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Preparation and properties of EPDM–clay hybrids

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Abstract

Ethylene propylene diene methylene linkage rubber (EPDM)–clay hybrids have been prepared by mixing with EPDM and organophilic clay via vulcanization process. When we used thiuram and dithiocarbamate for the vulcanization accelerator, EPDM–clay hybrid was prepared successfully. In this EPDM–clay hybrid, the silicate layers of the clay were exfoliated and almost dispersed to the monolayers. The tensile strength of the EPDM–clay hybrid loading 4 wt% clay exhibited 2.0 times higher value compared to that of neat EPDM at 25 °C. The storage moduli (E') of the EPDM–clay hybrid were also higher than that of neat EPDM. The gas permeability of EPDM–clay hybrid decreased 30% as compared with neat EPDM. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Vulcanization process; Montmorillonite; Transmission electron microscopy

1. Introduction

Clay is comprised of silicate layers having a 1 nm thick planar structure. It has been shown that the silicate layers can be dispersed at the molecular level (nanometer level) in a polymer matrix with the polymer existing between the silicate layers (two-dimensional space). In recent years, these types of nanometer composites (hybrid materials) have attracted great interest to many researchers since they frequently exhibit unexpected hybrid properties synergistically derived from the two components. In our previous works, we have synthesized nylon 6-clay hybrid (NCH) in which 1 nm thick silicate layers of clay minerals were exfoliated and homogeneously dispersed in the nylon 6 matrix [1]. The NCH exhibits various superior properties such as high strength, high modulus and high heat resistance compared to conventional nylon 6 [2]. Since then, other polymer–clay hybrids such as polyimide [3], epoxy resin [4–8], polystyrene [9–13], polycaprolactone [14], acrylic polymer [15], polyurethane [16], poly(ethylene terephathalate) [17], and polyolefins [18–21] have been reported.

Polyolefins, i.e. polypropylene (PP), polyethylene, and ethylene–propylene rubber are the most widely used polymers. Polyolefin–clay hybrid could not be prepared easily because polyolefin is hydrophobic and has poor miscibility with clay silicates. There is a direct-intercalation process in which PP is modified using maleic anhydride, followed by melt compounding [18–21]. It is a useful process from an industrial standpoint. However, because the modified process for ethylene propylene diene methylene linkage rubber (EPDM) is complicated, we studied a new intercalation method during the vulcanization process.

2. Experimental

2.1. Materials

The materials used for the preparation of the samples are purified montmorillonite (Kunipia-F) from Kunimine Ind. Co., octadecylamine from Wako Pure Chemical Co., and EPDM (Esupulen 505) from Sumitomo Chemical.

Vulcanization accelerators used were of five types of materials: thiourea (ethylenethiourea, NPV/C), thiazole (2-mercaptobenzothiazole, M), sulfenamide (*N*-cyclohexyl-2-benzothiazylsulfenamide, CZ), thiuram (tetramethylthiuram monosulfide, TS) and dithiocarbamate (zinc dimethyldithiocarbamate, PZ). Fig. 1 shows the structural formulae of these materials.

2.2. Preparation of organophilic clay

Sodium montmorillonite (80 g, cation exchange capacity: 119 mequiv./100 g) was dispersed in 5000 ml of hot water (about 80 °C) by using a homogenizer. Octadecylamine (31.1 g, 115 mmol) and conc. HCl (11.5 ml) were dissolved in hot water. This solution was poured into the montmorillonite–water solution with vigorous stirring by using the homogenizer for 5 min to yield white precipitates. The

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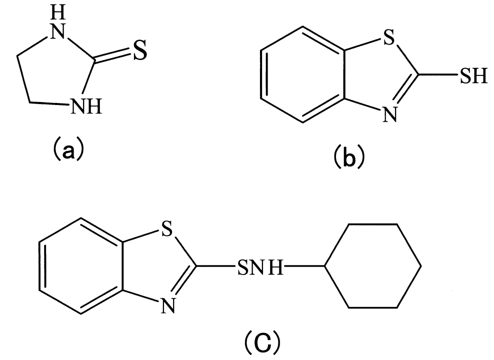

$[(CH_3)_2NC(S)]_2S$ (d)

$[(CH_3)_2NC(S)S]_2Zn$ (e)

Fig. 1. Structural formula of vulcanization accelerator (a) ethylenethiourea, NPV/C; (b) 2-mercaptobenzothiazole, M; (c) *N*-cyclohexyl-2-benzothiazylsulfenamide, CZ; (d) tetramethylthiuram monosulfide, TS; (e) zinc dimethyldithiocarbamate, PZ.

precipitates were collected and washed with hot water three times, and freeze-dried to yield an organophilic montmorillonite intercalated with octadecylammonuim. This material is abbreviated as C18-Mt. The inorganic content of C18-Mt was 69.2 wt% by measuring the weights before and after burning out its organic parts.

2.3. Preparation of EPDM–clay hybrids

Pellets of EPDM and the powder of C18-Mt, 7 phr (parts per hundred resin) were melt-blended at 200 °C by using a twin-screw extruder (Japan Steel Works Ltd, TEX30 α-45.5BW). The screw length was 1365 mm and *L*/*D* was 45.5. The obtained strands, zinc oxide 5 phr, stearic acid 1 phr, sulfur 1.5 phr and vulcanization accelerator 1.5 phr were compounded by using a mixing roll. Vulcanized EPDM was press molded at 160 °C for 30 min to yield rubber sheets (150 mm × 150 mm × 2 mm or 0.5 mm).

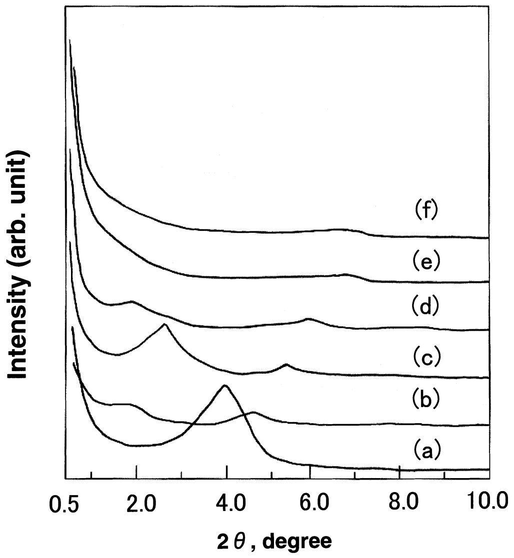

Fig. 2. XRD patterns of (a) C18-Mt and (b)–(f) EPDM–clay hybrid used five types of vulcanization accelerator: (b) ethylenethiourea, NPV/C; (c) 2-mercaptobenzothiazole, M; (d) *N*-cyclohexyl-2-benzothiazylsulfenamide, CZ; (e) tetramethylthiuram monosulfide, TS; (f) zinc dimethyldithiocarbamate, PZ.

2.4. Evaluation of dispersibility of the clay

The basal spacings of the clay were studied by means of wide angle X-ray scattering using a Rigaku RAD-B diffractometer with Cu Kα radiation at 30 kV and 30 mA. XRD patterns of the thin films of the hybrids were obtained. Transmission electron microscopy (TEM) observations were performed for the ultra thin sections of the films by Jeol-2000EX TEM using an acceleration voltage of 200 kV.

2.5. Measurement of mechanical properties and permeability

The tensile test was measured according to ASTM. The dynamic modulus was measured by using an Iwamoto VES-F viscoelastic meter. The storage modulus was obtained by sinusoidally vibrating the samples in tensile mode at 10 Hz. The permeability of nitrogen gas was measured by using a GTR-30 Yanaco gas permeation measuring system at 60 °C. EPDM–clay hybrid samples were sheets of 0.5 mm thickness, and the permeation area of gas is 16.2 cm^2.

3. Results

Fig. 2 shows the XRD pattern of C18-Mt and EPDM–clay hybrids by using five types of vulcanization accelerators. The peak between 2 and 5° appeared in the case of EPDM–clay prepared using NPV/C, M and CZ. It is clear that the clay silicate layers aggregate in the EPDM matrix. However, in the case of TS and PZ, a peak based on C18-Mt disappeared and there was a rise in the pattern at low scattering angle. This shows that the basal spacings of the clays were expanded. Fig. 3 shows TEM images of EPDM–clay hybrids using PZ vulcanization accelerator in which the dark lines are the cross sections of silicate layers of 1 nm thickness. The clay silicate layers were exfoliated and dispersed uniformly in EPDM as monolayers and a few layers. These EPDM materials that used TS and PZ as the vulcanization accelerator are called EPDM–clay hybrid and those used NPV/C, M and CZ as the vulcanization accelerator are called EPDM–clay composite in which the clay silicate layers are not exfoliated.

These EPDM–clay hybrids using TS and PZ as the vulcanization accelerator showed superior properties. To clarify the effect of hybridization with the clays, tensile tests of EPDM, EPDM–clay hybrids using TS and PZ and EPDM–clay composites using NPV/C, M and CZ were

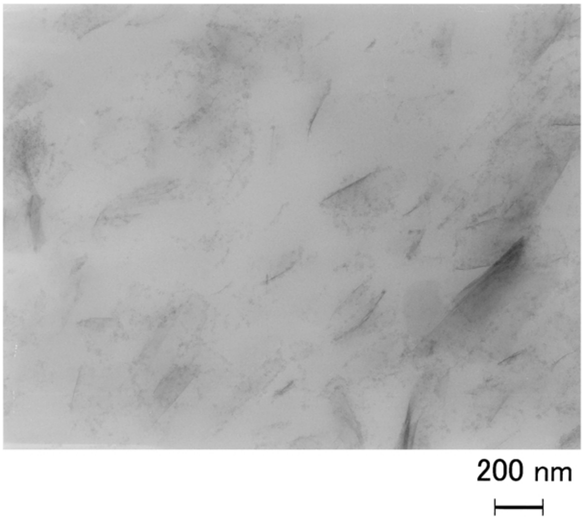

Fig. 3. TEM photograph of EPDM–clay hybrid.

done. Table 1 shows the results of the tensile test. The tensile strength of the EPDM–clay hybrids became higher than that of EPDM. The strength of the EPDM–clay hybrids using TS and PZ as the vulcanization accelerator was 2.0 times higher than that of EPDM. The 100% tensile stress of the EPDM–clay hybrids also increased compared to that of EPDM. The 100% tensile stress of the EPDM–clay hybrid using TS and PZ were 40% higher than that of EPDM. The elongation of the EPDM–clay hybrid using PZ was 520%. The dynamic storage moduli of the EPDM–clay hybrids were higher than that of EPDM.

Table 1 shows the permeability of nitrogen for the EPDM–clay hybrids and for EPDM. The permeability of the EPDM–clay hybrid using TS and PZ decreased 30% compared to EPDM.

4. Discussion

We consider the mechanism of EPDM intercalation into clay gallery, on the basis of experimental results. Fig. 4 shows the XRD patterns of various stages of the process of EPDM–clay hybrid preparation using PZ as the vulcanization accelerator. The first stage (Fig. 4(b)) is when EPDM and C18-Mt are melt compounded. The second stage (Fig. 4(c)) is when EPDM and C18-Mt and vulcanization agent are compounded using a mixing roll. The third stage (Fig. 4(d)) is after vulcanization at 160 °C. After vulcanization, XRD peaks based on clay layers disappeared at low angle. From these results, we conclude that the intercalation of EPDM molecules into clay galleries occurs during the time of mixing roll (formed the modified EPDM and intercalated into clay) and vulcanization process (exfoliated the clay and cured EPDM).

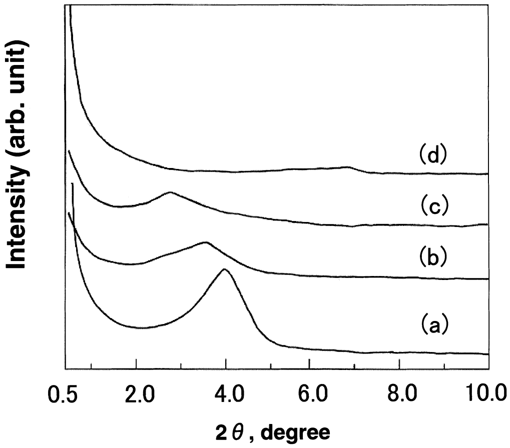

Fig. 4. XRD patterns of (a) C18-Mt and (b)–(d) each stage of EPDM–clay hybrid preparation process: (b) when EPDM and C18-Mt is melting compounded using extruder; (c) when EPDM and C18-Mt, vulcanization agent and vulcanization accelerator PZ is compounded using mixing roll; (d) after vulcanization at 160 °C.

When we used the vulcanization accelerator, thiuram (TS) and dithiocarbamate type (PZ), and EPDM–clay hybrids were prepared successfully. However, when thiourea (NPV/C), thiazole (M), and sulfenamide (CZ) types were used as accelerators, the dispersibility of clays in EPDM was insufficient. Thiuram and dithiocarbamate type vulcanization accelerators dissociate into radicals themselves when the temperature is raised. The radicals combine with carbon atoms in EPDM chains to polarize EPDM molecules. These EPDM molecules intercalate into the clay galleries through hydrogen bonds between the polar EPDM and the clay surface. The conceptual image of EPDM–clay hybrid material is illustrated in Fig. 5.

Table 1
Properties of EPDM–clay hybrid

Material	EPDM–clay					EPDM
Vulcanization accelerator	NPV/C	M	CZ	TS	PZ	PZ
Properties						
Tensile strength (MPa)	8.0	7.5	8.1	11.0	10.1	5.0
Elongation (%)	307	173	185	443	520	280
100% tensile stress (MPa)	1.9	1.8	1.7	2.3	2.3	1.6
Strage modulus (MPa)	5.5	5.3	5.8	6.0	6.2	3.3
N_2 permeability ($\times 10^{-9}$ cm^3 cm cm^{-2} sec^{-1} cmHg^{-1})	1.8	2.2	2.1	1.7	1.7	2.4

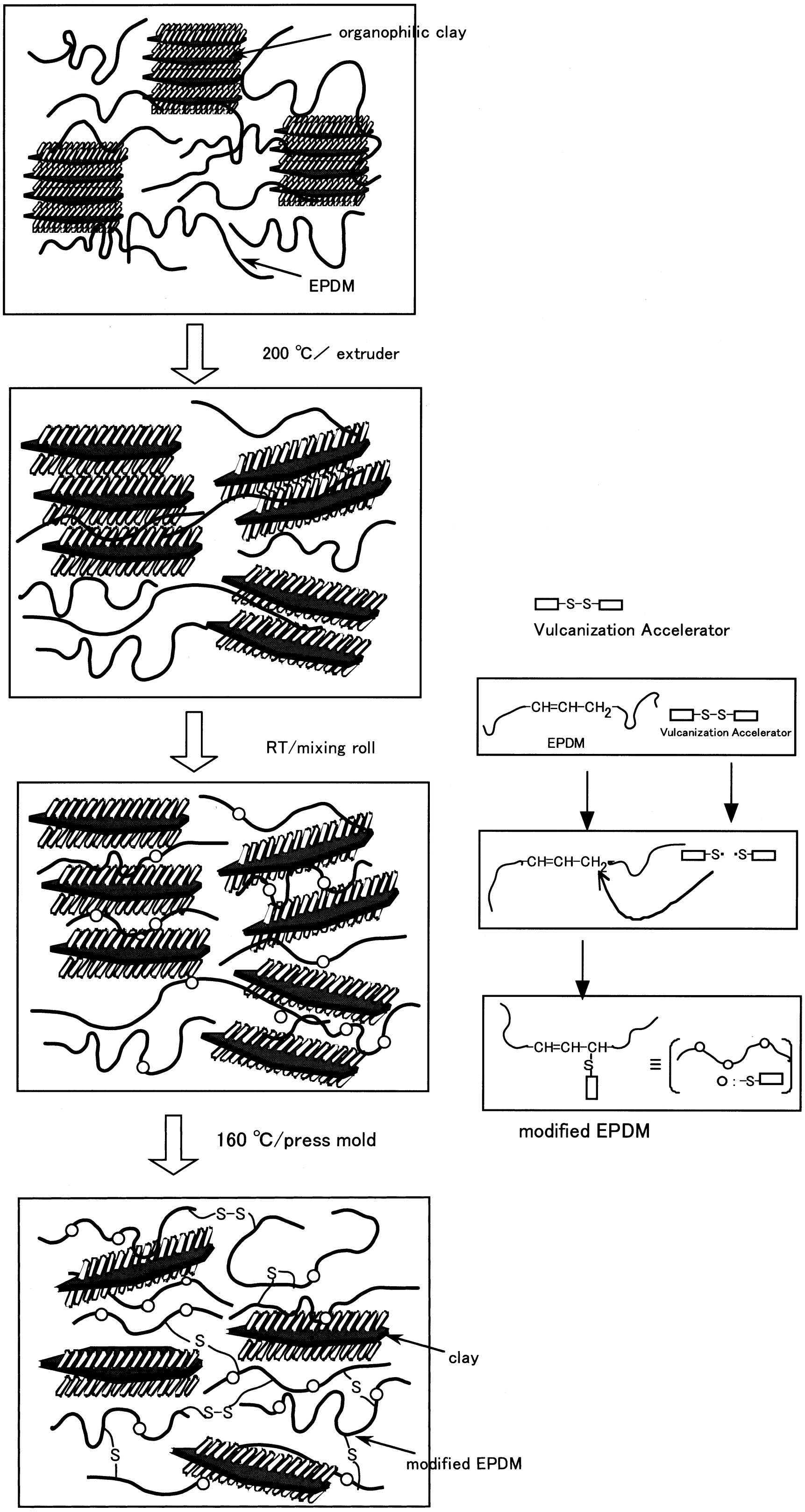

Fig. 5. Conceptual figure of vulcanization process of EPDM and intercalation into clay gallery.

The elongation of EPDM–clay hybrids increased remarkably. The mechanism about this point is not clear at present. We suppose that the stage of vulcanization weakens in the vicinity of the clay surface because of the steric hindrance.

5. Conclusion

We have prepared EPDM–clay hybrids via a vulcanization process using EPDM and an organophilic clay. In this material, the silicate layers were exfoliated and dispersed uniformly in EPDM. We found that the EPDM–clay hybrid was prepared successfully when thiuram (TS) and dithiocarbamate type (PZ) compounds were used for vulcanization accelerator. The modulus and strength of this material increased compared to EPDM. For example, the strength of the EPDM–clay hybrid is 2.0 times higher than that of EPDM. The gas permeability of the EPDM–clay hybrid decreased 30% as compared with EPDM.

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