: To improve the compatibility of bentonite with rubber matrix, organo-modified bentonite was synthesized with a silane coupling agent, [3-(2-aminoethylamino)propyl]trimethoxysilane (AEAPTMS) in the suspension of bentonite. The structure and characteristics of organo-modified bentonite were investigated using FTIR-spectroscopy, thermogravimetric analysis (TGA) and X-ray diffraction (XRD). Ethylene-propylene-diene monomer (EPDM) rubber/organo-bentonite composites were compounded by a two-roll mill. The vulcanization and mechanical properties were studied. Results showed that the concentration of hydrochloric acid and H_2O in the synthesis had significant influence on the modification of bentonite, which further contributed to the properties of the composites. Filled with 20 phr modified bentonite, the tensile strength and elongation at break of the rubber increased from 1.95 to 4.8 MPa and 300% to 500%, respectively.

Keywords: bentonite, [3-(2-aminoethylamino)propyl]trimethoxysilane, ethylene-propylene-diene monomer, mechanical properties.

Introduction

In recent decades, polymer-clay composites are of great interest due to their improved mechanical, rheological and thermal properties.[1-5] There are mainly two nano-structure in the prepared polymer-clay composites including intercalated and exfoliated structure in which the latter is more desirable due to better properties in various aspects.

The concept of polymer-clay composites is especially prospective in rubber industry. Conventionally, carbon black (CB) is extensively used as rubber filler due to its low cost and excellent performance in reinforcement. However, it suffers from its black color and pollution issues while applied as a rubber additive. Therefore, recent research work focuses on the development of substitutes for carbon black such as graphite,[6-8] silicon carbide,[9] metal salts[10] and different silicate,[11] in which clay is undoubtedly attractive because it is naturally originated, abundant and economical. Clay is with a high degree of mechanical and physical strength which is necessary as a reinforcing filler for rubber, mainly because of its high surface area, high aspect ratio and small particle size after exfoliation. However, related to the abundant hydroxyl groups on the surface of the layered structure and the metal ions in the

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galleries, bentonite is hydrophilic which makes it not so compatible with the rubber matrix whose surface is hydrophobic and with low energy. In that case, it is very difficult for clay to be dispersed homogeneously in rubber matrix. In the previous work, people made efforts in the improvement of compatibility during which different modifiers[12] were applied to make the surface of clay less hydrophilic. Among the modifiers, quaternary alkyl ammonium or phosphonium[13] such as hexadecyltrimethyl ammonium bromide (C16), octadecyltrimethyl ammonium chloride, dodecyltrimethyl ammonium bromide are most commonly used in the way of ion exchange with the internal and external cations[14] of the layered silicate. However, the exchange of ammonium or phosphonium salts is carried out in aqueous solution after which the clay becomes condensed solid blocks due to the dehydration. With silane coupling agents (SCA) modified, such as trialkoxysilanes, fine powder with particles in micro-size or even nano-size could be achieved. After hydrolyzation and condensation, silicon ether bonds form, with the SCA grafted onto the surface of clay and their functional groups branching out. By this mean, the polarity of the surface decreased significantly, becoming more compatible with the polymer matrix. The organic modification also weakens the interaction between layers leading to easily exfoliation during compounding.

Among the different types of clay, montmorillonite, hectorite and saponite[3,13,15,16] are most commonly used as rubber fillers. Bentonite is barely used as the rubber filler with only a few reports. Due to the presence of reactive -SiOH and -AlOH[17] at the interface, bentonite has great potential for the organic modification with trialkoxysilanes.

This research work focused on the optimization of synthesis of organo-modified bentonite. [3-(2-Aminoethylamino)propyl] trimethoxysilane (AEAPTMS) was selected as the modifier due to its two amino groups in the functional groups leading to strong interaction with the polymer molecules in the rubber matrix. Previously, there were already some reports on the amiable treatment of silicate[18-20] or other potential fillers[21-25] with silane coupling agents before compounding with rubber compounds. However, there is still few research work focusing on the important factors in the synthesis influencing on the catalyzation of the hydrolyzation and condensation between AEAPTMS and bentonite in alcohol-water system, the structure of bentonite as well as even the performances of final rubber composites. There are also reports on the *in-situ* addition of AEAPTMS in compounding on two-roll mill[18] or extruder.[26] However, as an adhensive, AEAPTMS always makes the mix-

ture excessively sticky during compounding on the two-roll mill leading to poor processibility. Therefore, modification of clay before the compounding is a better choice for the preparation of composites. In this research work, the modification of bentonite using AEAPTMS was carried out in methanol, catalyzed by hydrochloric acid in the existence of certain concentration of H_2O. After removing the solvent adequately, the modified bentonite was compounded with the EPDM matrix, together with other additives and sulfur powder as a crosslinker. Here we selected an intermediate bentonite loading of 20 phr as it was the best presentative to investigate the effect of some factors in the synthesis, such as the concentration of hydrochloric acid and H_2O on the vulcanization, mechanical properties and morphology of organo-modified bentonite/EPDM composites.

Experimental

Materials. Ethylene-propylene-diene monomer (EPDM), KEP2480 with ethylene content of 57.5%, ethylidene norbornene (ENB) of 8.9% and Mooney viscosity (ML (1+8) 125 °C) of 81 MU (Mooney Unit) was obtained from Kumho POLYCHEM. Bentonite (Bt) was purchased from YAKURI Pure Chem. [3-(2-Aminoethylamino)propyl]trimethoxysilane (AEAPTMS, ≥80%) was manufactured by Sigma-Aldrich. All other reagents for vulcanization were used as received: 2,2'-Dibenzothiazolyl disulfide (DM) was supplied by WAKO Pure Chem.; Stearic acid (above 95.0%), ZnO (above 99.0%) and sulfur powder (above 99.0%) were supplied by DAE-JUNG CHEM; *N*-Cyclohexyl-2-benzothiazolyl-sulfenamide (CBS) was supplied by T.C.I.. The carbon black was N550 (FEF) from CORAX.

Synthesis of Organo-modified Bentonite and Preparation of Composites. 25 g of Bt was first dispersed in 200 mL of methanol, stirred for 10 min. Certain amount of AEAPTMS was added into the flask and mixed for another 10 min. Then, certain amount of hydrochloric acid (35%, w/w) was added successively (see Table 1). The reaction was carried out for 8 h at room temperature.

The yield was filtrated, washed with methanol to remove the remained acid and AEAPTMS. Finally the yield was dried at 50 °C in vacuum for 72 h.

EPDM and modified Bt was mixed on a two-roll mill. The recipe of the blends was shown in Table 2. For the comparison purpose, unmodified bentonite/EDPM and carbon black/EPDM composites were also prepared. The optimum vulca-

Table 1. Concentration of Reagents

	Concentration of reagents (M)			Content of AEAPTMS (%)
	HCl	H₂O	AEAPTMS	
S1	0.39	1.32	0.15	4
S2	0.77	2.65	0.15	6
S3	1.15	3.97	0.15	9
S4	1.54	5.31	0.15	12
S5	1.92	6.62	0.15	14

Table 2. Ingredients for Compounding of EPDM/Bentonite Composites

Ingredients	(phr)
EPDM	100
Bt/CB	20
ZnO	5
Stearic acid	1.5
Accelerator CBS	3
Accelerator DM	1
Sulfur powder	1.5

nization time was determined using a Rheometer (MDR 2020) at a cure temperature of 160 °C. Then, the vulcanization was carried out in a heating press.

Characterization. Fourier transform infrared (FTIR) analysis of the modified Bt was conducted on a thin film about 200-300 μm using Perkin Elmer spectrum 100. Samples were scanned in the wave range between 650 and 4000 cm^{-1} with resolution of 4 cm^{-1}. Thermogravimetric analysis of modified Bt and the product was carried out with Perkin Elmer TGA 4000 by heating from 30 to 900 °C at a rate of 20 °C/min under the N₂ atmosphere. Hardness testing was tested on shore durometer type a according to ASTM D2240. Mechanical testing was performed according to the ASTM D412. All the results were measured by a Tinius Oisen H5KT-0401 testing machine with the average of three measurements.[24] The tensile fracture surface of compounds was coated with a thin layer of gold and then observed on a JSM-7500 FE-SEM (JEOL).[25] X-ray diffraction (XRD) was performed at 25 °C with Empyrean (manufactured by PANalytical) X-ray diffractometer using a Cu target, operated at 40 kV and 30 mA. X-ray diffraction data were obtained from 4° to 20° (2θ) at a rate of 2°/min.

Swelling Properties. Swelling test was conducted using toluene according to ASTM D 471-06. Initial weight (M_i) and swollen weight after 72 h of immersion in toluene (M_s) of the vulcanized specimens were measured. Swelling percentage

indicating the increase in mass due to toluene uptake and the swelling resistance of the vulcanized composites was calculated base on eq. (1).[17]

$$\text{Swelling } (\%) = [(M_s - M_i)/M_i] \times 100 \qquad (1)$$

Results and Discussion

Structure Determination. In this research work, FTIR analysis was carried out for the determination of certain chemical bonds before and after the modification. The spectra of three different samples is compared, including (a) unmodified bentonite, (b) AEAPTMS, (c) modified bentonite and (d) control sample (see Figure 1). As shown in Figure 1, the characteristic peaks appears at 3621, 3300~3400, 1636 and 1400~1500 cm^{-1} were attributed to the stretching vibration of O-H group, the stretching vibration and the bending vibration of H-O-H in the firmly bonded water and the absorption of CaCO₃. In addition, one strong peak for neat bentonite is observed at 900~1100 cm^{-1}, corresponding to the absorption of Si-O-Si stretching vibration. Si-O, Al-O, Ca-O vibrations at the surface of Bt are observed at around 795 cm^{-1}, which are not so specific. As shown in Figure 1, there are two weak peaks of stretching vibration at 3369 and 3289 cm^{-1} due to the characteristic -NH₂ group in AEAPTMS. The strong peaks of asymmetric and symmetric stretching of -C-H in CH₂ in the functional group are at 2850 and 2950 cm^{-1}. There is also -CH₂- scissoring vibration at 1464 cm^{-1}, AEAPTMS deformation vibration from the N-H bond at 1574 cm^{-1}, Si-O-C at 1189 and 1076 cm^{-1}, and Si-C vibration at 810 cm^{-1}.
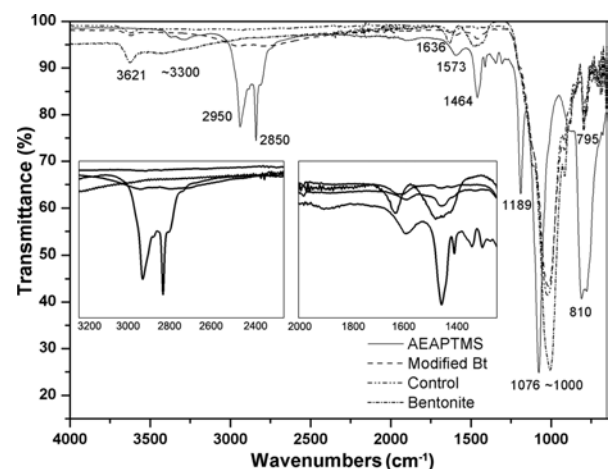

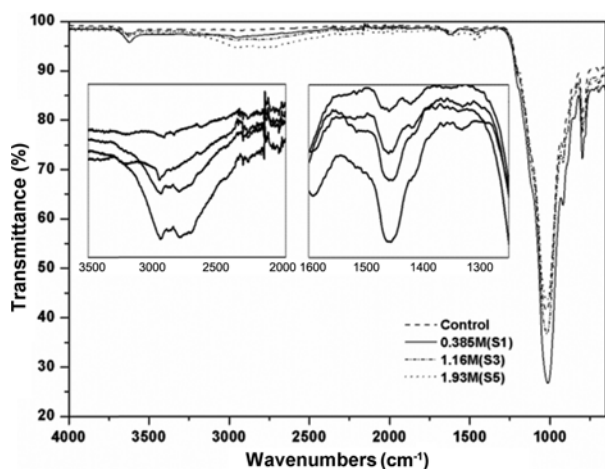**Figure 1.** FTIR spectroscopy of AEAPTMS, modified Bt, neat bentonite and the control sample.

Figure 2. FTIR spectroscopy of modified Bt with different concentrations of HCl.

Figure 3. Thermogravimetric analysis of modified Bt and neat Bt.

Figure 4. Thermogravimetric analysis of EPDM/Bt composites prepared with modified Bt and neat Bt: 30~455°C.

Though the absorption of some chemical bonds after the modification is not so significant because the modification just happens partly on the surface or interface, some differences could be observed compared to the unmodified Bt or control sample especially at 3000~2800 cm^{-1} and 1464 cm^{-1} due to the existence of -CH$_2$- groups. The modification could be further confirmed by increasing the concentration of the catalyst. Shown in Figure 2, as the concentration of HCl increased from 0.39 to 1.92 M, the absorption at 3000~2800 cm^{-1} and 1464 cm^{-1} is strengthened due to the increased productivity of the modification reaction.

Thermogravimetric Analysis. The TGA curves of the organo-modified Bt prepared with various HCl concentration and the EPDM/modified Bt composites is showed out in Figures 3 and 4, respectively.

The content of AEAPTMS in the organo-modified Bt is as follows (see Table 1): S1, 4%; S2, 6%; S3, 9%; S4, 12%; S5, 14%. That indicates when the concentration of HCl increases from 0.39 to 1.92 M (see Table 2), more AEAPTMS is hydrolyzed, leading to an increment of the content of AEAPTMS in the organo-modified Bt. Meanwhile, the decomposition temperature (T_d) of the organic layer is found to be approximately 300 °C, which is almost the same with that of the organo-modified Bt/EPDM composites, as shown in Figure 4. Compared with neat EPDM and unmodified Bt/EPDM composites, organo-modified Bt/EPDM have much higher T_d, indicating the improved thermal stability. This might be attributed to the improved dispersion state of organo-modified Bt in the EPDM matrix as well as the enhanced interfacial interaction.

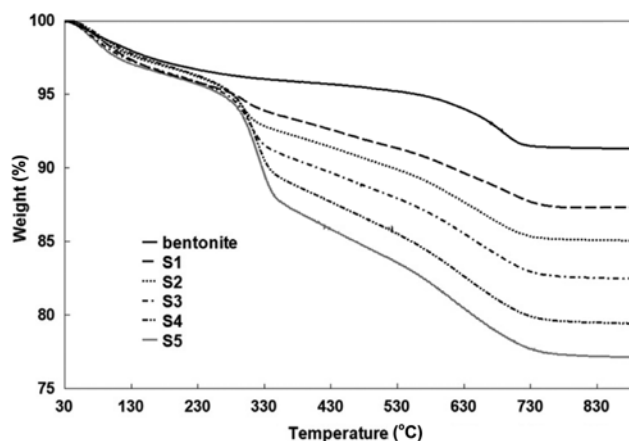**X-ray Diffraction.** For the determination of the intercalated or exfoliated structure, X-ray diffraction patterns of the unmodified Bt and organo-modified Bt were conducted. The strongest peak corresponds to the (001) plane reflections of the silicate layer aggregate.[26] As shown in Figure 5, for the unmodified Bt, it has an initial interlayer distance of about 1.27 nm. After the modification, all the organo-modified Bt have an interlayer distance around 1.81 nm, which suggests that AEAPTMS has been successfully inserted into the interlayer of Bt. Here, the little differences between 1.81, 1.80 and 1.82 nm may be result from the undulation of the experiment value. In our work, the peak in S2 is apparently sharper compared with that of other specimens, indicating that as the content of AEAPTMS in the composite increases until 6%, the ratio of intercalated Bt increases, accordingly. It is also believed that as the content of AEAPTMS increases continuously, there is a trend that the d_{001} peak at around 1.81 nm is
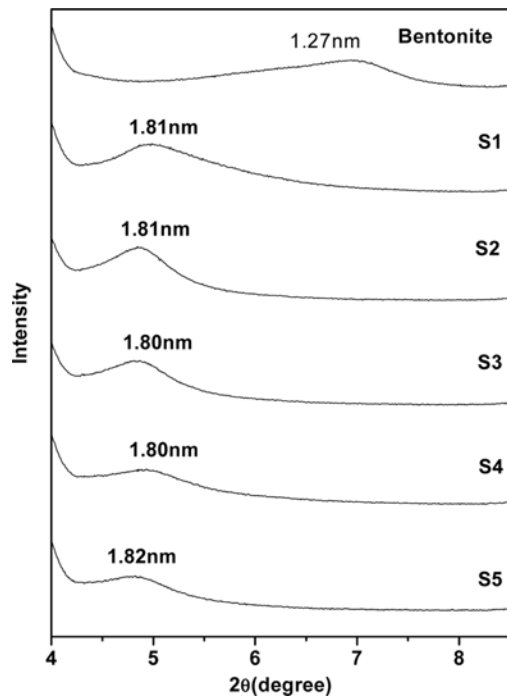
Figure 5. X-ray diffraction of modified Bt and neat Bt.

to disappear, showing that the intercalated Bt is partially exfoliated because of the weakened interaction between layers.

Scanning Electron Microscopy. Figure 6(a) and 6(b) show the FE-SEM micrograph of the tensile fractured surfaces of unmodified Bt/EPDM and organo-modified Bt/EPDM composites with 1000× magnification. As shown in Figure 6(a), the Bt particles are mostly with a diameter over 10 μm. Meanwhile, due to its poor compatibility with the rubber matrix, the particles are dispersed heterogeneously in their original aggregate state in the matrix, indicating a weak interaction between Bt and EPDM. After modification, the particle size of organo-modified Bt is significantly decreased as shown in Figure 6(b). Beyond that, the organo-modified Bt particles are "adhensive" with the matrix. It can be seen that the boundary is vague, suggesting that the compatibility of the organo-modified Bt particles with the matrix is improved apparently. That is believed to contribute a lot to the reinforcement of mechanical strength of the products. Comparing Figure 6(a) and 6(b) reveals an increase of roughness and tortuous path of the fracture surfaces in the condition that Bt is modified. This could be explained by the better compatibility between EPDM and the modified Bt and enhanced fracture energy.[27,28]

Vulcanization and Mechanical Properties. The vulcanization curves are shown in Figure 7 while the vulcanization characteristics, expressed in terms of optimum curing time,
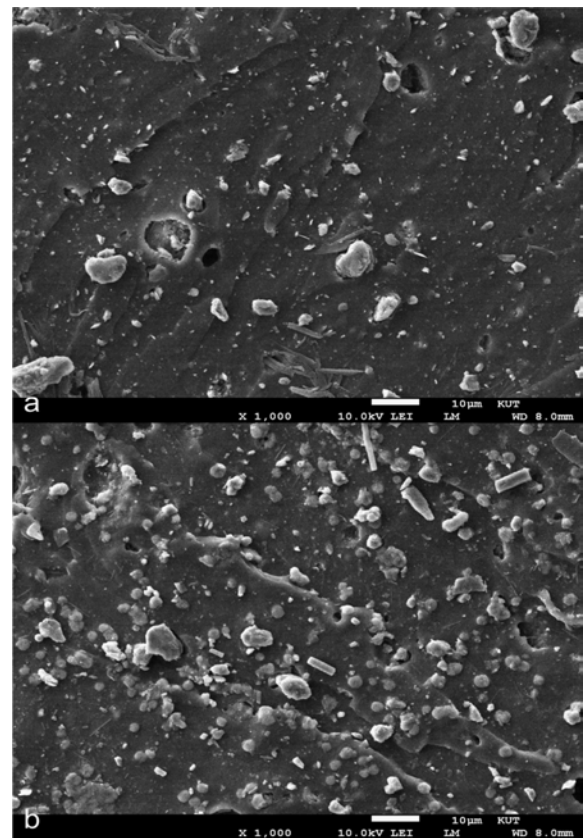

Figure 6. SEM microphotograph of (a) unmodified Bt/EPDM composites; (b) organo-modified Bt/EPDM composites.

tc90, minimum and maximum torque value, ML and MH are summarized in Table 3. The torque values of ML and MH increases to 8.6 and 36 lb-in respectively when the AEAPTMS content reaches 6.26%, above which the torque values start to decrease. Different from the trend of torque values, tc90 increases continuously. It is possible that AEAPTMS acts as a curing barrier for the crosslinking of sulfur powder in the
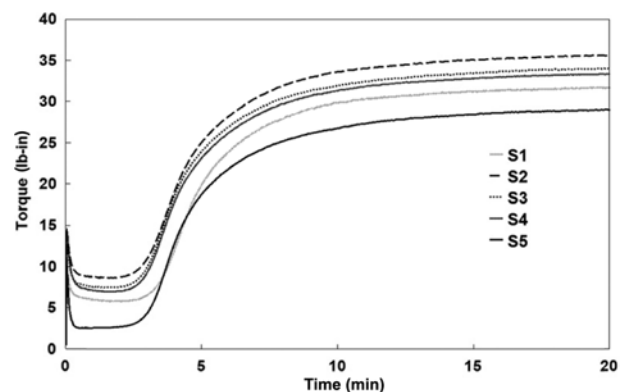

Figure 7. Vulcanization curves of modified Bt.

Table 3. Rheological Properties during Vulcanization

	ML (lb-in)	MH (lb-in)	tc90 (min)
S1	5.8	34.0	09'16"
S2	8.6	36.0	09'30"
S3	7.4	34.4	09'43"
S4	6.9	33.8	09'43"
S5	2.5	29.4	09'53"

rubber matrix because of its interaction with EPDM. Meanwhile, the linear or steric structure of hydrolyzed AEAPTMS might contribute to a weakened thermo-conductivity, either. A third possible reason is that the curing accelerators, such as CBS and DM are attracted onto the surface of organo-modified Bt due to the formation of hydrogen bond between them.

The influence of the content of AEAPTMS on the tensile properties and shore A hardness of organo-modified Bt/EPDM
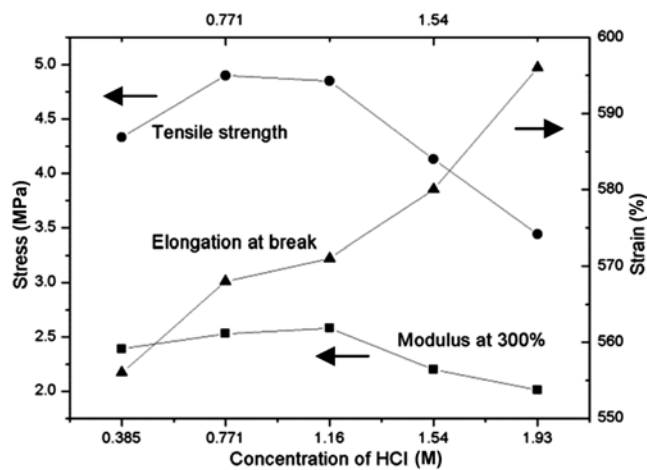
Figure 8. Mechanical properties of EPDM/modified Bt composites.
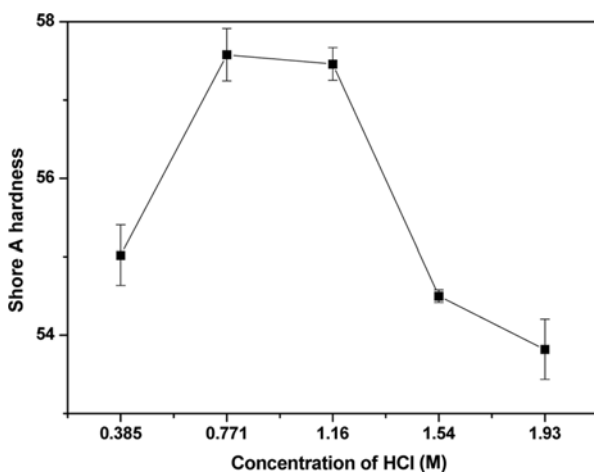
Figure 9. Shore A hardness of modified Bt (S1-S5).

composites were shown in Figures 8 and 9, respectively. In the condition that the concentration of H_2O in the reaction is low, the swelling of the layered Bt barely happens. A percentage of AEAPTMS is hydrolyzed but not so effective for the intercalation of the layered structure of Bt. As the content of hydrolyzed AEAPTMS increased, the hardness of EPDM matrix becomes decreased while the elongation at break increased gradually. Generally, the trend of shore A hardness is same with that of tensile strength as the content of AEAPTMS increases. The dispersion of modified Bt is greatly improved because the modification enlarges the distance between layers while the surface of Bt becomes hydrophobic.

Figure 10 shows the comparison of stress-strain curves of neat EPDM, unmodified Bt/EPDM, organo-modified Bt/EPDM and carbon black/EPDM composites. As is shown in Figure 10, after the modification, the tensile strength and elongation at break are all greatly improved compared with the neat EPDM or unmodified Bt-filled EPDM. The tensile strength is even higher than EPDM filled with carbon black.

Swelling Properties. Because of the uptake of organic solvent, the volume of the specimens increases accordingly. Therefore, the swelling percentage becomes an important measure for the description of swelling properties. It is well known that the smaller the swelling percentage is, the stronger the swelling resistance of the composite is. Figure 11 illustrates the swelling percentage of organo-modified Bt/EPDM composite as a function of immersion time. It is shown that all the specimens filled with unmodified Bt or modified Bt have much lower swelling percentages related to neat EPDM, whose swelling percentage is as high as 195%. It is believed that the
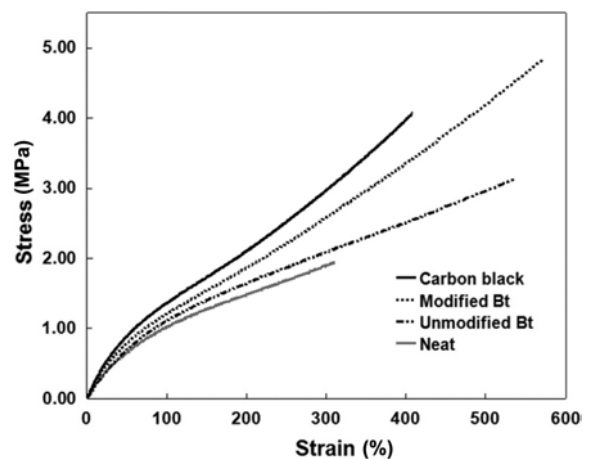
Figure 10. Comparison of mechanical properties of EPDM/modified Bt and other specimens.
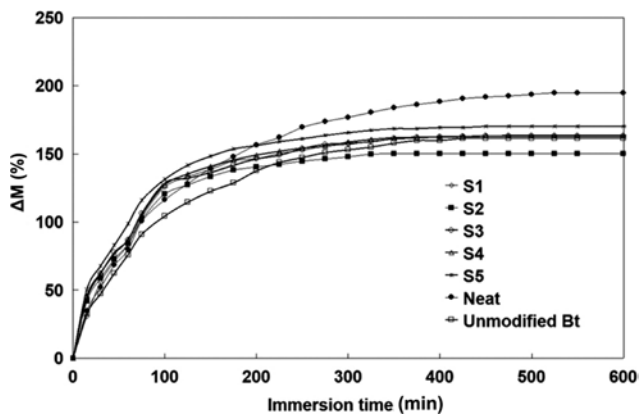
Figure 11. Swelling properties of EPDM samples filled with modified Bt, unmodified Bt and neat EPDM.

hydrophilic Bt acts an effective barrier for the uptake of toluene which is non-polar. S2 shows the lowest swelling percentage which is only 150%, contributing to the most homogeneous dispersion of Bt in the matrix and the proper content of AEAPTMS. For S1, the modification is not so significant which contributed little to the dispersion of Bt. Meanwhile, if the content of AEAPTMS is too high, the swelling percentage increases gradually. That could be explained with the increment of the hydrophobic group which is highly amiable to toluene.

Conclusions

In this study, some important factors influencing the characteristics of the modified Bt and the products were investigated. It was proved that with the concentration of the catalyst increased, the hydrolyzation of AEAPTMS was reinforced. The content of AEAPTMS in the modified Bt and the products was characterized and determined by FTIR and TGA. Results show that the content of AEAPTMS increased consistently with the concentration of hydrochloric acid increased during the modification reaction. Considering the self-condensation of AEAPTMS, the modified Bt for reinforcement of EPDM was achieved after optimization with a proper content of AEAPTMS. The relationship between the content of AEAPTMS and the vulcanization and mechanical properties of the EPDM/modified Bt composites was also studied. When the content of AEAPTMS was in the range of 6~9% in the modified Bt, the best tensile strength (4.9 MPa) could be achieved, which was 150% higher than that of neat EPDM. The elongation at break was also increased from 300% to more than 500%. These improvements were due to the improved dispersion state as well as enhanced interfacial interaction, which was evidenced using the XRD, SEM and swelling testing.

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