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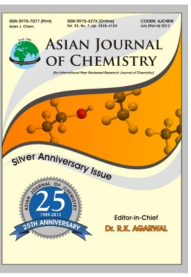

X-Ray Diffraction and X-Ray Photoelectron Spectroscopy Characterization of Maleic Anhydride-Grafted Ethylene-Propylene-diene Terpolymer Based Thermoplastic Elastomers†

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Maleic anhydride-grafted ethylene-propylene-diene terpolymer (MAH-*g*-EPDM) based thermoplastic elastomers were characterized by X-ray diffraction and X-ray photoelectron spectroscopy. The analysis focused on the formation of ionomers between MAH-*g*-EPDM and zinc oxide. The X-ray diffraction patterns of the thermoplastic elastomers showed different peak intensities of zinc oxide according to the formulations. The X-ray photoelectron spectroscopy spectra of the thermoplastic elastomers showed a shift in the binding energies of carbon and oxygen atoms. The degree of ionomer formation was estimated from percentage crystallinity determined by the XRD patterns and from difference in the relative intensities of the C1s and O1s peaks in the X-ray photoelectron spectroscopy spectra.

Key Words: MAH-*g*-EPDM, Ionomer, X-ray diffraction, X-ray photoelectron spectroscopy.

INTRODUCTION

Maleic anhydride (MAH) is a useful functional monomer for the graft modification of polymers[1-4]. The application of maleic anhydride on the non-polar backbone of polymers has overcome the disadvantages of the low surface energy of these polymers[5-7]. Maleic anhydride-grafted polymers have good affinity to metal or metal oxides such as Cu, CuO and ZnO. This improves the hydrophilicity of the polymer surface and the adhesion of rubber with polar/non-polar materials[8-12].

Ethylene-propylene-diene terpolymer (EPDM) is a synthetic rubber composed of ethylene, propylene and unsaturated diene. Its advantage is weather, heat and solvent resistance, which continues to grow in a wide variety of applications[13-18]. Maleic anhydride-grafted ethylene-propylene-diene terpolymer (MAH-*g*-EPDM) as a compatibilizer in polymer blends has been reported to be useful for improving the properties of the blends[10,19-21].

An ionomer is an ion-containing copolymer crosslinked by metal ions[22,23]. In general, metal cations such as Na^+, Zn^{2+} and Ca^{2+} are used, while CO^{2-} and SO^{3-} are used as anions to form an ionomer. When the ionomer is heated, crosslinks formed by ions will lose their attraction, but the crosslinks reform again during cooling giving it good mechanical properties[24-26].

X-ray photoelectron spectroscopy (XPS) and X-ray diffraction of polymeric materials can detect and characterize chemical changes or contamination on the surface[27-31]. XRD is used widely to evaluate the polymer crystallinity because it can provide qualitative identification for quantitative estimations of the crystalline phases[32,33]. X-ray photoelectron spectroscopy is a quantitative spectroscopic technique to measure the elemental composition and chemical bonding state. The binding energy of an atomic electron is dependent on the chemical environment with other atoms. Because of these features, a range of polymers including elastomers have been analyzed by XRD and XPS[34-36].

In this study, thermoplastic elastomers composed of MAH-*g*-EPDM, zinc oxide and other ingredients were characterized by XRD and XPS. The thermoplastic elastomers may have ionic bonds (pseudo-crosslinkers or reversible crosslinkers) between the maleic acid groups of MAH-*g*-EPDM and zinc oxide. The effect of the zinc oxide content and the kinds and contents of other additives on the formation of ionic bonds was examined. The level of the ionomer formation was investigated using the percentage crystallinity of zinc oxide particles and relative peak intensities of carbon and oxygen.

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EXPERIMENTAL

Royaltuf 498 (MAH functionality 1.0 %) of Chemtura Co. was employed as an MAH-*g*-EPDM. Songnox 1076 (octadecyl 3-(3,5-di-*t*-butyl-4-hydroxyphenyl)- propionate) of Songwon Industrial Co. was used as an antioxidant. Zinc oxide and zinc stearate were purchased from Aldrich Co. Formulation of the thermoplastic elastomers was shown in Table-1.

TABLE-1
FORMULATION (phr)

Sample no.	1	2	3	4	5	6
Royaltuf 498	100	100	100	100	100	100
Songnox 1076	0.3	0.3	0.3	0.3	0.3	0.3
Zinc oxide	1	3	5	5	5	5
Zinc stearate	0	0	0	5	0	0
Octadecyl amine	0	0	0	0	5	0
Stearic acid	0	0	0	0	0	5

XRD was performed using a D-max 2500/PC diffractometer (Rigaku Co.) with CuK$_\alpha$ radiation. The accelerating voltage and electric current were 40 kV and 100 mA, respectively. The samples were scanned from 5º to 35º (or 40º) at a scan speed of 2 º/min and from 5º to 80º at a scan speed of 4 º/min. The degree of crystallinity determined by XRD was calculated as the percentage of the scattered intensity of the crystalline phase over the sum of the scattered intensities of the crystalline and amorphous phases. The percentage crystallinity was acquired from the peak at 5º to 40º 2θ using XRD analysis software (Mdi Jade 6.0).

XPS (Sigma Probe of ThermoVG Scientific Co.) of the thermoplastic elastomers was performed using an AlK$_\alpha$ source (15 kV and 100 W). High-resolution surveys (pass energy = 20 eV) with a step size of 0.1 eV for C1s and O1s were recorded. The binding energies were corrected by reference to the hydrocarbon component at 285.0 eV. Deconvolution of the XPS spectrum was acquired from the C1s and O1s regions by peak fitting.

RESULTS AND DISCUSSION

XRD analysis: Fig. 1 shows the XRD patterns of ZnO. The three high intensity peaks at 31.8º, 34.5º and 36.3º 2θ were assigned to the (100), (002) and (101) planes of the ZnO hexagonal phase crystal, respectively. Fig. 2 shows XRD patterns of the thermoplastic elastomers. The XRD patterns were separated into the crystalline and amorphous regions. The shapes of crystalline peaks were sharp, whereas the amorphous peak was very broad. A typical XRD pattern of the elastomer is fully amorphous[37-39]. All XRD patterns of the thermoplastic elastomer samples have an amorphous peak of A and crystalline peaks of B and C. These peaks were assigned to MAH-*g*-EPDM because the crystalline peaks, B and C, were not observed in the XRD pattern of ZnO. The crystalline peaks of D, E and F were assigned to the typical ZnO crystal as shown in Fig. 1. According to the ZnO peaks in the XRD patterns of the thermoplastic elastomers, some zinc oxide did not participate in the formation of ionomers and still remained in the sample. The relative intensities of peaks B and C were relatively unchanged irrespective of the formulations, whereas those of peaks D, E and F changed according to the kinds and contents of the ingredients, particularly the zinc oxide contents.

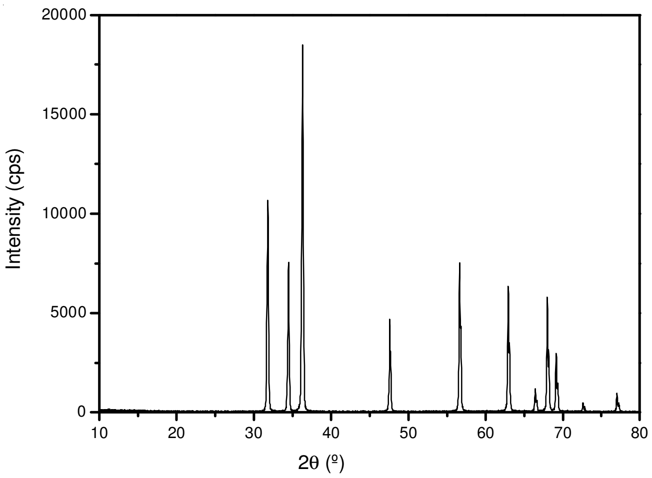


Fig. 1. XRD pattern of ZnO

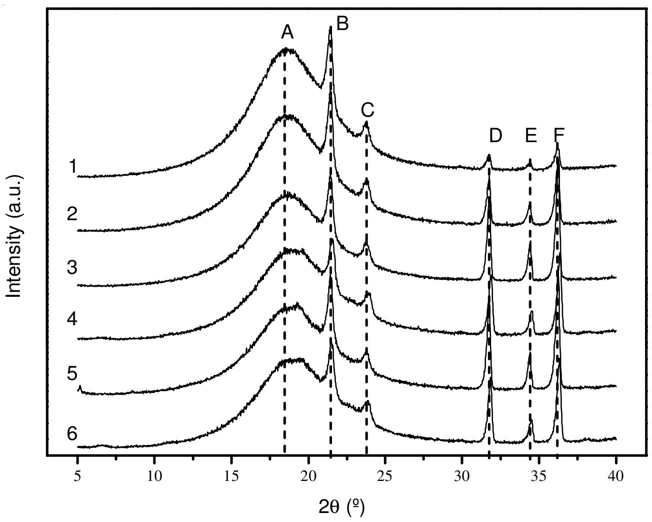


Fig. 2. XRD patterns of the thermoplastic elastomers. The numbers indicate the samples No. as described in the formulation

The degree of the ionic bonds formed between maleic acids of the MAH-*g*-EPDM and ZnO was estimated using the percentage crystallinity. The crystallinity was determined from the XRD pattern using the software (Mdi Jade 6.0). The percentage crystallinity (X_c, %) was calculated using eqn. (1) and the results are listed in Table-2.

$$X_c = I_c/(I_c + I_a) \tag{1}$$

where I_c and I_a are the sums of the intensities of the crystalline and amorphous regions, respectively.

Table-3 summarizes the normalized percentage crystallinity (= X_c/ZnO content) of the thermoplastic elastomers. The normalized percentage crystallinity increased with increasing

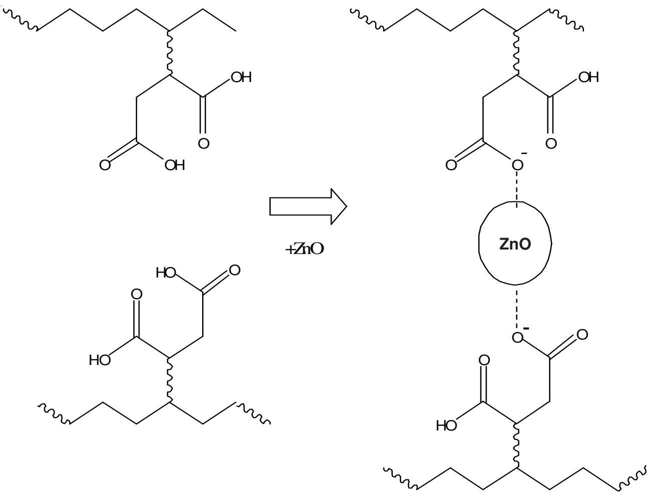
TABLE-2
PERCENTAGE CRYSTALLINITY (X_c, %) OF THE ZnO CRYSTALLINE PEAKS OF D, E, F AND SUM OF THEM (D + E + F)

Sample No.	1	2	3	4	5	6
A : D	0.5	1.8	3.5	2.8	3.8	3.0
A : E	0.2	0.7	1.5	1.0	1.4	1.0
A : F	0.9	2.7	5.5	4.1	5.6	4.2
A : (D + E + F)	1.6	5.2	10.5	7.9	10.8	8.2

the ZnO content. The difference in the normalized percentage crystallinity of the samples with the ZnO contents of 3 and 5 phr (the difference was 0.4) was higher than that of the samples with the ZnO contents of 1 and 3 phr (the difference was 0.2). This means that the increase of the ionomer formation decreased with increasing the ZnO content. The ionomers can be formed between the maleic acid groups of the MAH-*g*-EPDM and zinc oxide particles as shown in **Scheme-I**.

TABLE-3
NORMALIZED PERCENTAGE CRYSTALLINITY
(X_c/ZnO CONTENT)

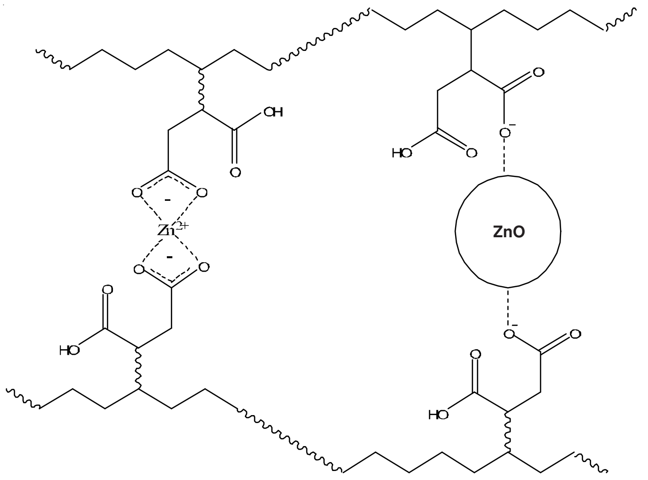
Sample no.	1	2	3	4	5	6
A : D	0.5	0.6	0.7	0.6	0.8	0.6
A : E	0.2	0.2	0.3	0.2	0.3	0.2
A : F	0.9	0.9	1.1	0.8	1.1	0.8
A : (D + E + F)	1.6	1.7	2.1	1.6	2.2	1. 6



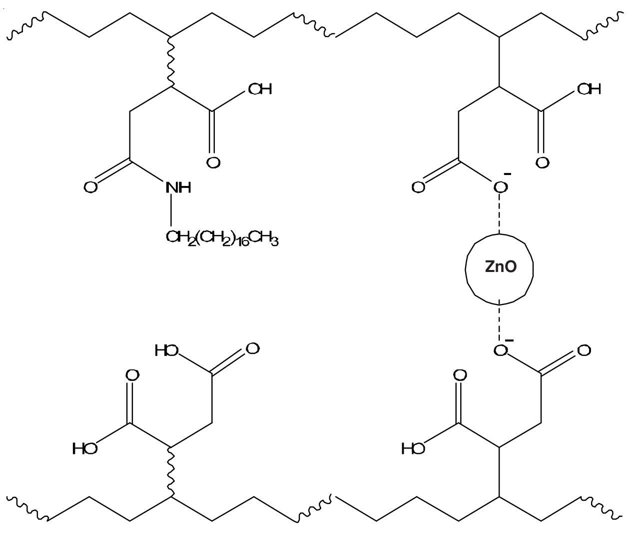
Scheme-I: Ionomer formation between MAH-*g*-EPDM and ZnO particle

The normalized percentage crystallinity of the thermoplastic elastomers containing zinc stearate or stearic acid (the samples no. 4 and 6, respectively) were lower than that of the thermoplastic elastomer only containing the same zinc oxide content (the sample no. 3). On the other hand, the normalized percentage crystallinity of the thermoplastic elastomers containing octadecyl amine (ODA) was higher than that of the sample no. 3. These results suggest that the degree of ionomer formation was enhanced by adding stearic acid or zinc stearate whereas it was reduced by adding octadecyl amine. Stearic acid or zinc stearate may stimulate the release of Zn^{2+} to improve the ionomer formation. Zinc stearate can release Zn^{2+}, while stearic acid reacts with zinc oxide particle to generate zinc stearate and release Zn^{2+}. Therefore, by adding stearic acid or zinc stearate, new ionic bonds between the maleic acid groups and Zn^{2+} are formed as shown in **Scheme-II**. An acid/base reaction between the basic amine group of octadecyl amine and the maleic acid occurs to form a peptide bond, which prevents the maleic acid group from generating the ionic bonds with zinc oxide particles as shown in **Scheme-III**.

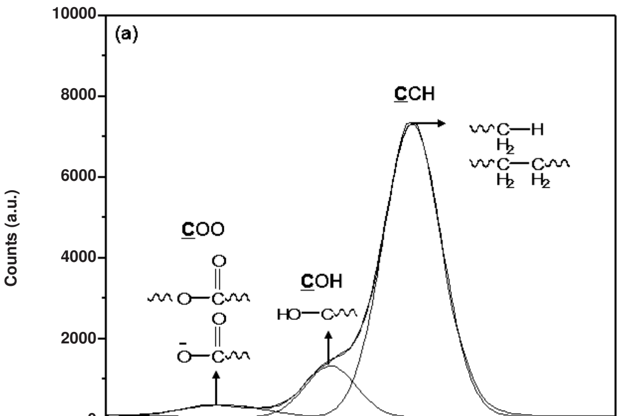
XPS analysis: Fig. 3 shows XPS spectrum of the sample no. 5. The peak in C1s region can be deconvoluted into three (**C**CH, **C**OH and **C**OO) or four (**C**CH, **C**N, **C**OH and **C**OO) parts. The peak at 285.0 eV was assigned to **C**-C or **C**-H. The peak at 286.3-286.6 eV was assigned to alcohol, amine, or amide. The peak at 288.0-289.0 eV results from a carbon-oxygen double bond (**C**=O) due to amide and carboxylate (relative lower binding energy) and the higher binding energy attributed to carboxylic acid or ester.



Scheme-II: Ionomer formation of MAH-*g*-EPDM with ZnO particle and zinc ion (Zn^{2+})



Scheme-III: Prevention of ionomer formation by octadecyl amine



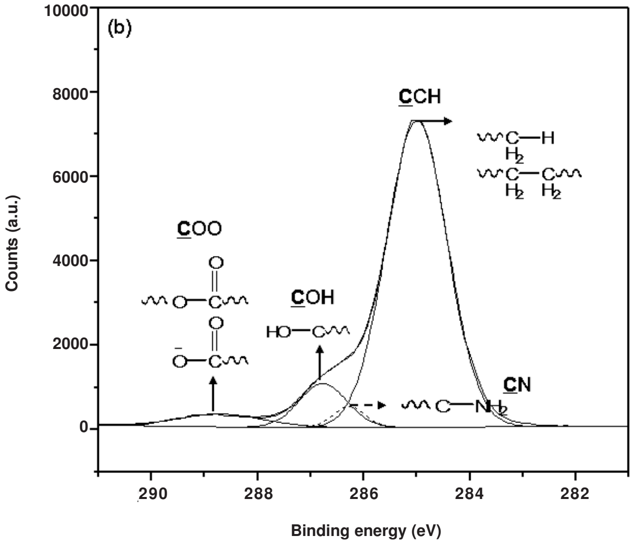


Fig. 3. XPS spectrum of the sample no. 5. Two deconvolution methods of the C1s region with three (a) and four (b) peaks

Fig. 4 shows O1s region XPS spectrum of the sample no. 5. The O1s peak can be deconvoluted into four parts of C-**O**H, **O**=C-O, Zn**O** and O=C-**O**. The Ols peak was deconvoluted into the following peaks: (1) the C-**O**H peak at 532.5 eV due to alcohol, (2) the **O**=C-O peak at 531.6 eV related to carboxylic acid, ester, amide and carboxylate, (3) the Zn**O** peak at 530.7 eV and (4) the O=C-**O** peak at 533.5 eV related to carboxylic acid, ester and amide[40,41]. Tables 4 and 5 summarize the assignments of the Cls and O1s peaks components and the materials affecting the C1s and O1s peaks, respectively.

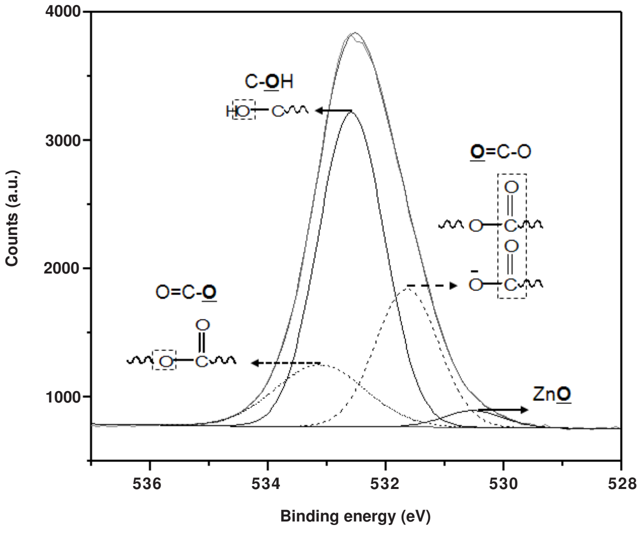


Fig. 4. XPS spectrum of the sample no. 5. The O1s region was deconvoluted into four peaks

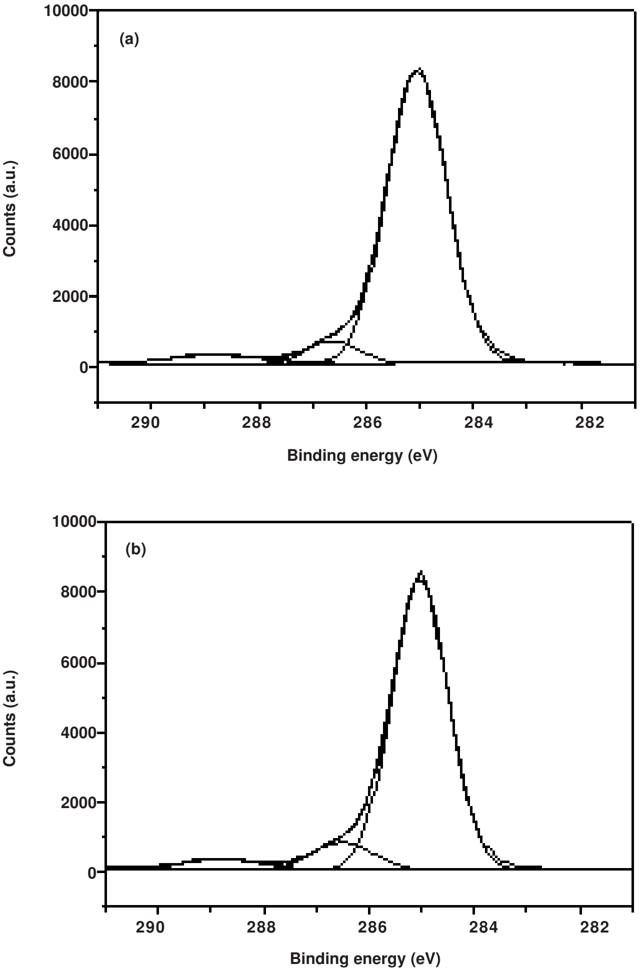
The C1s peak was deconvoluted into three parts of **C**CH (285.0 eV), **C**OH (286.5 eV) and **C**OO (288.7 eV), because deconvolution of the **C**N peak from the neighboring peaks was not reasonable as shown in Fig. 3(b). Fig. 5 shows the C1s region of XPS spectra of the thermoplastic elastomer samples. There were some differences in the peak intensities depending on the sample formulations. The highest intensity **C**CH peak at 285.0 eV was assigned to an aliphatic environment. Therefore every other peak in this region was normalized to this peak. The **C**OH peaks might be affected by the alcohol group of the antioxidant. The **C**OO peaks at 288-289 eV were

TABLE-4
ASSIGNMENT OF THE DECONVOLUTED Cls AND O1s PEAKS IN THE XPS SPECTRA

Peak	Binding energy (eV)	Function	Functional group
C1s	285.0	**C**-(C or H)	Hydrocarbon
	286.3	**C**-N	Amine
	286.6	**C**-OH	Alcohol
	289.0	O=**C**–O	Acid, ester
O1s	530.7	Zn**O**	Zinc oxide
	531.6	**O**=C-O	Acid, ester
	532.5	C-**O**H	Alcohol
	533.5	O=C–**O**	Acid, ester

TABLE-5
AFFECTING MATERIALS ON THE C1s AND O1s PEAKS IN THE XPS SPECTRA

Peak	Materials
CCH	Royaltuf 498, Songnox 1076, zinc stearate, octadecyl amine, stearic acid
COH, C-**O**H	Songnox 1076
CN	octadecyl amine
COO, **O**=C-O, O=C–**O**	Royaltuf 498, Songnox 1076, carboxylate, zinc stearate, stearic acid
Zn**O**	Zinc oxide



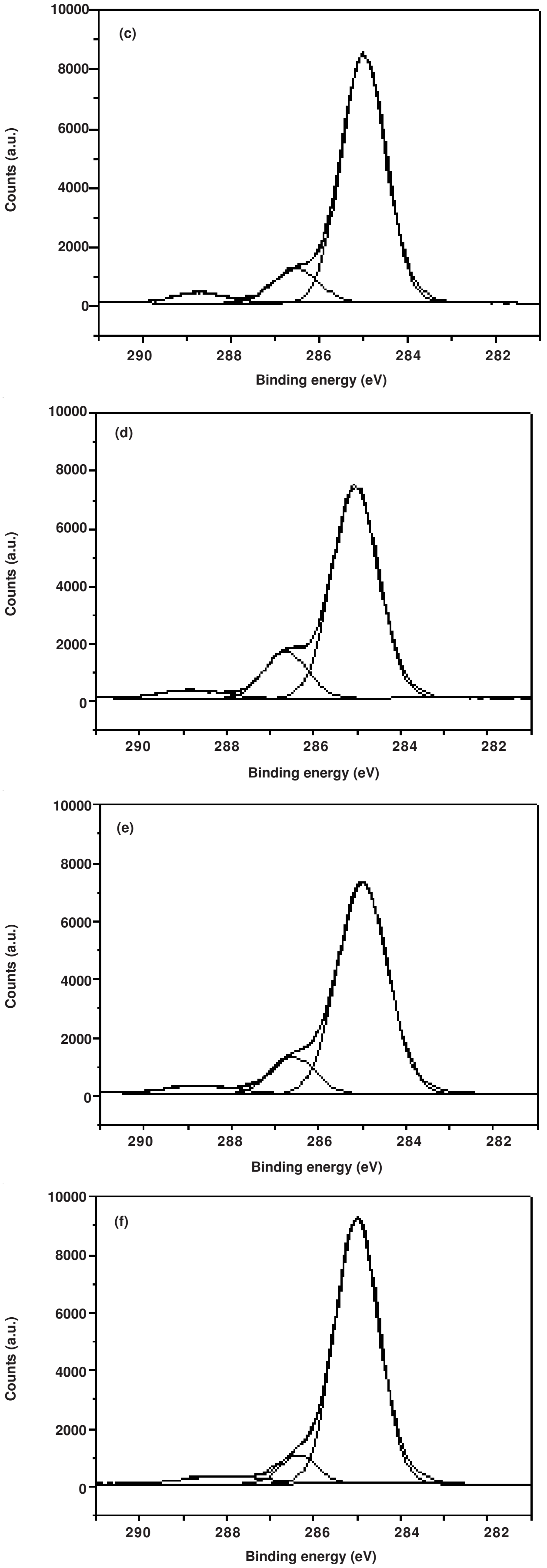


Fig. 5. XPS spectra of the C1s region of the samples No. 1 (a), 2 (b), 3 (c), 4 (d), 5 (e) and 6 (f)

assigned to the carboxylic acids, esters, or carboxylate related to the formation of an ionomer. The binding energy of carbon decreased slightly (about 0.3 eV) when the carboxylic acid groups of the maleic acids changed to carboxylates by the formation of ionomers[42]. The C1s peak of maleic acid appears at 289 eV, while the C1s peak of carboxylate to form the ionomer was observed at 288.7 eV. Fig. 6 shows the expanded XPS spectra of the <u>C</u>OO peak region from 287 to 292 eV. The binding energy shifted to lower energy as the zinc oxide content increased. The binding energy of samples no. 1, 2 and 3 were, 288.77, 288.76 and 288.68 eV, respectively. This means that the formation of the ionomers increased with increasing the zinc oxide content (Table-6).

TABLE-6
PEAK INTENSITY RATIOS OF THE O1s PEAKS
(NORMALIZED WITH THE PEAK AT 285 eV of C1s)

Sample no.	1	2	3	4	6
C-**O**H	30.8	30.9	32.8	42.5	18.3
O=C–O	6.3	7.8	13.6	16.7	8.0
O=C–**O**	7.0	6.4	8.7	8.5	5.4
Zn**O**	0.4	0.9	1.5	1.0	0.8

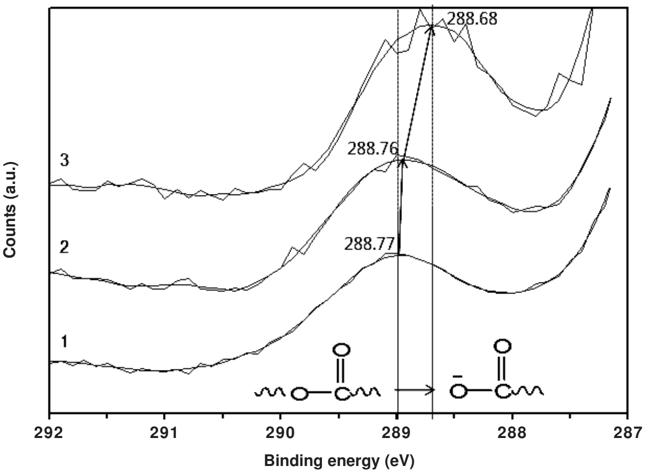


Fig. 6. XPS spectra of the TPEs (binding energy : 292-287 eV). The numbers indicate the samples No. as described in the formulation

Fig. 7 shows XPS spectra of the O1s region of the thermoplastic elastomers. The relative intensity of the Zn**O** peak at 530.7 eV increased with increasing the ZnO content. The relative intensity of the Zn**O** peak was reduced by adding zinc stearate or stearic acid. This means that zinc stearate or stearic acid reacts with zinc oxide particle to generate Zn^{2+} and form zinc ionomers. The same trends were observed in the XRD patterns as discussed above. The **O**=C-O and O=C-**O** peaks are related to various chemicals such as carboxylic acid, ester, amide and carboxylate. Therefore, the degree of the ionomer formation could not be determined using the **O**=C-O and O=C-**O** peak abundances.

Conclusion

The normalized percentage crystallinity increased with increasing the ZnO content. The ionomers were formed between the maleic acid groups of MAH-*g*-EPDM and zinc oxide and the increase of the ionomer formation decreased with increasing the ZnO content. The addition of zinc stearate

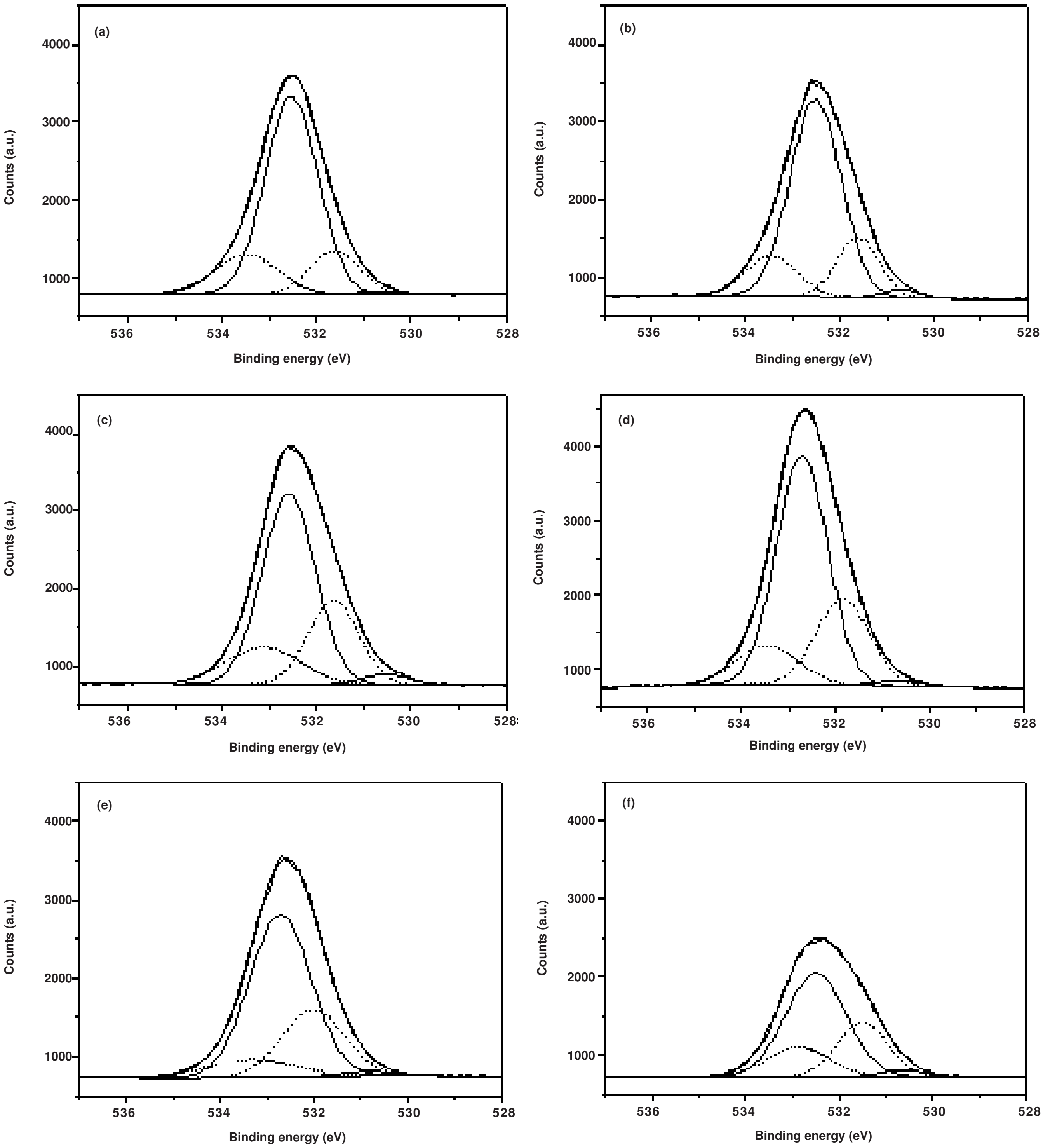


Fig. 7. XPS spectra of the O1s region of the samples No. 1 (a), 2 (b), 3 (c), 4 (d), 5 (e) and 6 (f)

or stearic acid increased the normalized percentage crystallinity, whereas the addition of octadecyl amine decreased the crystallinity. For the XPS analysis, the relative peak intensity of Zn**O** increased with increasing the ZnO content and was decreased by adding zinc stearate or stearic acid. Stearic acid and zinc stearate release Zn^{2+} to improve the ionomer formation, whereas octadecyl amine prevents the ionomer formation. The analysis results using XRD and XPS showed similar trends. The percentage crystallinity in XRD and the relative intensity of ZnO in XPS are important factors for determining the degree of ionomer formation of the thermoplastic elastomers.

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