Preparation and properties of high-performance recyclable ethylene propylene diene rubber

Jung-Soo Kim,[1] Jong-Woo Bae,[1] Jin-Hyok Lee,[1] Young-Hee Lee,[2] Han-Do Kim[2]

[1]Industrial Materials Fusion Technology Center, Korea Institute of Footwear and Leather Technology, Busan 614-100, Korea
[2]Department of Organic Material Science and Engineering, Pusan National University, Busan 609-735, Korea
Correspondence to: H.-D. Kim (E-mail: kimhd@pusan.ac.kr)

ABSTRACT: To obtain high-performance recyclable ethylene propylene diene rubber (EPDM), EPDM was chemically functionalized as follows: EPDM was grafted with citraconic acid (CCA) by radical melt polymerization to produce a grafted EPDM (EPDM-g-CCA), and EPDM-g-CCA was reacted with various amino acids by melt condensation reaction to give amidated copolymers (EPDM-g-CCA-2-Am, EPDM-g-CCA-7-Am, and EPDM-g-CCA-12-Am, where the n indicates the carbon number of amino acid), and then ionomers (EPDM-g-CCA/n-Am/Io) were prepared by melt reaction of EPDM-g-CCA/n-Ams with Zinc oxide (ZnO)/zinc stearate (ZnSt). The mechanical properties/compression set (CS) resistance (elasticity)/recyclability of pristine EPDM, EPDM-g-CCA, EPDM-g-CCA/n-Am, and ionomers sheet samples were compared. The tensile strength/modulus, tear strength, and elasticity of samples were mostly increased in the order of ionomers>EPDM-g-CCA/n-Ams>EPDM-g-CCA>pristine EPDM. The properties of ionomers increased significantly with increasing the carbon number in amino acid up to seven, and then levelled off or decreased a little. The tensile strength/elasticity (compression set resistance) of recyclable ionomer (EPDM-g-CCA/7-Am/Io) was found to be ∼9.42/∼2.31 times of pristine EPDM, respectively. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42718.

INTRODUCTION

It is well known that ethylene propylene diene rubber (EPDM) rubber is a terpolymer of ethylene, propylene, and diene monomers. A third, nonconjugated diene monomer can be terpolymerized in a controlled manner to maintain a saturated backbone and place the reactive unsaturation in a side chain available for vulcanization or polymer modification chemistry. The two most widely used diene termonomers are primarily ethylidene norbornene (ENB) followed by dicyclopentadiene (DCPD). Versatility in EPDM design and performance has resulted in broad usage in automotive weather-stripping and seals, glass-run channel, radiator, garden and appliance hose, tubing, belts, electrical insulation, roofing membrane, rubber goods, plastic impact modification, thermoplastic vulcanizates, and motor oil additive applications.[1–3]

Maleic anhydride (MA) and its isostructural analogues (maleic, fumaric, citraconic, and itaconic acids and their amide, imide, ester, and nitrile derivatives) as reactive polyfunctional monomers are being widely used in the preparation of reactive functional polymers with various structures to make high performance materials. Chemical modification of conventional polymers by free radical grafting and graft-(co)polymerization methods has received much academic and practical interest. The free radical melt grafting of polyfunctional monomers onto EPDM using reactive extrusion/mixing system is very important in the chemical modification methods of EPDM rubber. These methods allow to imparting a variety of functional groups to conventional polymers such as polyolefin and EPDM. The most studies were related with MA grafting of polypropylene (PP) in the melt using various types of extruders and mixers. The MA functionalization of PP was investigated by Gaylord and Mishra[4] and Ho *et al.*[5]

In general, the crosslinking of elastic materials is necessary to obtain the required rubber properties, such as high elasticity, high toughness, and good solvent resistance. The main industrial technologies for rubber crosslinking using sulfur vulcanization and peroxide curing, involve irreversible covalent crosslinking, which prevents melt processing and strongly complicates recycling.[6] An attractive solution to overcome the recycling problem is to use elastomers exhibiting thermoplastic behavior, so-called thermoplastic elastomers (TPEs). Ideal TPEs combine the service properties of crosslinked elastomers with the melt processing properties of thermoplastics.

The introduction of a small number of ionic groups into the polymer chains with acid/base groups can result in profound changes in the properties of modified polymers, also known as ionomers.[7–9] Ionomers are another class of material with thermoreversible crosslinks. Depending on the content of these ionic groups, the ionic aggregates can exist as multiplets, which function as physical crosslinks, or as clusters, consisting of the ion pairs and hydrocarbon chains, often leading to micro-phase separation.[10–13] The reversibility of the ionic crosslinks is based on the increased mobility of the ionic aggregates at elevated temperatures. Therefore, ionomer-based on polymers with a low Tg can be used as TPEs, if the ionic associations are sufficiently decreased at the processing temperature.[14–16]

The question of the disposal of used polymer has gained increasing importance in public discussions because of the environment problems resulting from the rapid increase in plastic wastes. In general, melt recycled polymers exhibit unsatisfactory mechanical properties because of their degradation during melt reprocessing. The reproducing involves several high-temperature shearing cycles that facilitate the occurrence of thermal and/or mechanical degradation, consequent chemical and physical changes, and the deterioration of the final properties. Therefore, an in-depth understanding of the influence of melt processing/recycling on the properties of thermoplastics is essential for effective mechanical recycling of used thermoplastics and thermoplastics scraps.

Ionomers with different cations such as zinc, potassium, sodium, and copper cations, are obtained via the neutralization of a polymer containing acid groups with metal compounds for different degrees of neutralization.[7,17–20] Ionic rubbers are mostly prepared by the metal ion neutralization of acid functionalized rubbers, such as carboxylated styrene-butadiene rubber and carboxylated nitrile rubber.[18,21–23] Generally, ionic rubbers under ambient conditions exhibit moderate to high tensile and tear strength and high elongation. Generally, sulfonated, maleated, and citraconated EPDM rubber were obtained from the reactions of EPDM with sulfate, maleic anhydride, and citraconic acid, respectively. Ionic rubbers based on sulfonated EPDM rubber[19,24,25] and maleated EPDM have been studied by several workers.[26–28] However, ionic rubber based on citraconated EPDM has not been studied as a potential ionomer. Therefore, understanding the effect of melt processing/recycling on the properties of citraconated EPDM-based ionomers is very important for reusing. Our previous study examined citraconated EPDM (EPDM-g-CCA) and mechanical properties and recyclability of EPDM-g-CCA ionomers.[29] We found that the mechanical properties and compression set (CS) resistance increased in the order of EPDM-g-CCA ionomers > EPDM-g-CCA > pristine EPDM. On the other hand, there are few reports on amino acid reacted EPDM-g-CCA (EPDM-g-CCA-n-Ams) prepared from the melt reaction between EPDM-g-CCA and amino acids with different chain lengths, and on the properties of EPDM-g-CCA-n-Ams and their ionomers.

In this study, to obtain high performance functional EPDM was grafted with citraconic acid by free-radical melt polymerization to produce a functional grafted EPDM (citraconated EPDM:

EPDM-g-CCA), and EPDM-g-CCA was reacted with various amino acids containing different chain length by melt condensation reaction to give chemically modified EPDM (EPDM-g-CCA-n-Ams: EPDM-g-CCA-2-Am, EPDM-g-CCA-7-Am, and EPDM-g-CCA-12-Am, where the n indicates the number of carbon atoms in amino acids), and then a series of ionic thermoplastic elastomers (ionomers: EPDM-g-CCA/n-Am/Io) were prepared by melt reaction of EPDM-g-CCA/n-Ams with neutralizing agent (ZnO)/ionic plasticizer (zinc stearate (ZnSt)). The properties of pristine EPDM, EPDM-g-CCA, EPDM-g-CCA/n-Am series, and ionomers EPDM-g-CCA/n-Am/Io series sheet samples were compared. The effect of amino acids with different chain lengths on the mechanical properties and the recyclability of these materials were also investigated.

EXPERIMENTAL

Materials

The EPDM (contents of ethylene, propylene, and ethylidene norbornene: 70, 25.5, and 4.5 wt %, respectively, KUMHO POLYCHEM, Korea), citraconic acid (CCA, Aldrich Chemical, Milwaukee, WI), 2,5-Dimethyl-2,5-di(tert-butyl peroxy)-hexane (T-101, Akzo Novel Co.), Zinc oxide (ZnO, PJ Chemtec Co., Korea), Zinc stearate (ZnSt, Aldrich Chemical, Milwaukee, WI), glycine (2-Am, Aldrich Chemical, Milwaukee, WI), 7-aminoheptanoic acid (7-Am, Aldrich Chemical, Milwaukee, WI), 12-aminododecanoic acid (12-Am, Aldrich Chemical, Milwaukee, WI), toluene (Junsei Chemical Co.), and acetone (Junsei Chemical Co.) were used without further purification. The chemical name, structural formula, molecular weight (MW), and melting temperature of various amino acids with different chain length are shown in Table I.

Preparation of EPDM-g-CCA, EPDM-g-CCA/Am Series, and EPDM-g-CCA/Am/Io Series

Citraconated EPDM (EPDM-g-CCA) was prepared by melt grafting from citraconic acid (CCA)/EPDM/free radical initiator [2,5-dimethyl-2,5-di(tert-butyl peroxy) hexane: L-101] using Haake Rheocorder (Rheocord 9000, Haake Co., Germany) under 50 rpm, at 160°C for 15 min. The EPDM-g-CCA with 1.78% of percent grafting and 18.0% of gel content was prepared by free radical melt graft copolymerization of pristine EPDM (100 g) with citraconic acid (CCA, 2 g)/initiator (L-101, 0.04 g).[29] Percent grafting (%) of EPDM-g-CCA was determined by the following equation:
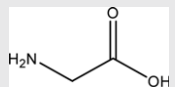
$$\text{Percent grafting } (\%) = \left[(W_g - W_o)/W_o \right] \times 100 \qquad (1)$$

where the dry weights of EPDM-g-CCA extracted in acetone at 40°C for 48 h and pristine EPDM are W_g and W_o, respectively. Gel content (wt %) was determined by the following equation:

$$\text{Gel content } (\text{wt } \%) = (W_{insoluble}/W_T) \times 100 \qquad (2)$$

where the $W_{insoluble}$ is the dry weight of insoluble EPDM-g-CCA after extraction in boiling xylene for 24 h and the W_T is the dry weight of EPDM-g-CCA extracted in acetone at 40°C for 48 h.

Table I. Various Amino Acids with Different Chain Length in This Study

Chemical name (Abbreviation)	Structural formula	Molecular weight (g/mol)	Melting temperature (°C)
Glycine (2-Am)		75.07	233
7-aminoheptanoic acid (7-Am)		145.20	192–195
12-aminododecanoic acid (12-Am)		215.33	185–187

A series of amidated copolymers (EPDM-g-CCA-2-Am, EPDM-g-CCA-7-Am, and EPDM-g-CCA-12-Am, where the n indicates the carbon number of amino acid) were prepared by melt condensation reaction of EPDM-g-CCA with various amino acids, and then ionomers (EPDM-g-CCA/n-Am/Io) was made by melt reaction of EPDM-g-CCA-n-Am with neutralizing agent (ZnO)/ ionic plasticizer (zinc stearate) using Haake Rheocorder (Rheocord 9000, Haake Co., Germany) under 50 rpm, at 160°C for 15 min. Scheme 1 shows the preparation process of high-performance recyclable EPDM.

The sheet samples (thickness: 2 mm) of pristine EPDM, EPDM-g-CAA, EPDM-g-CCA/n-Ams, and ionomers and recycled samples were prepared by compression- molding under 180°C for 10 min after milling using open mill (Yasuda Seiki Co., Model 191-TM, 6") at 160–170°C. The sample code, compounding components, and properties of pristine EPDM, EPDM-g-CCA, EPDM-g-CCA/n-Ams, and ionomers prepared in this study are given in Table II.

Characterization

A Fourier transform infrared spectrometer (FTIR 6200, Jasco, Japan) with attenuated total reflectance (ATR) was used to confirm chemical structure of sheet samples. For each samples, 32 scans at 4 cm^{-1} resolution were collected in the transmittance mode and recorded in the rage of 4000~500 cm^{-1}. The stress–strain curves were measured using dumbbell shaped specimens according to ASTM D412 using a Instron universal testing machine (UTM, Model: 3345, Instron) at a crosshead speed of 500 mm/min. Tear strength was measured using the Instron UTM 3345 using a 90° nick cut-crescent sample according to ASTM D624. The elastic and permanent elongations were determined using stress–strain cycling test according to international standard ISO 9856. The density was measured at 23°C using CCl$_4$-n-heptane density gradient column method according to ASTM D1505. Melt flow index (MFI) is defined as the mass of polymer, in grams, flowing 10 min through a capillary of a specific diameter and length by pressure applied via prescribed alternative gravimetric weights for alternative prescribed temperature.[30–32] MFI measurement of samples was carried out on a Melt Indexer CS127-604 (CSI) according to ISO 1133, where the test temperature was set 190°C and the nominal load was 2.16 kg. The hardness was measured using a Shore A durometer

(Asker, Kobunshi Co., Japan) according to ASTM D2240. The compression set (CS) % was measured on cylindrical samples with a diameter of 300 mm and a thickness of approximately 10 mm. For the CS measurements, the samples were compressed between two parallel plates with a linear deformation of 25% at 70°C for 22 h. The CS was determined after 30 min of relaxation time at room temperature without deformation, according to ASTM D395. The CS of the samples was calculated using the following equation:

$$CS\,(\%) = [(t_0 - t_f)/(t_0 - t_s)] \times 100 \qquad (3)$$

where t_0 is the original thickness of sample (1 cm), t_f is the thickness of recovered sample after compressed at 70°C for 22 h and subsequently cooling down to room temperature for 30 min, and t_s is the thickness (0.75 cm) of compressed sample. Measurements on each sample were repeated five times and the average was considered as the characteristic value.

RESULTS AND DISCUSSION

Identification of Pristine EPDM, EPDM-g-CCA, EPDM-g-CCA/n-Am, and EPDM-g-CCA/n-Am/Io Film Samples

FTIR spectroscopy is a useful technique to study the modification of EPDM, since the position and intensity of the carbonyl (C═O) stretching vibration bands in functionalized EPDM samples change upon reaction. Figure 1 shows the FTIR spectra of pristine EPDM, EPDM-g-CAA, EPDM-g-CCA/n-Am, EPDM-g-CCA/n-Am/Io. An overview of assignments of the characteristic FTIR bands is given in Table III.

The pristine EPDM shows the characteristic peaks of the C═H stretching vibration peak at 2915 and 2848 cm^{-1}, the small C═C stretching peak at 1685 cm^{-1}, and the strong peaks around at 1465, 1435, and 1376 cm^{-1}, which are originating from EPDM back bone of long aliphatic chains, symmetric deformation of the methyl group of polypropylene in EPDM copolymer, the methyl group of the diene (CH$_3$─C═C) and the symmetric deformation band of methyl group, respectively. The EPDM-g-CCA sample had the characteristic peaks of EPDM (2915, 2848, 1465, 1435, and 1376 cm^{-1}) and the C═O stretch peak at 1702 cm^{-1} of the carboxylic acid in CCA, indicating the presence of CCA in EPDM. The EPDM-g-CCA/n-Am samples had the characteristic peaks of EPDM (2915, 2848, 1465,
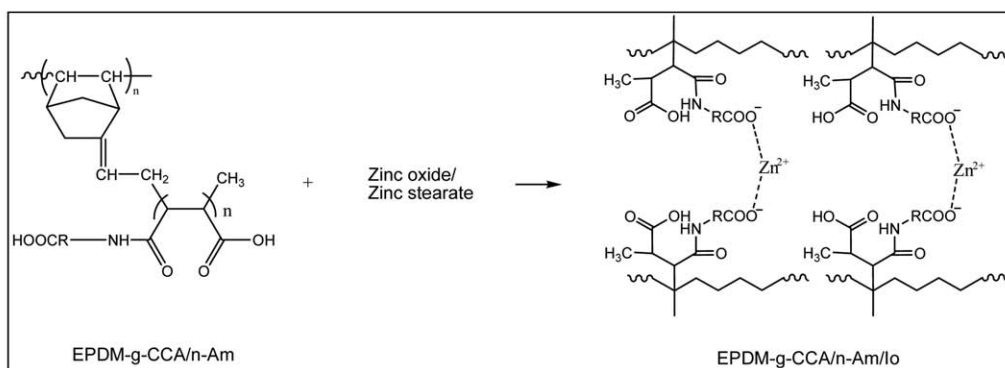
(a) Grafting: EPDM + Initiator /CCA → EPDM-g-CCA
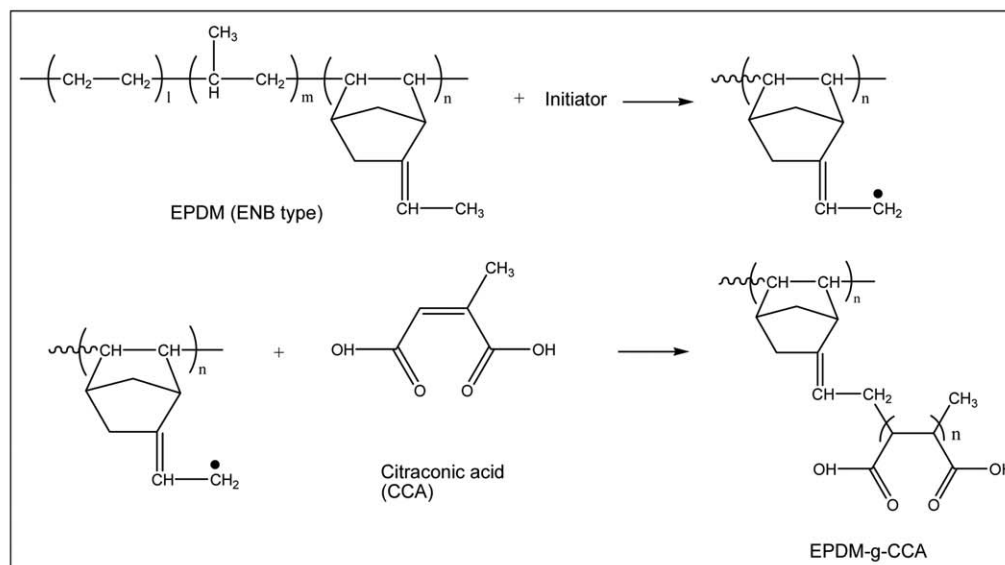
(b) Treating of amino acid: EPDM-g-CCA + Amino acids → EPDM-g-CCA/n-Am
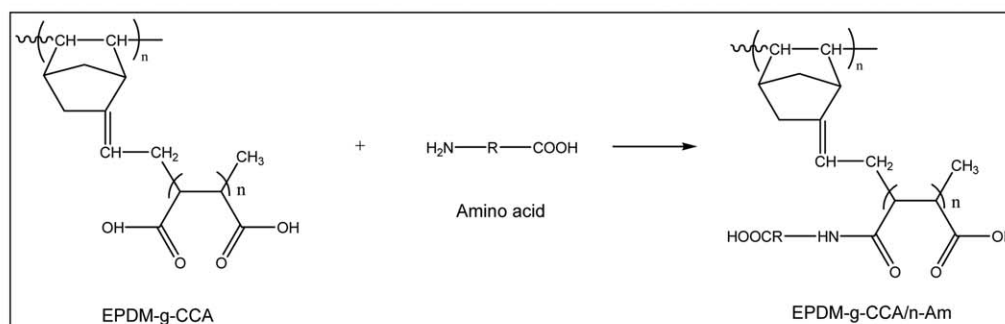
(c) Ionomerization: EPDM-g-CCA/n-Am + ZnO/Zn stearate → EPDM-g-CCA/n-Am/Io

Scheme 1. The preparation process of high-performance recyclable EPDM.

1435, and 1376 cm^{-1}), the C=O stretching peak at 1702 cm^{-1}, and additional amide (I) C=O stretch peak at 1646 cm^{-1} and amide N–H stretching peak at 3570 cm^{-1} in the range of 3500~3700 cm^{-1} indicating the occurrence of amidation reaction between carboxylic acid and amino acid. The EPDM-g-CCA/n-Am/Io samples show the characteristic peaks of EPDM (2915, 2848, 1465, 1435, and 1376 cm^{-1}), the C=O stretch peak at 1702 cm^{-1}, amide (I) C=O stretch peak at 1646 cm^{-1}, amide

Table II. Sample Code, Compounding Components, and Properties of Pristine EPDM, EPDM-g-CCA, EPDM-g-CCA/n-Am Series, and EPDM-g-CCA/n-Am/Io Series

Sample code	Compounding components							Mechanical properties							
	EPDM	EPDM-g-CCA	Amino acid	ZnO	ZnSt	Specific gravity	MFI (g/10min)	Tensile strength (MPa)	Elongation at break (%)	100% Modulus (MPa)	Elastic elongation at 100% extension (%)	Permanent elongation at 100% extension (%)	Tear strength (kN/m)	Hardness (Shore A)	Compression set (%)
Pristine EPDM	100	–	–	–	–	0.86	12	1.96	810	0.78	7	93	19.61	46.5	90
EPDM-g-CCA	–	100	–	–	–	0.88	10	5.78	975	1.08	10	90	22.50	56.5	89
EPDM-g-CCA/2-Am	–	100	1 (2-Am)	–	–	0.88	10	5.90	900	1.23	11	89	24.23	55.5	88
EPDM-g-CCA/7-Am	–	100	1 (7-Am)	–	–	0.88	10	7.94	920	1.28	13	87	31.24	56.5	85
EPDM-g-CCA/12-Am	–	100	1 (12-Am)	–	–	0.88	10	7.23	925	1.26	12	88	30.32	56.5	86
EPDM-g-CCA/2-Am/Io	–	100	1 (2-Am)	5	5	0.93	9	11.07	910	1.42	40	60	40.34	66.5	55
EPDM-g-CCA/7-Am/Io	–	100	1 (7-Am)	5	5	0.93	9	18.42	925	2.12	55	45	43.30	67.5	39
EPDM-g-CCA/12-Am/Io	–	100	1 (12-Am)	5	5	0.93	9	17.54	965	1.83	53	47	42.52	67.5	40
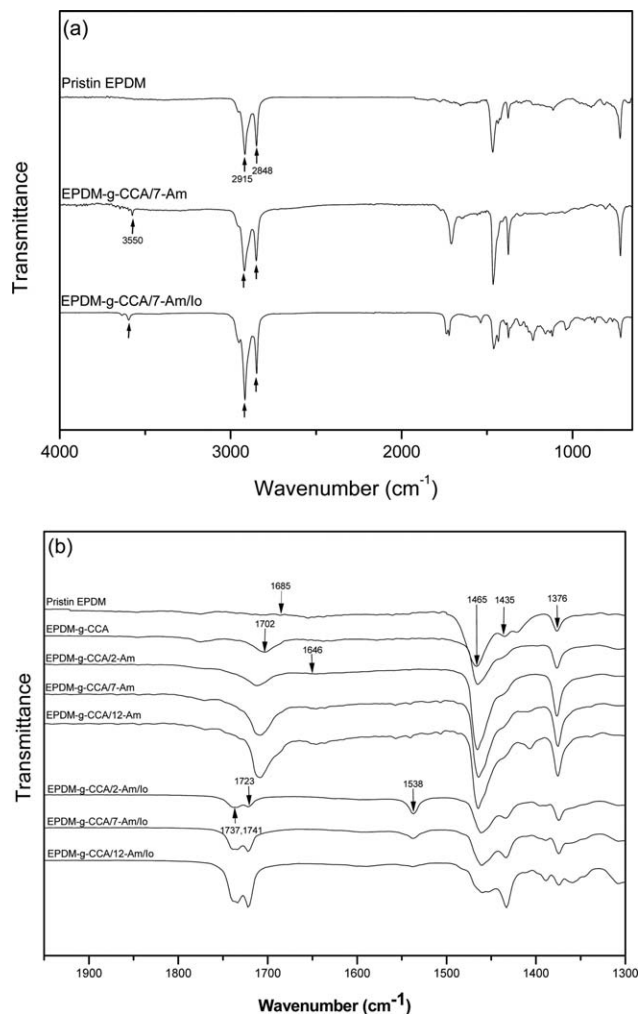
Figure 1. FTIR spectra of pristine EPDM, EPDM-g-CCA, EPDM-g-CCA/ n-Am, and EPDM-g-CCA/n-Am/Io series film samples; (a) in the range of $4000\sim500\,cm^{-1}$ and (b) in the range of $1900\sim1300\,cm^{-1}$ (magnified spectra).

group peak at 3570 cm^{-1}, and zinc carboxylate salt peak at around 1538 cm^{-1} which originated from the C=O stretching vibration of metal-carboxylate salts,[33] indicating the successfully formation of ionomers (EPDM-g-CCA/n-Am/Io). Additionally, the intensity of carboxylate peak at 1538 cm^{-1} was found to decrease very slightly with increasing the carbon number of amino acids. This should be due to the decrease of the fraction of acid group in amino acids by increasing the carbon number of amino acids at the fixed wt % of amino acids (1 wt %).

Specific Gravity and Melt Flow Index of Pristine EPDM, EPDM-g-CCA, EPDM-g-CCA/n-Am, and EPDM-g-CCA/n-Am/Io Series

In the case of EPDM-g-CCA/Am/Io series samples, ZnO could function as a Zn ion supplier (neutralization agent) and filler, whereas Zn stearate could perform as a Zn ion supplier and plasticizer. Table II shows the specific gravity and melt flow index (MFI) of pristine EPDM, EPDM-g-CCA, EPDM-g-CCA/

Table III. Assignments of Characteristic FTIR Transmittance Band of Pristine EPDM, EPDM-g-CCA, EPDM-g-CCA/n-Am, and EPDM-g-CCA/n-Am/Io Series

Sample designation	Assignment	Wavenumber (cm^{-1})
EPDM	C—H stretching vibration	2915, 2848
	C=C stretching vibration	1685
	CH$_3$ group in PP	1465
	CH$_3$ group in diene group (CH$_3$–C=C)	1435
	CH$_3$ group (symmetric deformation band)	1376
EPDM-g-CCA	C—H stretching vibration	2915, 2848
	CH$_3$ groups in EPDM	1465, 1435, 1376
	Carboxylic acid C=O	1702
EPDM-g-CCA/n-Am	C—H stretching vibration	2915, 2848
	CH$_3$ groups in EPDM	1465, 1435, 1376
	Carboxylic acid C=O	1702
	Amide (I) C=O stretch	1646
	Amide N–H stretching	3570
EPDM-g-CCA/n-Am/Io	C—H stretching vibration	2915, 2848
	CH$_3$ groups in EPDM	1465, 1435, 1376
	Carboxylic acid C=O	1702
	Carboxylate C=O	1538, 1737, 1741
	Amide group	3570

n-Am, and EPDM-g-CCA/n-Am/Io samples prepared in this study.

The specific gravity of pristine EPDM, EPDM-g-CCA, EPDM-g-CCA/n-Am, and EPDM-g-CCA/n-Am/Io series was 0.86, 0.88, 0.88, and 0.93, respectively. The specific gravity of ionomers EPDM-g-CCA/n-Am/Io was notably higher than those of pristine EPDM, EPDM-g-CCA, and EPDM-g-CCA/n-Am. This phenomenon was due to the presence of ZnO (density: 5.61 g/cm^3). The specific gravity of EPDM-g-CCA is equal to those of EPDM-g-CCA/n-Ams. However, their specific gravities are higher a little than pristine EPDM. This should be attributable to the polar carboxylic groups in EPDM-g-CCA and EPDM-g-CCA/n-Ams.

The melt flow index (MFI) is a measure of the ease of flow of a thermoplastic polymer melt. Melt flow rate is an indirect measure of molecular weight. MFI of a polymer is related directly to the melt viscosity, which depends on the molecular weight (MW) and structure (branching/crosslinking). In particular, for practical applications, MFI is a critical factor determining the melt processability and usability requirements of customers of thermoplastic polymers. The MFIs of pristine EPDM, EPDM-g-CCA prepared by melt processing for ones, EPDM-g-CCA/n-Am prepared by melt processing for twice and EPDM-g-CCA/n-Am/Io series by melt processing of three times were 12, 10, 10, and 9, respectively. The MFI decreased in the order of pure EPDM < EPDM-g-CCA = EPDM-g-CCA/n-Am < EPDM-g-CCA/n-Am/Io. The lowest MFI value of ionomer EPDM-g-CCA/n-Am/Io formed by melt processing of three times should be due to the run number (three times) of melt processing and neutralization of ZnO.

Mechanical Properties of Pristine EPDM, EPDM-g-CCA, EPDM-g-CCA/Am, and EPDM-g-CCA/Am/Io Series

Table II also shows the tensile strength, elongation at break, elastic/permanent elongation at 100% elongation, 100% modulus, tear strength, Shore A hardness, and compression set% of pristine EPDM, EPDM-g-CCA, EPDM-g-CCA/n-Am, and EPDM-g-CCA/n-Am/Io samples prepared in this study.

Figure 2 shows the stress–strain curves of the pristine EPDM, EPDM-g-CCA, EPDM-g-CCA/n-Am, and EPDM-g-CCA/n-Am/Io series film samples. The tensile strength/elongation at break of pristine EPDM, EPDM-g-CCA, EPDM-g-CCA/n-Am, and EPDM-g-CCA/n-Am/Io series were 1.96 MPa/810%, 5.78 MPa/975%, 5.90~7.94 MPa/900~925%, and 11.07~18.42 MPa/910~965%, respectively. The tensile strength and 100% modulus increased in the following order: EPDM-g-CCA/n-Am/Io > EPDM-g-CCA/n-Am > EPDM-g-CCA > pristine EPDM. This indicated that the tensile strength and 100% modulus were markedly increased due to grafting, subsequent amidation, and subsequent neutralization processes. The elongation at break of EPDM-g-CCA/n-Am was lower than that of EPDM-g-CCA. This might be due to the polar amide group in EPDM-g-CCA/n-Am. However, the elongation at break increased with increasing the carbon number of amino acid (see Figure 3). This should be attributed to the increase of flexible methylene group number in amino acid. The EPDM-g-CCA/n-Am had lower elongation at break than their corresponded ionomers. This might mainly be attributable to the role of plasticizer stearate. In order to measure a sample's elastic and permanent elongation characteristics, the industry has adopted international standard ISO 9856. With each tensile stress below break load, the sample is subjected to an elongation (100%) which, upon stress relief, partly
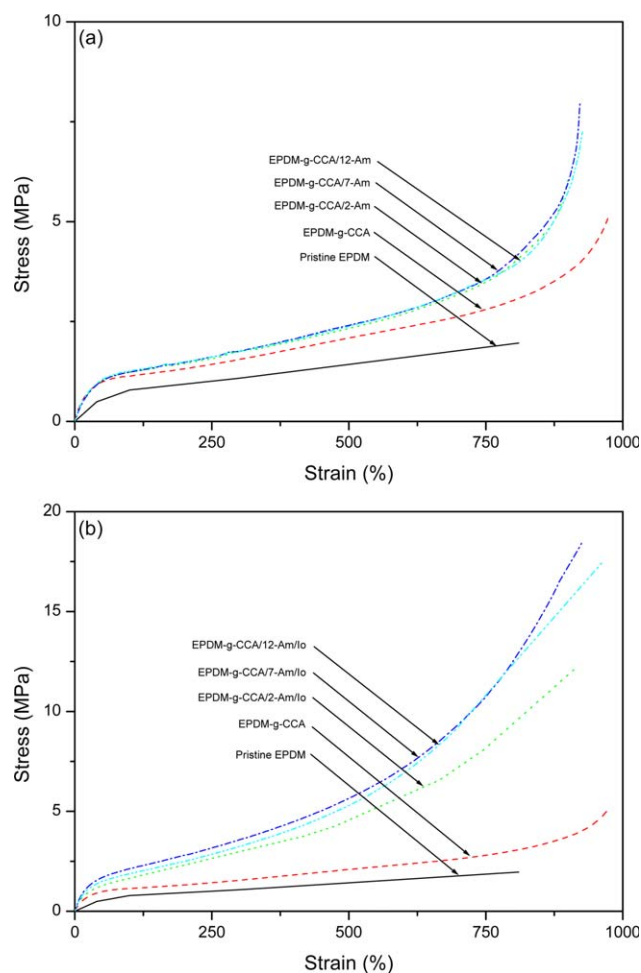
Figure 2. Stress–strain curves of (a) pristine EPDM, EPDM-g-CCA, and EPDM-g-CCA/Am series and (b) pristine EPDM, EPDM-g-CCA, and EPDM-g-CCA/Am/Io series samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

recovers (elastic elongation) and partly remains (permanent elongation). It was found that the elastic elongation at 100% elongation increased in the order of EPDM-g-CCA/n-Am/Io > EPDM-g-CCA/n-Am > EPDM-g-CCA > pristine EPDM. Thus, the permanent elongation at 100% elongation increased in the order of pristine EPDM > EPDM-g-CCA > EPDM-g-CCA/n-Am > EPDM-g-CCA/n-Am/Io. The elastic elongation value of EPDM-g-CCA/n-Am/Io series samples increased significantly with increasing the carbon number of amino acid up to seven, and then decreased a little (see Table II). The tear strengths of pristine EPDM, EPDM-g-CCA, EPDM-g-CCA/n-Am, and EPDM-g-CCA/n-Am/Io series were 19.61, 22.50, 24.23–30.32, and 40.34–43.30 MPa, respectively. The tear strength also increased markedly in the order of EPDM-g-CCA/n-Am/Io > EPDM-g-CCA/n-Am > EPDM-g-CCA > pristine EPDM. The tensile strength of functionalized EPDM (EPDM-g-CCA/7-Am/Io) was found to be ~9.42 times of pristine EPDM. This increase of tensile strength should be related with lower MFI due to cross-linking, stronger interfacial interactions, and addition of inorganic particles (ZnO).

These higher mechanical properties of ionomers EPDM-g-CCA/n-Am/Io series samples compared to EPDM-g-CCA/n-Am and

EPDM-g-CCA should be due to the ionic bonds (ionic cluster) of ionomers. These mechanical properties of ionomers increased significantly with increasing the carbon number of amino acid up to seven, and then levelled off or decreased a little (see Figure 3). This might be attributable to the increase of mobility in amidated amino acid moiety for easy formation of hydrogen bonds and ionic bonds with increasing the carbon number of amino acid up to seven. Therefore, the 7-aminoheptanoic acid (7-Am) was found to be suitable for improving the mechanical properties of EPDM. The Shore A hardness of pristine EPDM, EPDM-g-CCA, EPDM-g-CCA/n-Am, and EPDM-g-CCA/n-Am/Io series were 46.5, 56.5, 55.5~56.5, and 66.5~67.5, respectively. The hardness also increased in the order of EPDM-g-CCA/n-Am/Io > EPDM-g-CCA/n-Am > or = EPDM-g-CCA > pristine EPDM. This indicates that materials with both strongly polar functional group (amide group) and inorganic filler ZnO tend to have higher hardness.

Generally, a compression set test measures the ability of rubber compounds to retain their elastic properties after prolonged compressive stress. The compression set is the end result of progressive stress relaxation, which is the steady decline in the sealing force when an elastomer is compressed over a long period of time. The compression elasticity is inversely proportional to the compression set%. A lower compression set results in
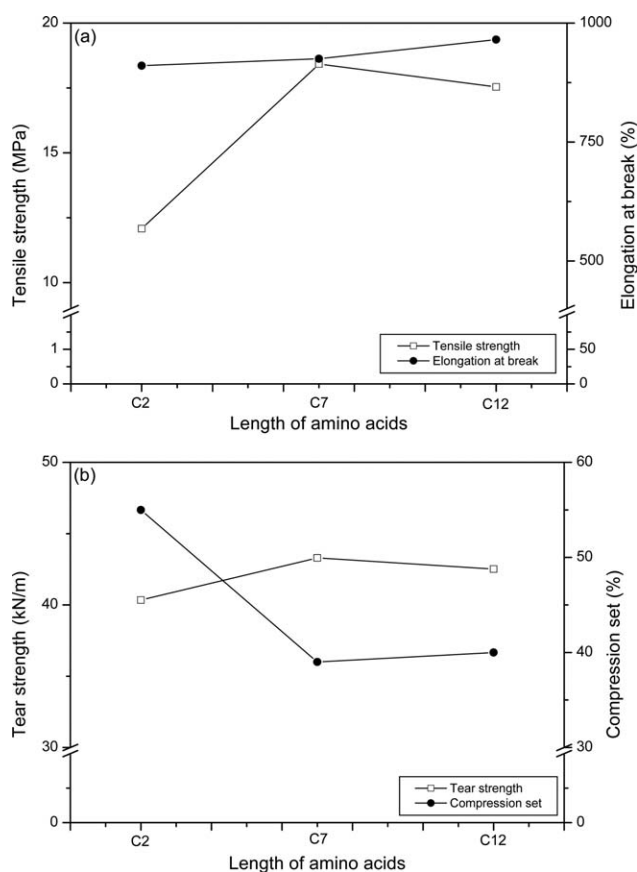

Figure 3. (a) Tensile strength and elongation at break (b) tear strength and compression set of ionic thermoplastic elastomer according to chain length of amino acid.
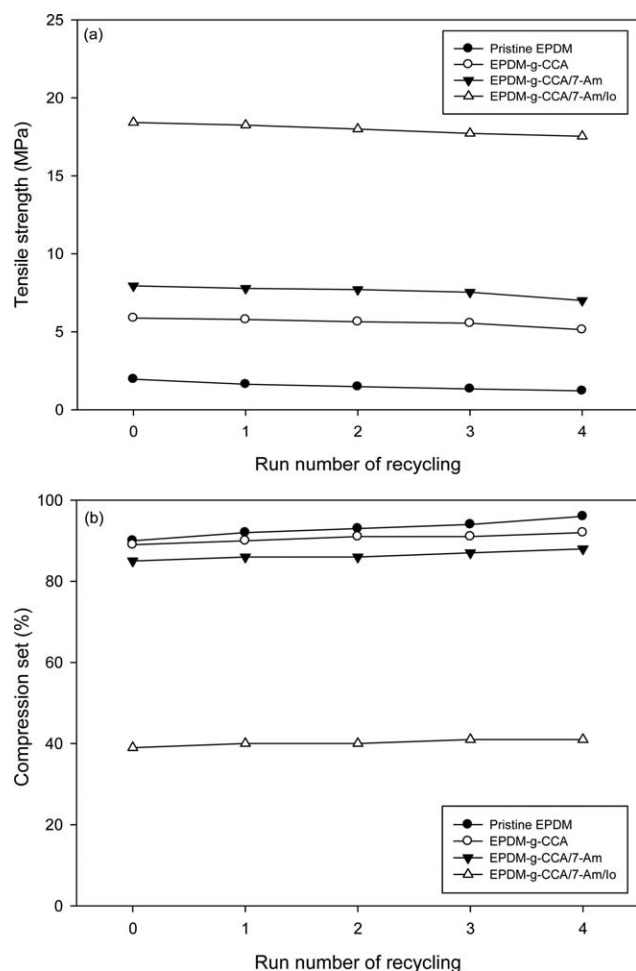
Figure 4. The effect of run number of recycling on (a) the tensile strength and (b) compression set of pure EPDM, EPDM-g-CCA, EPDM-g-CCA/7-Am, and EPDM-g-CCA/7-Am/Io sample.

improved sealing and a longer service life. The compression set% of pristine EPDM, EPDM-g-CCA, EPDM-g-CCA/n-Am, and EPDM-g-CCA/n-Am/Io series were 90, 89, 88~85, and 55~39%, respectively. The compression set% values of EPDM-g-CCA/n-Am series samples and EPDM-g-CCA/n-Am/Io series samples decreased a little with increasing the carbon number of amino acid up to seven, and then increased a little (see Figure 3). However, the compression set% value was found to be markedly decreased from 90 for pristine EPDM to 55–39 for

ionized samples (EPDM-g-CCA/n-Am/Io series samples). The elasticity (compression set resistance) of functionalized EPDM (EPDM-g-CCA/7-Am/Io) were found to be ~2.31 times of pristine EPDM.

From these results, it was also found that the 7-aminoheptanoic acid (7-Am) was highly suitable modifying agent for improving the elasticity of EPDM.

Recyclability of Pristine EPDM, EPDM-g-CCA, EPDM-g-CCA/7-Am, and EPDM-g-CCA/7-Am/Io Samples

Plastic recycling is the process of recovering scrap or waste and reprocessing the plastic into useful products. Figure 4 shows that the effect of run number of subsequent melt mixing (reprocessing, recycling) on the tensile strength and compression set% of pristine EPDM, EPDM-g-CCA, EPDM-g-CCA/7-Am, and EPDM-g-CCA/7-Am/Io samples. The tensile strengths of pristine EPDM, EPDM-g-CCA, EPDM-g-CCA/7-Am, and EPDM-g-CCA/7-Am/Io samples with 0, 1, 2, 3, and 4 times of subsequent melt mixing were 1.96~1.21 MPa, 5.78~5.13 MPa, 7.94~7.00 MPa, and 18.42~17.70 MPa, respectively. The compression set% for pristine EPDM, EPDM-g-CCA, EPDM-g-CCA/7-Am, and EPDM-g-CCA/7-Am/Io samples obtained by subsequent melt recycling for once/four times were 90/93, 89/92, 85/88, and 39/41, respectively. As the run number of subsequent melt recycling increased, the tensile strength decreased a little, but the compression set% increased a little. However, all these samples had no significant changes in tensile strength and compression set% with increasing recycling up to four times. The effects of run number of recycling of properties of the ionomer EPDM-g-CCA/7-Am/Io sample are shown in Table IV. The specific gravity, MFI and Shore A hardness were nearly not changed with increasing run number of subsequent melt recycling. As the run number of recycling increased, the tensile strength, 100% modulus, tear strength, and the elongation at break decreased, however, the gel content and compression set% of sample increased a little. This suggests that the ionomer EPDM-g-CCA/7-Am/Io prepared in this study have strong potential as a recyclable high performance material.

CONCLUSIONS

Ethylene propylene diene rubber (EPDM) was chemically modified to improve its mechanical properties: EPDM was grafted with citraconic acid by free-radical melt polymerization to produce a grafted copolymer (citraconated EPDM: EPDM-g-CCA), and EPDM-g-CCA was reacted with various amino acids

Table IV. The Effect of Run Number of Recycling on the Properties of Ionomer EPDM-g-CCA/7-Am/Io Sample

Run number of recycling	Gel content (wt %)	Specific gravity	MFI (g/10 min)	Mechanical properties					
				Tensile strength (MPa)	Elongation at break (%)	100% Modulus (MPa)	Tear strength (kN/m)	Hardness (Shore A)	Compression set (%)
0	18.0	0.93	9	18.42	925	2.12	43.30	67.5	39
1	18.1	0.92	9	18.35	920	2.08	42.12	67.5	40
2	18.1	0.92	9	18.10	914	2.05	41.81	67.5	40
3	18.2	0.92	9	18.02	911	2.01	41.54	66.5	41
4	18.3	0.92	10	17.70	909	1.99	41.52	66.5	41

containing different chain length by melt condensation reaction to give amidated EPDM-g-CCA (EPDM-g-CCA-n-Ams: EPDM-g-CCA-2-Am, EPDM-g-CCA-7-Am, and EPDM-g-CCA-12-Am, where the n indicates the number of carbon atoms in amino acids), and then a series of ionic thermoplastic elastomers (ionomers: EPDM-g-CCA/n-Am/Io) were prepared by melt reaction of EPDM-g-CCA/n-Ams with neutralizing agent ZnO/ionic plasticizer zinc stearate.

In this study, the mechanical properties/compression set% of pristine EPDM, EPDM-g-CCA, EPDM-g-CCA/Am, and EPDM-g-CCA/Am/Io were compared, and the melt recyclability of these materials was also investigated.

The specific gravity, tensile strength, 100% modulus, and tear strength were mostly increased in the order of EPDM-g-CCA/n-Am/Io ionomer > EPDM-g-CCA/n-Am > EPDM-g-CCA > pristine EPDM, whereas the compression set% was in the opposite order. There were no significant changes in mechanical properties and compression set% with increasing the run number of melt recycling up to four times, indicating that the recyclability of these materials was mostly retained after chemical modification with successive melt recycling. The compression set resistance (elasticity) was found to be markedly improved from 90% of EPDM to 55∼39% of ionomers. The mechanical properties and elasticity of ionomers increased with increasing the carbon number of amino acid up to seven, and then levelled off or decreased a little. These results suggest that the recyclable ionomer EPDM-g-CCA/7-Am/Io prepared in this study have high potential as a new high performance thermoplastic elastomer.

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