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Properties of Thermoplastic Elastomers Made of MAH-*g*-EPDM, Zinc Oxide and Amino Acids†

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Thermoplastic elastomers were prepared by mixing maleic anhydride-grafted ethylene-propylene-diene terpolymer (MAH-*g*-EPDM), zinc oxide and amino acids. 4-Amino-2-methoxybenzoic acid (MBA), 4-aminosalicylic acid, 12-aminolauric acid and L-glutamine were employed as the amino acids. The thermoplastic elastomers were analyzed by infrared spectroscopy (IR), solvent extraction, crosslink density and physical properties. The amino acids reacted with maleic acid groups of the MAH-*g*-EPDM and zinc oxide to form ionomers. Like cured elastomers, it is possible that crosslink densities of the thermoplastic elastomers are measured using the solvent swelling method. Compared to the specimen without amino acids, crosslink densities of the thermoplastic elastomers decreased due to the long crosslinkages. Crosslink density of the sample containing 12-aminolauric acid was lower than the others. Physical properties of the sample containing 4-aminosalicylic acid were better than the others. This can be explained by the hetero-crosslinkages.

Key Words: Thermoplastic elastomer, MAH-*g*-EPDM, Zinc ionomer, Amino acid.

INTRODUCTION

Thermoplastic elastomers have attracted considerable attention in commercial and research fields because they have the processing properties of thermoplastics as well as the performance of typical elastomers[1-6]. An ionomer is a polymer with a small mole fraction of ionic groups bonded to the polymer backbone[7,8]. It is not a chemically crosslinked polymer but a type of thermoplastic elastomer with a reversible crosslinker. Ethylene-propylene-diene terpolymer (EPDM) is a popular synthetic rubber with good weather resistance and electrical resistivity[9-12]. Modification of rubbers with maleic anhydride (MAH) is a useful way of imparting the compatibility to immiscible polymer blends as well as improving the interfacial adhesion in polymeric composites[13-15]. MAH-grafted EPDM (MAH-*g*-EPDM) is one of the useful MAH-modified elastomers[16,17].

In the present work, thermoplastic elastomers composed of MAH-*g*-EPDM, zinc oxide and amino acid were prepared. Ionic bonds can be formed between the amino acid-modified maleic acid groups and zinc oxides. The thermoplastic elastomers were characterized by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), solvent swelling behaviours including crosslink density and physical properties. Physical properties of rubber vulcanizates depend on their crosslink densities. In general, crosslink densities of cured elastomers are measured using a swelling method[18,19].

EXPERIMENTAL

Royaltuf 498 of Chemtura Co. was employed as an MAH-*g*-EPDM (MAH functionality 1.0 %). Songnox 1076 (octadecyl 3-(3,5-di-*t*-butyl-4-hydroxy phenyl)-propionate) of Songwon Industrial Co. was used as an antioxidant. Zinc oxide, zinc stearate, 4-amino-2-methoxy benzoic acid (MBA), 4-amino salicylic acid (ASA), 12-amino lauric acid (ALA), L-glutamine (LG), decalin, toluene and xylene were purchased from Aldrich Co. Formulation of the compounds was shown in Table-1.

The components were mixed in an electrically heated mixing chamber (nominal volume 60 mL) of a Haake Rheocorder. The rotor speed was 50 rpm. The compounds were prepared as follow: (1) the MAH-*g*-EPDM and amino acid were loaded together into the mixer and mixed for 3-5 min at 160 ºC, (2) the other additives of zinc oxide, zinc stearate and antioxidant were compounded into the mixture of MAH-*g*-EPDM and amino acid for 15 min at 180 ºC. The sample sheets were prepared by pressing at 200 ºC for about 10 min in a compression mold (10 MPa, 2 mm thickness).

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TABLE-1 FORMULATION (phr)				
Compound	MBA	ASA	ALA	LG
Royaltuf 498	100.0	100	100	100
Songnox 1076	0.3	0.3	0.3	0.3
Zinc oxide	5.0	5.0	5.0	5.0
Zinc stearate	5.0	5.0	5.0	5.0
4-Amino-2-methoxybenzoic acid	0.5	0.0	0.0	0.0
4-Aminosalicylic acid	0.0	0.5	0.0	0.0
12-Aminolauric acid	0.0	0.0	0.5	0.0
L-glutamine	0.0	0.0	0.0	0.5

The samples were analyzed by ATR-FTIR (Perkin-Elmer spectrum100) with zinc selenide (ZnSe) crystal. Crosslink densities of the samples were measured using the swelling method. The samples were soaked in a swelling solvent for 2 days at room temperature and the weights of the swollen samples were measured. And they were dried and their weights were measured. Decalin (ε = 2.2), toluene (ε = 2.38) and xylene (ε = 2.4) were employed as the swelling solvents. The swelling ratio (Q) was calculated by eqn. (1)

$$Q = (W_s - W_u)/W_u \quad (1)$$

where W_s and W_u are the weights of the swollen and unswollen samples, respectively. In general, the reciprocal swelling ratio (1/Q) was used as the apparent crosslink density.

The tensile properties were measured according to ASTM D 412 using an Instron universal testing machine (UTM, model 3345) at a crosshead speed of 500 mm/min. The tear strength was measured according to ASTM 624-86 using an Instron UTM 3345. The compression set was measured according to ASTM D 395.

RESULTS AND DISCUSSION

Fig. 1 shows ATR-FTIR spectra of the thermoplastic elastomers. The principal absorption bands originating from the MAH-*g*-EPDM were 1714, 1740 and 1775 cm^{-1} corresponding to carboxylic acid, ester group and cyclic anhydride, respectively[20,21]. The absorption band of carboxylic acid at 1714 cm^{-1} was attributed to the hydrolysis of anhydride groups. The absorption band at 1775 cm^{-1} is a characteristic peak of a cyclic anhydride. The anhydride group was not observed in the ATR-FTIR spectra. This means that the residual maleic anhydrides in MAH-*g*-EPDM changed to maleic acid by the additives. The broad band around 1590 cm^{-1} was assigned to the asymmetric carboxylate stretching region due to the formation of ionomer[22]. An ionomer formation between MAH-*g*-EPDM and zinc oxide particle was described in **Scheme-I**.

The apparent crosslink densities (1/Qs) measured with decalin, toluene and xylene were summarized in Table-2. The 1/Q values measured using toluene were higher than the others, whereas those measured using decalin were lower than the others irrespective of the samples. The 1/Q values of the sample 12-amino lauric acid were lower than the others irrespective of the swelling solvents. For the samples 4-amino-2-methoxy benzoic acid, 4-amino salicylic acid and L-glutamine, the order of the 1/Q values varied slightly depending on the swelling solvents. The order of the 1/Q values obtained using decalin and toluene was L-glutamine > 4-amino-2-methoxy benzoic acid, 4-amino salicylic acid > 12-amino lauric acid, while that obtained using xylene is 4-amino salicylic acid > 4-amino-2-methoxy benzoic acid, L-glutamine > 12-amino lauric acid. The sample without any amino acid was prepared and its apparent crosslink density was also measured to compare those of the thermoplastic elastomers. The apparent crosslink densities of the thermoplastic elastomers were reduced by adding amino acid as listed in Table-3. This might be due to the long ionic bonds by amino acids. The amine groups of amino acids can react with the maleic acid groups of MAH-*g*-EPDM to form peptide bonds and the acid groups of the amino acids can form ionic bonds with zinc oxide. Therefore, the length of the ionic bonds may become longer. Ionic bonds between the amino acid-treated MAH-*g*-EPDM and ZnO particle for 4-amino-2-methoxy benzoic acid, 4-amino salicylic acid, 12-amino lauric acid and L-glutamine were described in **Schemes II-V**, respectively.

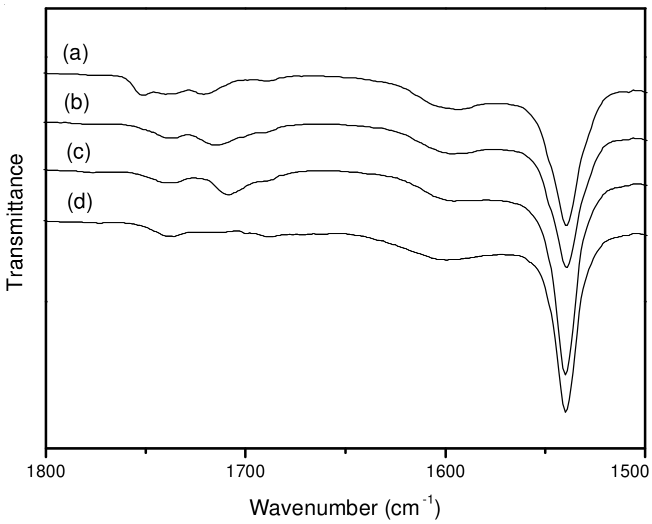
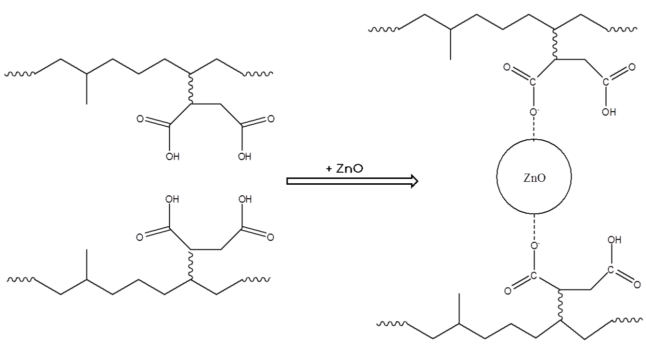


Fig. 1. ATR-FTIR spectra of the samples 4-amino-2-methoxy benzoic acid (a), 4-amino salicylic acid (b), 12-amino lauric acid (c) and L-glutamine (d)

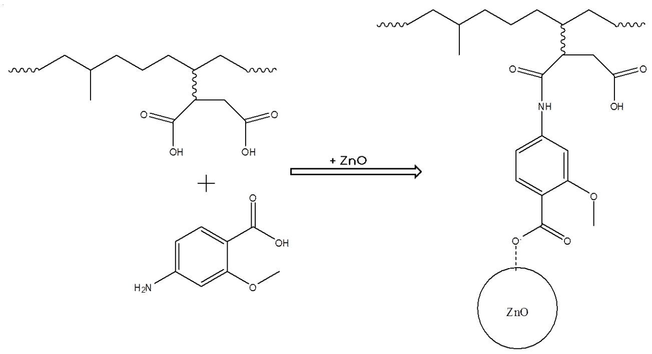


Scheme-I: Ionomer formation between MAH-*g*-EPDM and ZnO particle

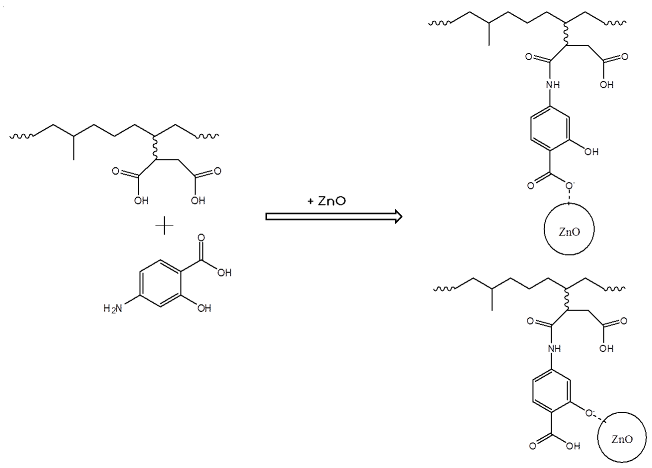
TABLE-2 APPARENT CROSSLINK DENSITIES (1/Q) OF THE TPEs MEASURED WITH DIFFERENT SWELLING SOLVENTS				
Compound	MBA	ASA	ALA	LG
Decalin (ε = 2.2)	0.19	0.19	0.18	0.20
Toluene (ε = 2.38)	0.28	0.28	0.26	0.29
Xylene (ε = 2.4)	0.25	0.26	0.23	0.25

TABLE-3
RATIOS OF THE APPARENT CROSSLINK DENSITIES (**1/Q**) OF THE TPEs COMPARED WITH THE APPARENT CROSSLINK DENSITY OF SPECIMEN WITHOUT ANY AMINO ACID

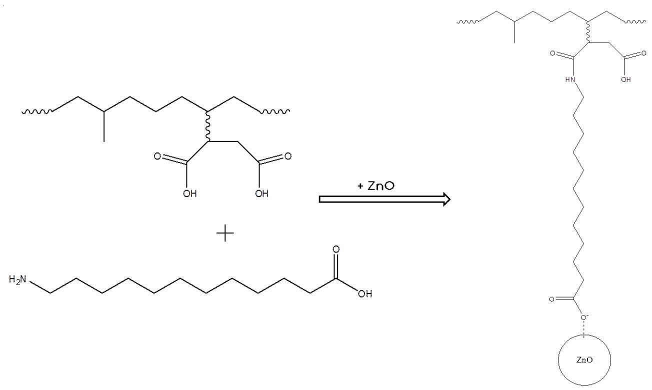
Compound	MBA	ASA	ALA	LG
Decalin	0.79	0.79	0.75	0.83
Toluene	0.93	0.93	0.87	0.97
Xylene	0.81	0.84	0.74	0.81



Scheme-II: Ionomer formation of 4-amino-2-methoxy benzoic acid treated MAH-*g*-EPDM and ZnO particle

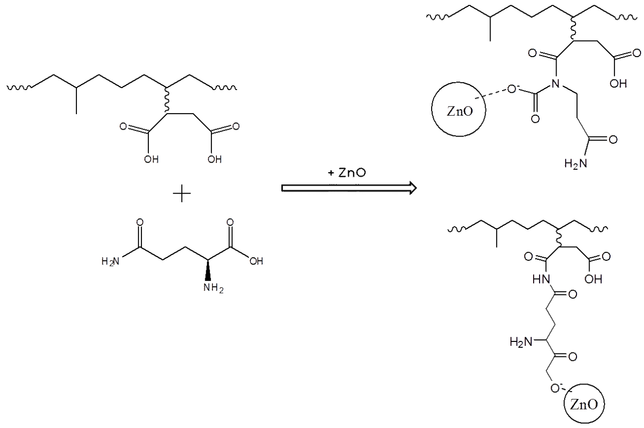


Scheme-III: Ionomer formation of 4-amino salicylic acid treated MAH-*g*-EPDM and ZnO particle



Scheme-IV: Ionomer formation of 12-amino lauric acid treated MAH-*g*-EPDM and ZnO particle

Some organic materials were extracted by the solvent swelling. The weight losses by toluene or xylene were much larger than those by decalin as listed in Table-4. This indicates that decalin did not completely extract the free organic materials. Besides the organic additives such as the antioxidant and



Scheme-V: Ionomer formation of L-glutamine treated MAH-*g*-EPDM and ZnO particle

TABLE-4
WEIGHT LOSSES OF THE TPEs BY SOLVENT EXTRACTION (wt %)

Compound	MBA	ASA	ALA	LG
Decalin	1.60 ± 0.33	2.34 ± 0.28	1.73 ± 0.45	1.77 ± 0.50
Toluene	5.27 ± 0.12	5.68 ± 0.20	5.09 ± 0.08	5.51 ± 0.49
Xylene	5.22 ± 0.16	5.67 ± 0.26	5.47 ± 0.12	5.21 ± 0.39

unreacted amino acids, unbound polymers that did not to participate in building the ionic bonds can be extracted with a solvent such as toluene or xylene. The difference in the weight losses by toluene and xylene was negligible. The weight losses by toluene and xylene were larger than 5 wt %, which is much higher than expected because the content of the organic additives in the samples was less than 1 wt % as listed in Table-1. The large amounts of extracted materials indicate the existence of uncrosslinked (or unbound) polymers.

In general, crosslink density of a rubber vulcanizate is calculated using the Flory-Rehner eqn. (2).

$$X_c = -[\ln(1-\nu_2) + \nu_2 + \chi\nu_2^2]/[V_1(\nu_2^{1/3} - \nu_2/2)] \quad (2)$$

where ν_2 is the volume fraction of the crosslinked polymer, χ is the interaction parameter between the polymer and solvent, V_1 is the molar volume of the swelling solvent. The ν_2 is obtained by eqn. (3).

$$\nu_2 = (m_2/\rho_2)/[(m_2/\rho_2) + (m_1/\rho_1)] \quad (3)$$

where m_1 and m_2 are the solvent and specimen weights at equilibrium swelling, respectively and ρ_1 and ρ_2 are the densities of swelling solvent and unswollen vulcanizate, respectively. Crosslink densities of the thermoplastic elastomers were calculated by the Flory-Rehner equation (2). The parameters of EPDM were employed as those of the MAH-*g*-EPDM. The crosslink densities were calculated using the data for toluene because the interaction parameter between EPDM and toluene is available from a literature[23]. Densities of toluene (ρ_1) and EPDM (ρ_2) are 0.865 and 0.87 g/cm^3, respectively. The V_1 is 106.3 cm^3/mol. The χ values were obtained from the literature; of $\chi = 0.429 + 0.218\ \nu_2$.[23] The X_cs were listed in Table-5. The order of the X_cs was L-glutamine > 4-amino-2-methoxy benzoic acid > 4-amino salicylic acid > 12-amino lauric acid. The order of the X_cs was well consistent with that of 1/Qs. Therefore, properties of the thermoplastic elastomers can be explained using the apparent crosslink densities if the interaction parameter used to measure the crosslink density is unavailable. A comparison of the sample without the amino acids showed that the crosslink densities were reduced by about 10 % (6-14 %).

Physical properties of the thermoplastic elastomers were summarized in Table-6. Physical properties of the sample 12-amino lauric acid were worse than the others. This might be due to the lower crosslink density. However, even elongation at break of the sample 12-amino lauric acid was smaller than that of the sample 4-amino-2-methoxy benzoic acid. The modulus, tear strength and compression set of the sample 4-amino salicylic acid were better than those of the others, even though it had a relatively low crosslink density. This might be due to the effect of heterocrosslinkages as shown in **Scheme-III**. 4-Aminosalicylic acid has carboxylic acid and acidic alcohol functional groups that form ionic bonds with zinc oxide particle.

TABLE-5
CROSSLINK DENSITIES (X_c, mol/cm^3) OF THE TPEs AND THE CROSSLINK DENSITY RATIOS COMPARED TO THE SPECIMEN WITHOUT ANY AMINO ACID. TOLUENE WAS USED AS THE SWELLING SOLVENT

Compound	Crosslink density (X_c, mol/cm^3)	Crosslink density ratio
MBA	1.03×10^{-4}	0.90
ASA	0.98×10^{-4}	0.86
ALA	0.86×10^{-4}	0.75
LG	1.07×10^{-4}	0.94

TABLE-6
PHYSICAL PROPERTIES OF THE TPEs

Compound	MBA	ASA	ALA	LG
Elongation at break (%)	940	845	885	825
Modulus at 100 % (MPa)	2.16	2.26	2.06	2.06
Modulus at 300 % (MPa)	3.34	3.73	3.04	3.63
Tensile strength (MPa)	17.07	15.79	13.44	15.70
Tear strength (MPa)	3.73	3.92	3.43	3.73
Compression set (%)	55	47	60	50

Conclusion

Properties of thermoplastic elastomers made of MAH-*g*-EPDM, zinc oxide and amino acid (4-amino-2-methoxy benzoic acid, 4-amino salicylic acid, 12-amino lauric acid, or L-glutamine) were investigated using ATR-FTIR, solvent extraction, apparent crosslink density and crosslink density as well as physical properties. The amine groups of amino acids reacted with the maleic acid groups to form peptide bonds and the residual acid groups reacted with zinc oxide particle to form ionomers. The apparent crosslink densities (1/Qs) of the thermoplastic elastomers were reduced by adding amino acid due to the long ionic bonds. The order of the 1/Qs was L-glutamine > 4-amino-2-methoxy benzoic acid, 4-amino salicylic acid > 12-amino lauric acid. The existence of unbound (or uncrosslinked) polymers was confirmed using a solvent extraction test. The order of the crosslink densities (Xcs) obtained by the Flory-Rehner equation was L-glutamine > 4-amino-2-methoxy benzoic acid > 4-amino salicylic acid > 12-amino lauric acid. Physical properties of the sample 12-aminolauric acid were worse than the others due to the relatively lower crosslink density. Modulus, tear strength and compression set of the sample 4-amino salicylic acid were better than the others due to the effect of hetero crosslinkages.

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