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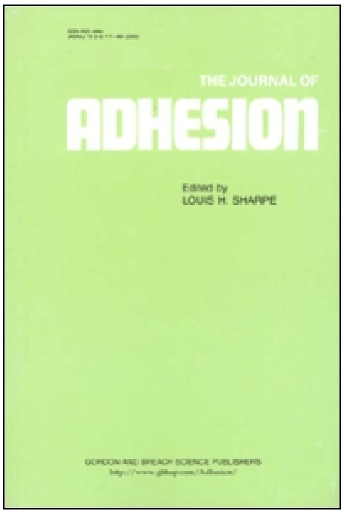

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The Adhesion Properties of an Ozone Modified Thermoplastic Olefin Elastomer*

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The adhesion properties of a thermoplastic olefin elastomer (TPO) after ozone exposure are studied with attenuated total reflection infrared spectroscopy (ATR), the lap shear test, and contact angle measurement. The ozone treatment is applied after the TPO is dip-coated with acrylic acid (AA) that is mixed with benzophenone, benzoyl peroxide (BPO), and azobisisobutyronitrile initiators. ATR spectra confirm the presence of grafted AA on TPO, the amount of which depends on the ozone exposure time and the type of initiator applied. The total surface energy, the polar component, and lap shear strength (LSS) of the grafted TPO increase with increasing ozone exposure time and also vary with the initiator. All AA-grafted TPOs have much greater LSS than the TPO without AA. The greatest LSS is obtained from the specimen grafted with AA and BPO. In addition, the small differences in surface energies and failure strains associated with the great changes in LSS obtained from various specimens implies that the nature of the grafted layer has a significant effect on the adhesion strength.

Keywords: Thermoplastic olefin elastomer; ozone; grafting; acrylic acid; adhesion

I. INTRODUCTION

Thermoplastic olefin elastomers (TPO), which consist of dispersions of ethylene-propylene-diene rubber particles (EPDM) in a polypropylene (PP) matrix, have been used extensively in the automotive industry,

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building materials, and commodity products to replace conventional rubber materials because of their good mechanical, elastic, processing, and recycling properties. The increasing functional and styling needs demand that the thermoplastic olefins be easily adhered to other materials.

In general, TPO has a low energy surface because of its hydrocarbon constituents and is difficult to bond. Many methods such as bulk grafting, compounding, and various surface grafting techniques, have been proposed to modify the surface of aliphatic polymers into a polar surface with a high surface energy to facilitate adhesion [1–7]. Among these common methods, ozone has been applied successfully in treating polymers such as PP, polyethylene (PE), polyethylene terephthalate, and polyurethane (PU) to improve adhesion [8–13]. It is well recognized that polar carbonyl, carboxyl, and hydroperoxide species are generated on the ozonized polymer surface [13, 14]. The as-formed polar functional groups are responsible for the increase of the surface energy and improvement in the wettability.

Moreover, the hydroperoxides on the ozonized surface can serve as active sites to induce radical polymerization of monomers containing C=C bonds and result in surface grafting of functional monomers onto the target polymer surface [9]. Different vinyl monomers were successfully grafted on PE and PP surfaces through this ozone-induced grafting reaction [8, 9, 13]. Yamauchi *et al.* have shown that methyl methacrylate could be graft copolymerized onto the ozonized PP [8]. It was indicated that ozone could generate peroxyl radicals which were converted to hydroperoxide and then broken by heating to form alkoxyl and hydroxyl radicals to initiate graft copolymerization [8].

A similar result was obtained by Fujimoto *et al.* They found that the polymeric peroxides were capable of initiating graft polymerization of acrylamide onto PE and PU surfaces [9]. The amounts of peroxide produced were dependent on the ozone concentration, the ozone exposure time, and the kind of the polymer used. It was also shown that ozone-induced peroxides were not only on the outermost surface layer but also underneath the surface [9]. Dasgupta also found that the surface of PE and PP could be grafted with acrylamide in aqueous solution under an ozone environment [13]. The extent of grafting reaction depended on the temperature, the agitation speed, and the concentration of ozone. It is believed that hydroperoxides generated on the PE and PP surfaces provide effective sites for surface grafting.

In this study, the surface of TPO is first dip-coated with acrylic acid (AA) in the presence of different initiators and then exposed to ozone to initiate the surface-grafting reaction of AA onto the TPO. AA has been readily grafted onto PE and PP surfaces through UV, plasma, and laser techniques [15–24]. The method used here is demonstrated to be a good alternative to the commonly-used ozone exposing then surface coating (grafting) process in which the grafting efficiency is easily affected because the active radicals on the ozone-treated surface are liable to be contaminated before the surface grafting process. In this study, the modified surfaces are characterized by attenuated total reflection infrared spectroscopy (ATR), contact angle measurement, and lap shear strength measurement (LSS).

II. EXPERIMENTAL

The TPO used was Santoprene 203-50, consisting of EPDM (with ethylidene norbornene as the comonomer) dispersed in PP, from Advanced Elastomer Systems. The TPO, with a width of 3 cm and thickness of 0.5 mm, was extruded at 210°C (die temperature). The extruded material had a crystallinity about 21% as determined by differential scanning calorimetry. Specimens with the size of $2.5 \times 1.3\ \text{cm}^2$ were cut from the strip parallel to the extruding direction. The specimens were ultrasonically cleaned twice in 99% pure acetone solvent for 5 minutes at room temperature and then vacuum dried 3 hours before use.

An acetone solution containing 1 mole/liter (M) acrylic acid (AA, $CH_2{=}CHCOOH$) and 0.2 M initiators was prepared. The AA was purchased from Merck. Three different initiators, benzoyl peroxide (BPO, $(C_6H_5CO)_2O_2$), benzophenone (BP, $C_6H_5COC_6H_5$), and azobisisobutyronitrile (AIBN, $[(CH_3)_2(CN)C]_2N_2$), were used (also from Merck). TPO specimens were immersed in the three as-prepared grafting solutions for five minutes, taken out, and vacuum dried for two hours. These coated TPO specimens were subsequently exposed to ozone (1.2 amp, 4 1/min, Sumitomo SG-01A ozone generator) for various periods of time, ultrasonically rinsed twice with acetone for five minutes, and vacuum dried before analysis. The concentrations of ozone generated within 20, 40, 60, 80, and 100 minutes under selected operating conditions were 4484, 8902, 13320, 17738, and 22156 mg/l, respectively (determined by titration method).

In ATR analysis, the treated TPO specimens were pressed against a Ge(60°) crystal under a constant 32 oz-in torque with a torque wrench, and placed in an ATR accessory made by Harrick Scientific Co. Two hundred scans were acquired at a resolution of 4 cm^{-1} from 4000 cm^{-1} to 600 cm^{-1} on a Perkin-Elmer 1725 Fourier Transform infrared spectrophotometer. Difference spectra were obtained by subtracting the baseline spectrum of a clean Ge(60°) crystal.

For surface energy measurements, a contact angle goniometer (as Model 100–00 from Ramé-Hart, Inc.) equipped with a video camera was used. Three standard liquids, double-distilled water, formamide, and ethylene glycol, were applied on the surface of the grafted TPO. The drop size was approximately about 0.01 ml. Fifty readings were averaged to obtain one contact angle value.

Lap shear strength (LSS) measurements were performed in accordance with ASTM standard D-1002. The grafted TPO samples were sandwiched between two acid-etched 1020 cold-rolled steel substrates ($2.5 \times 10.2\ \text{cm}^2$, from China Steel Co.) with a room-temperature-cured, two-part epoxy adhesive (707-AB from Great Eastern Resins Industrial Co., mixing ratio of resin/curing agent (an amidoamine) = 1/1.4). The metal etching procedures were described previously [25]. A piece of 0.2 mm diameter fishing line was used as the spacer to keep the bond-line thickness constant. After a seven-day cure at room temperature, the residual epoxy adhesive along the bondline edges was trimmed using a razor blade. Then the LSS specimens were tested to failure on an Instron using a crosshead rate of 1.3 mm/min. Five specimens were tested for each measurement.

III. RESULTS AND DISCUSSION

(A) ATR Analyses

Representative ATR difference spectra obtained from the TPO modified with AA and BPO after ozone exposure are shown in Figure 1.

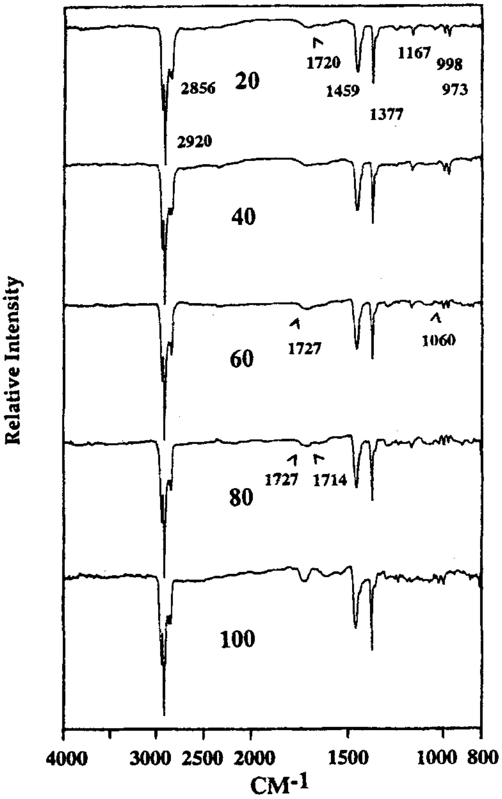

FIGURE 1 The ATR spectra obtained from TPO modified with AA and BPO after 20, 40, 60, 80, and 100 minutes ozone exposure.

The bands characteristic of the EPDM and PP are clearly identified [14]. The characteristic bands of the asymmetric and symmetric stretching vibrations of CH_2 in TPO appear at 2920 and 2856 cm^{-1}, respectively. The band near 1459 cm^{-1} is from the asymmetric deformation of $—CH_2—$groups. The characteristic bands of CH_3 are shown at 1377 and 1167 cm^{-1}. In addition, the small band near 998 cm^{-1} is from —CH and CH_3; the band near 973 cm^{-1} is due to CH_3 and C—C.

As shown in the Figure 1, the band near 1720 cm^{-1} increases in intensity with an increase in the ozone exposure time. Since AA has a strong band characteristic of COOH near 1727 cm^{-1}, the increase is an indication of the substantial amounts of grafted AA on TPO. The previous result indicated that TPO was oxidized to form carboxyl and carbonyl groups, with the bands near 1746 and 1714 cm^{-1}, respectively, under ozone [14]. These two bands could also contribute to the observed changes in intensities. However, it is clearly observed in Figure 1 that the band near 1720 cm^{-1} splits into two bands around 1714 and 1727 cm^{-1}. No band near 1746 cm^{-1}, which is intense after only 20 minutes ozone exposure on uncoated TPO, is present [14]. Moreover, although other strong characteristic bands of AA are mixed with bands of TPO and are unidentified, the band near 1060 cm^{-1} from AA becomes noticeable and increases in intensity after 60 minutes exposure. As a result, it is evident that AA is present on TPO and increases in amounts with the ozone exposure time.

The detected AA may come from either homopolymerized AA or grafted AA (AA reacted with TPO). In this study, both kinds of AA are expected to be generated. Ozone attacks BPO and AA first since they are on the surface of the TPO. An absence of the 1746 cm^{-1} band and a much smaller 1714 cm^{-1} band observed in Figure 1 confirm that the attack of TPO by ozone is screened by the presence of AA and BPO on the TPO surface. The abundant radicals generated from BPO will then react with AA and TPO. The great concentration of BPO used could increase the possibility of primary termination between radicals, thereby decreasing the possibility of forming long-chain AA homopolymer. The small or loosely bounding AA homopolymers would be rinsed off during the ultrasonic cleaning procedure described in the experimental section. It is believed that AA detected in Figure 1 is from either grafted AA or tightly-entangled AA homopolymer.

In the case of AIBN, a similar result was obtained. Figure 2 shows representative ATR difference spectra obtained from the TPO modified with AA and AIBN after ozone exposure. The characteristic bands observed in Figure 1 also appear in Figure 2 except that the band near 1714 cm^{-1} is more intense in Figure 2. The band near 1727 cm^{-1} (from AA) is clearly seen in the spectrum taken after 100 minutes of ozone treatment. The difference in intensities between Figures 1 and 2 is attributed to the difference in radical decomposition rates between AIBN and BPO. AIBN has a greater decomposition rate than BPO; therefore, AIBN is consumed faster than BPO

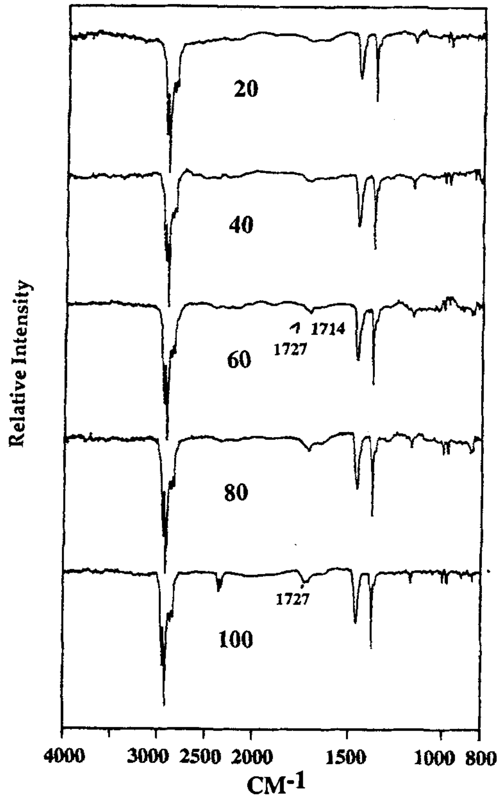

FIGURE 2 The ATR spectra obtained from TPO modified with AA and AIBN after 20, 40, 60, 80, and 100 minutes ozone exposure.

and this allows different amounts unreacted ozone to go through the coated AA and AIBN layer (~0.16 micrometer thick) and oxidize TPO to form carbonyl species or radicals. The differences in reaction efficiencies with ozone, and the differences in chain transfer constants, initiator efficiencies, and primary termination rates between the two initiators are all related to the extent of the grafting reaction. These effects are beyond the scope of this study and need to be further investigated.

The band near 1714 cm^{-1} is also significant in Figure 3 which gives the ATR difference spectra obtained from the TPO modified with AA and BP. There is only a small shoulder near 1727 cm^{-1} after ozone

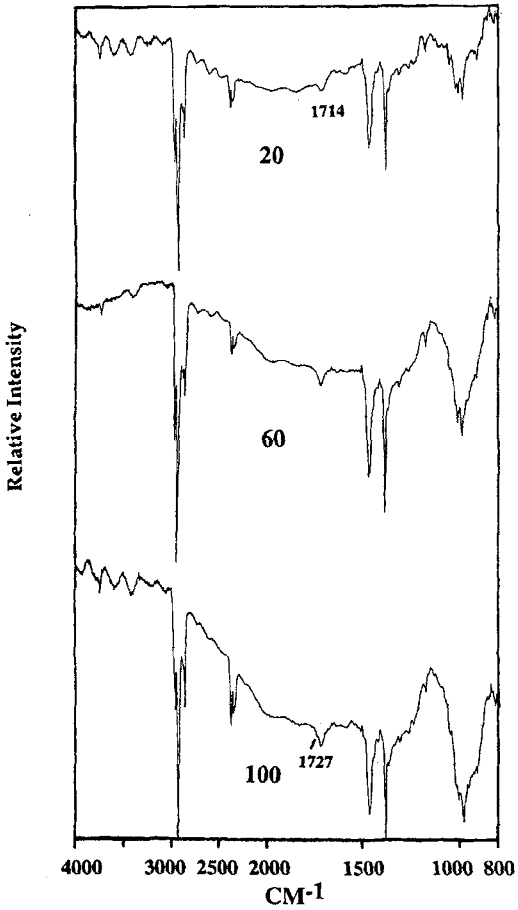

FIGURE 3 The ATR spectra obtained from TPO modified with AA and BP after 20, 60, and 100 minutes ozone exposure.

exposure. Comparison of Figures 1 and 2 with Figure 3 indicates that the amounts of AA detected on TPO are smaller with the use of BP than with the use of BPO and AIBN. This may result from the fact that BP is a photosensitized initiator which has properties different from the thermally initiated BPO and AIBN. The radical initiation process of BP (and with AA) under ozone could be quite different from those of BPO and AIBN. The origin of this difference deserves to be studied.

(B) The Surface Energy

Table I lists contact angles and surface energies calculated from different TPO surfaces. The polar and dispersion components are calculated from the equations proposed by Schultz *et al.* [26] Before ozone exposure, TPO has a high water contact angle and a low surface energy near 28.5 ergs/cm^2. Although TPO consists of hydrocarbon chains, a polar component is detected and is attributed to the chemicals (such as vulcanizers) in the crosslinked EPDM, as well as oxidized species fromed during the processing. This was confirmed in the previous ATR analyses [14].

As shown in Table I, the contact angles on TPO decrease after ozone treatment. The calculated total surface energy and the polar component of the blank TPO (no treatment) increase while the

TABLE I The contact angles and surface energies of different specimens

Reaction	*Time (min)*	*Contact angle (degree)*			*Surface energy (ergs/cm^2)*		
		A	*B*	*C*	R_d	R_p	*Total*
No	*No*	*79*	*66*	*59*	*17.6*	*10.9*	*28.5 (1.0)*
	20	70	64	58	8.7	23.9	32.6 (0.1)
O_3 only	40	65	61	57	6.3	31.3	37.6 (0.8)
	60	63	61	56	5.1	35.0	40.1 (0.6)
	80	61	60	55	4.5	38.1	42.6 (0.7)
	100	59	59	54	3.9	41.2	45.1 (0.7)
	20	67	64	57	7.2	27.3	34.5 (0.1)
AA	40	65	60	56	7.2	30.1	37.3 (0.7)
+	60	63	58	54	7.2	31.8	39.0 (0.8)
BPO	80	59	57	53	5.0	39.1	44.1 (1.3)
	100	56	56	52	3.8	44.4	48.2 (1.4)
	20	68	63	57	7.8	26.6	34.4 (0.2)
AA	40	66	60	56	8.0	28.1	36.1 (0.6)
+	60	63	59	55	6.4	33.0	39.4 (0.9)
AIBN	80	60	58	54	5.0	38.2	43.2 (1.2)
	100	59	57	53	5.0	39.1	44.1 (1.3)
	20	62	62	59	3.3	39.7	43.0 (1.5)
AA	40	60	60	58	3.1	42.1	45.2 (2.2)
+	60	58	58	56	3.7	43.1	46.8 (2.9)
BP	80	57	57	55	3.3	44.7	48.0 (2.5)
	100	56	56	55	3.2	46.2	49.4 (3.2)

A: water, *B*: formamide, *C*: ethylene glycol
R_d: dispersion component, R_p: polar component
( ): standard deviation
Standard deviation of all contact angles is about degree.

dispersion component decreases with the ozone exposure time. The total surface energy becomes 45.1 ergs/cm^2 after 100 minutes exposure. This is attributed to the formation of polar OH, C=O, and COO species on the TPO surface during ozone exposure [14].

Similarly, as AA is applied on the TPO, the contact angle decreases and the surface energy increases after ozone treatment. The total surface energies after 100 minutes ozone exposure follow the order of BP $\sim$ BPO $>$ blank $\sim$ AIBN (when standard deviations are considered) while the differences among them are not as great as those obtained from ATR spectra. This is attributed to the fact that the sampling sensitivities and depths of the ATR and the contact angle measurements are very different. However, considering the results obtained from ATR analyses, it is obvious that the increases in polar component and total surface energy are from the contributions of both species oxidized and AA reacted on TPO.

It is also evident that the rates of changes in contact angles (= change in contact angle/treating time) depend on the type of the initiator added. From Table I and Figure 4, the rates of increases in the total surface energies and the polar components during the early stage of ozone exposure are in the order of BP $>$ BPO $\sim$ AIBN $\sim$ blank TPO. It is believed that the difference in efficiencies of the three initiators can result in different amounts and forming rates of reacted AA and oxidized species on TPO.

Although the relation between surface energy and adhesion strength is still in debate, the result obtained here gives supporting evidence about how monomer and initiator can affect the extent and rate of reaction among AA, initiator, and TPO during ozone exposure.

(C) The Lap Shear Strength (LSS)

The specimens prepared without TPO have a LSS near 1000 psi (6.9 MPa) (standard deviation (SD) = 78 psi (5.4 KPa), failure strain = 2.9%) and cohesive failure is observed in the adhesive layer between the steel substrates as noted by the presence of large amounts of adhesive on both failed steel surfaces. This proves that the etching process of the steel generates a strong adhesive/steel interface and the lap shear strength is limited by the bulk adhesive.

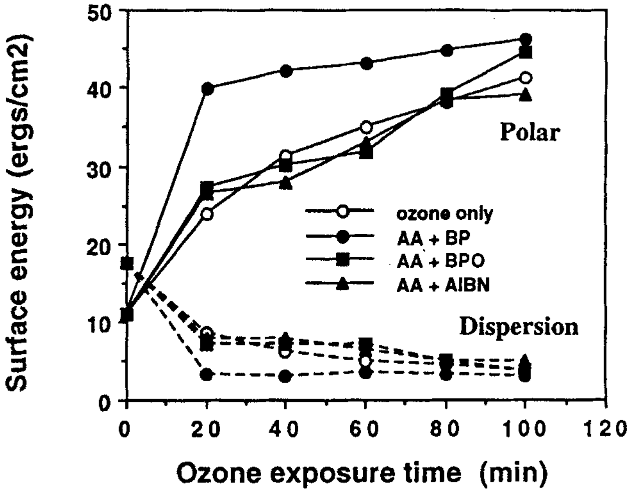

FIGURE 4 The surface energies of specimens prepared with grafted TPO.

The LSS obtained from various specimens are shown in Table II and Figure 5. The ozone treatment results in the LSS of the uncoated TPO increasing from 55 (0.38 MPa) to 118 psi (0.81 MPa) after 100 minutes exposure. The clear TPO failure surfaces obtained from these uncoated specimens after the lap shear test indicate that the failure loci of these specimens are near the TPO. Before ozone exposure, the specimens prepared with the untreated TPO have negligible strength. The improvement in adhesion strength is limited on the uncoated

TABLE II The lap shear strength obtained from various specimens

Specimen		*20 min*	*40 min*	*60 min*	*80 min*	*100 min*
O_3 only	psi	55 (1)	74 (7)	105 (8)	109 (9)	118 (17)
	%	0.66 (0.10)	0.72 (0.15)	0.60 (0.11)	0.71 (0.12)	0.76 (0.10)
AA + BPO	psi	409 (29)	607 (34)	706 (32)	821 (29)	864 (26)
	%	1.06 (0.10)	2.50 (0.66)	2.76 (0.51)	2.97 (0.38)	4.10 (0.24)
AA + AIBN	psi	344 (26)	368 (34)	387 (26)	471 (41)	561 (20)
	%	1.10 (0.10)	1.25 (0.11)	1.52 (0.09)	1.85 (0.12)	2.10 (0.15)
AA + BP	psi	257 (14)	350 (16)	432 (9)	505 (36)	613 (16)
	%	1.39 (0.08)	1.51 (0.19)	1.60 (0.21)	2.18 (0.37)	2.62 (0.18)

psi: LSS (lb/in^2), 145 psi = 1 MPa, %: strain ratio (percentage)
( ): standard deviation.

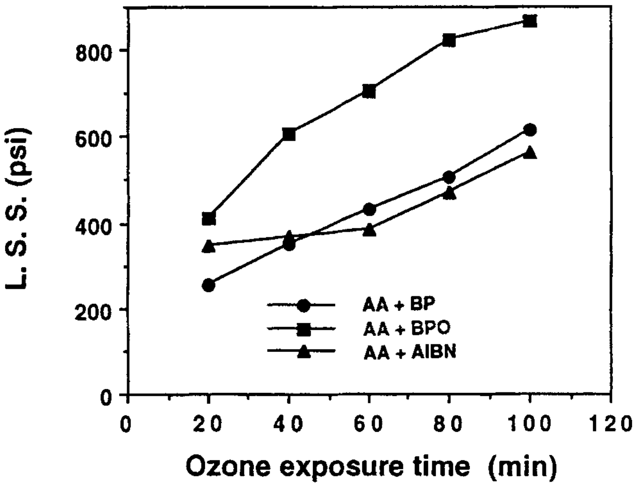

FIGURE 5 The lap shear strengths of specimens prepared with grafted TPO.

TPO even though the polar component of the surface energy increased from 10.9 to 41.2 ergs/cm^2 after 100 minutes ozone treatment. This result may imply that the polar functional groups generated during ozone exposure do not react with the epoxy resin to form strong bonds and have little effect in increasing the LSS.

However, the adhesion strength can be greatly improved when AA is introduced. It is shown that the specimen prepared with AA and BPO has a LSS near 490 psi (2.8 MPa) after only 20 minutes ozone treatment (see Tab. II and Fig. 5). The LSS also increases with the treating time and reaches 864 psi (5.96 MPa) after 100 minutes. It is important to notice that all grafted specimens show clean failure surfaces on the TPO sides. The significant improvement is attributed to the presence of AA on the TPO since little enhancement is obtained from specimens without AA. The use of AA in improving adhesion properties of various polymers have been verified by many researchers [15–24]. In this case, the significant increase is due to the reaction of AA with the epoxy adhesive since COOH groups of AA can open the epoxide groups and chemically bond with the epoxy resin. Moreover, the AA layer on TPO can offer the opportunity for diffusion and entanglement of adhesive molecules which can also enhance adhesive strength.

As shown in Table II, the type of initiator applied also affects the LSS. The LSS of specimens prepared with the AA-grafted TPO increases with increasing the ozone exposure time and follow in the order of BPO > BP ~ AIBN after 60 minutes exposure. This trend is different from that obtained from the surface energies. This confirms that the polar groups generated on the blank TPO surface during ozone exposure have little effect in increasing LSS, and significant increase in LSS obtained is due to the presence of AA.

The difference in LSS among the three initiators is consistent with the result obtained from ATR analyses in which a more intense absorption band from AA is found on the specimen using BPO than on specimens using BP and AIBN. The rate of increase in LSS can also give information of the grafting efficiencies of different initiators. Although the nature of AA reacted on the TPO can not be clearly identified, the amount of AA is closely related to the LSS. The previously-mentioned entanglement and reaction of AA with epoxy chains may explain this relationship.

Interestingly, the LSS obtained from the specimen coated with only AA and without any initiator is 596 psi (4.1 MPa) (SD = 16 psi (0.11 MPa)) after 100 minutes ozone treatment. The value is close to that from the specimen with BP but greater than that from AIBN. This indicates that ozone is capable of initiating the grafting reaction without the presence of external initiators. The differences in LSS comes from either the change in amounts of grafted AA mentioned before or the change in structures of reacted AA as described below.

As shown in Table II, the failure strain differs as different initiators are used. The maximal strains obtained from AA-grafted specimens using BPO, AIBN, and BP are 4.10, 2.10, and 2.62%, respectively. Although the change in LSS may result in difference in strains, the variation in structures of the grafted AA layer is also a contributing factor. For example, the fact that a similar strain with a quite different LSS was obtained from specimens prepared with three initiators after 20 minutes ozone treatment indicates that a structural difference is present among grafted layers (see Tab. II). The rigidity of the TPO/AA/epoxy interfacial layer could be affected by the amount of AA grafted, the degree of entanglement between AA and epoxy, and the degree of preferential adsorption of constituents in the adhesive. It is believed that the type of initiator applied can result in these structural changes because of its effect on the grafting efficiency.

Furthermore, the failure strains of the specimens prepared with AA and BPO after 80 and 100 minutes ozone exposure are 2.97 and

4.10%, respectively, which are even higher than the failure strain of the adhesive itself (2.90%). Such large failure strains could result from the strong interaction between AA and the adhesive which causes deformation of the elastic TPO material. This result also implies that the grafted AA layer is capable of enduring greater elongation than the adhesive alone.

From results obtained from ATR, surface energy, and LSS measurements of various specimens, it is concluded that the adhesion strength of the TPO depends on the grafting efficiencies and the structures of the grafted layers which are dependent on the initiator and the ozone exposure time. Although the greatest strength is obtained only after a relatively long exposure time (100 minutes), the experimental conditions applied here can be viewed as a starting point and modified to minimize the ozone treating time and improve the efficiency of the current method.

IV. CONCLUSIONS

The ozone-induced surface grafting reaction of acrylic acid (AA) onto a thermoplastic olefin elastomer (TPO) surface was demonstrated. The ozone treatment was applied after the TPO surface was coated with AA and three different initiators. ATR spectra confirmed that AA was effectively grafted onto the TPO surface. The amounts of AA grafted increased with the ozone exposure time and changed with the type of initiator used. The total and the polar component of surface energies obtained from the grafted TPO also increased with the ozone exposure time, and followed in the order of BP $\sim$ BPO $>$ AIBN, while the lap shear strength increased in the order of BPO $>$ BP $\sim$ AIBN after long time exposure. The small differences in surface energies and breaking strains but the great changes in lap shear strengths among specimens indicated that the adhesion strength of the TPO could be significantly affected by the nature of the grafted layer.

Acknowledgements

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