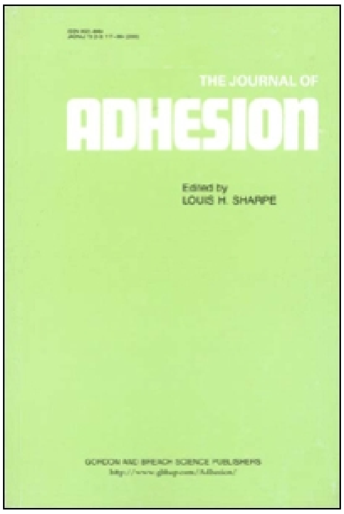

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Dynamic Mechanical and ESCA Studies of Aluminium-Aluminium Bonding by an Epoxidised Natural Rubber-Polyacrylic Acid Blend

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A polyacrylic acid (PAA)-epoxidised natural rubber (ENR) blend becomes crosslinked during high temperature moulding and such a blend was found to be a good adhesive for aluminium (Al)-aluminium (Al) bonding. The joint strength can be improved by the incorporation of silica filler into the adhesive up to a loading of 5 phr. However, higher filler loading causes deterioration of the joint strength. Electron Spectroscopy for Chemical Analysis (ESCA) studies of the peeled and then leached Al surface shows that the ENR phase of the blend is primarily responsible for the adhesion with the Al surface. With the increase in filler loading adhesion with Al increases at the cost of crosslinking between the component polymers. This is substantiated by dynamic mechanical analyses of the blends and joints (that is, Al/blend/Al composites). The changes in dynamic mechanical properties of the blends due to Al adhesion could be correlated with the peel strength of the Al/blend/Al joints.

KEY WORDS polyacrylic acid; epoxidised natural rubber; aluminium-aluminium bonding; dynamic mechanical analysis; peel strength; ESCA studies.

INTRODUCTION

While studying a Brabender-mixed blend of ENR and PAA, it was observed that the blend undergoes thermally-induced crosslinking during high temperature moulding.[1] Preliminary results indicated that this type of blend adhered strongly with Al foil and that the extent of adhesion depends on the incorporation of silica filler into the blend. The present paper reports the results of an investigation on adhesion between the Al foil and the blend on the basis of dynamic mechanical analyses and ESCA studies.

Recently De and co-workers have reported that rubber-rubber blends can be used for Al-Al bonding.[2–4] Incorporation of silica filler in the adhesive enhances its bonding ability presumably through the formation of Al—O—Si linkages.[5] Dynamic mechanical studies revealed that the attachment of the Al foil on the rubber

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*Corresponding author.

blend caused changes in the dynamic mechanical properties of the rubber blend[6] in the same way as caused by the incorporation of reinforcing filler in rubbers.[7–8,10–11]

EXPERIMENTAL

Details of the materials used are given in Table I.

Preparation of the PAA/ENR Blends:

Compositions of the gum and silica-filled blends are given in the Table II. Mixing was done at 180°C and at a rotor speed of 90 rpm. ENR was first masticated in a Brabender Plasticorder PLE-330 for 1 min., followed by blending with PAA for another 11 min. In the case of the silica-filled blend, ENR was first masticated for 1 min. Then silica was added and mixed for another 3 min. Finally, PAA was added and the ENR-silica-PAA mix was blended for an additional 11 min.

Preparation of the Al/Adhesive/Al Joints:

Aluminium foils (Vickers Hardness No. 52.7) were cut to 150 × 200 mm^2 sizes and cleaned with acetone. Approximately 3 g of the blend was placed between the two aluminium foils. This assembly was moulded under a pressure of 5 MPa, at a temperature of 190°C, in a hydraulic press. Part of the metal foil assembly was not

TABLE I
Details of the materials used

Materials	Description[a]	Source
Epoxyprene-50, abbreviated as ENR	$\overline{M}n = 131$ $\overline{M}w = 446.1$	Kumpulan Guthrie Berhad Malayasia
Polyacrylic acid, abbreviated as PAA	Copolymer of acrylic and methacrylic acids. Average mol. wt. range Mr 500 – 1000	Fluka Switzerland

[a] Molecular weight in Kg/mol.

TABLE II
Blend compositions[a]

	Blend designation				
Materials	A	B	C	D	E
PAA	50	50	50	50	50
ENR	50	50	50	50	50
Silica[b]	0	2	5	7	10

[a] Parts by weight.
[b] Vulcasil-S (Bayer, Germany).

filled with the blend and was kept outside the mould during moulding. This part was fixed in the grips of the Zwick Universal Tensile Testing Machine during testing of the joint strength. The overall dimensions of the test specimen were 100 mm × 25 mm, while the bonded region was 50 mm × 25 mm. Figure 1(a) shows a schematic diagram of the Al/adhesive/Al joints.

Determination of the Peel Strength of Al/Adhesive/Al Joint:

The 180° peel (T-peel) strength was determined in accordance with ASTM D 413 using a Zwick Universal Tensile Testing Machine, model 1445. The test specimen

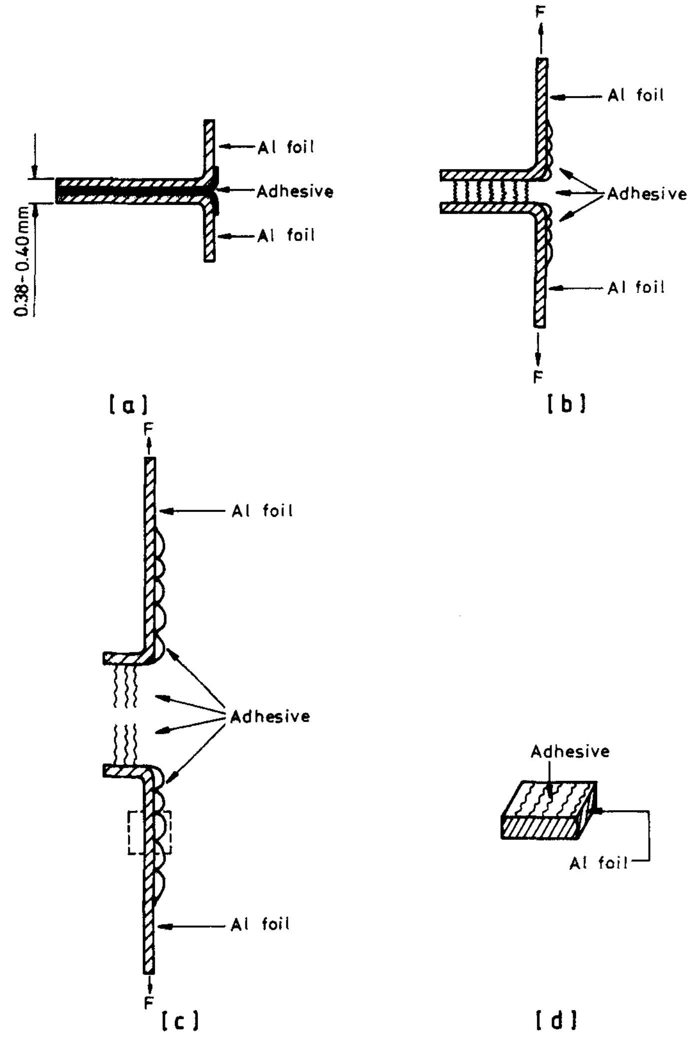

FIGURE 1 Schematic diagram of the adhesive joint during peeling: (a) before peeling; (b) during peeling; (c) after peeling; (d) peeled aluminium surface for ESCA.

was fitted horizontally in the grips of the testing machine through the non-bonded part of the metal foils. A steady load was applied at a rate of 50 mm/min until separation was complete. Figs. 1b–1c show the change in sample geometry as the peel test proceeds.

The peel strength, in terms of force/width, was calculated from the plot of the force *versus* displacement, according to the formula given by Hata[12]

$$F/b = \frac{W}{1 - \cos\theta} \tag{1}$$

where F is the peel force, b is the width, W is the work of adhesion and θ is the peel angle.

In the present case, $\theta = 180°$ and thus the peel strength is given by,

$$W = \frac{2F}{b} \tag{2}$$

Here, F is expressed in Newtons and b is in meters.

ESCA Studies:

The following three samples were prepared for ESCA studies: (i) aluminium foil; (ii) aluminium surface from which the gum adhesive had been leached; and (iii) aluminium surface from which the silica-filled adhesive had been leached.

Sample Preparation for the ESCA Studies Was as Follows:

Aluminium foil: Aluminium foil of size 3 mm × 3 mm was cleaned with acetone and kept in a vacuum oven for 168 hrs. at room temperature.

Peeled and Leached Aluminium Samples (Al/Blend/Al):

Composites as previously described were first prepared by moulding at 190°C at a pressure of 5 MPa for 120 min. The peeled samples were cut to 3 mm × 5 mm size. These peeled samples were immersed in chloroform (solvent for ENR) for 24 hrs. and then in methanol (solvent for PAA) for another 24 hrs. Next the samples were kept for 8 hrs. at room temperature. These leached samples were used for ESCA studies. Fig. 1(d) shows the sample geometry used for the ESCA studies.

Sample Preparation for Dynamic Mechanical Analysis:

The Brabender mixed blends were moulded in a Teflon coated mould (4 cm × 8 cm × 1.5 cm) in a hydraulic press at a temperature of 190°C and a pressure of 5 MPa. All the samples were moulded for 120 min. Al foil bonded blends were prepared by moulding each blend with the Al foil of size 3 cm × 4 cm, attached on both sides of the blend. Figure 2 shows the sample geometry. Al foil was fixed in the mid portion of the sample. The two ends of the moulded sheets were kept free for holding in the clamps of the dynamic mechanical analyser.

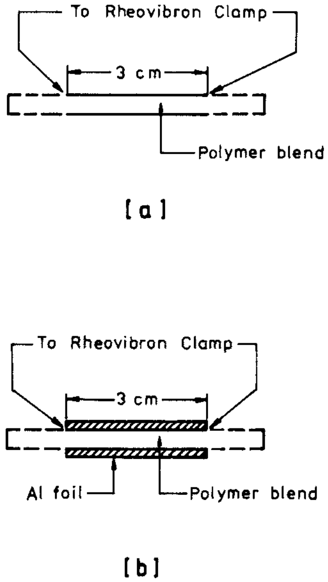

FIGURE 2 Schematic diagram of the Rheovibron sample.

Dynamic Mechanical Analysis:

Dynamic mechanical analyses of the samples (3 cm × 0.64 cm × 0.17 cm) were carried out using a Rheovibron, model DDV-III-EP (Orientec Corporation, Japan) at a strain amplitude of 0.0025 cm and a frequency of 3.5 Hz. Each sample was scanned from −50°C to +200°C at the rate of temperature rise of 2°C/min.

RESULTS AND DISCUSSION

Figure 3 shows the storage modulus *versus* temperature plots of the silica-filled 50/50 PAA/ENR blends and the same blends sandwiched between two Al foils. It was observed that for both the blend and the sandwich composite, the storage modulus increases with an increase in filler loading. This is believed to be due to polymer-filler interaction, as has been reported by several authors.[13–15] Secondly, at a particular filler loading, the storage modulus of the sandwich composite is higher than that of the blend. It is believed that the adhesion between Al and the blend plays an important role in enhancing the storage modulus.

Table III shows the storage modulus values at 100°C of the blends and the corresponding sandwich composites. Figure 4 shows the plots of the ratio of storage moduli of the filled to the gum blends *versus* volume fraction of the silica filler. The

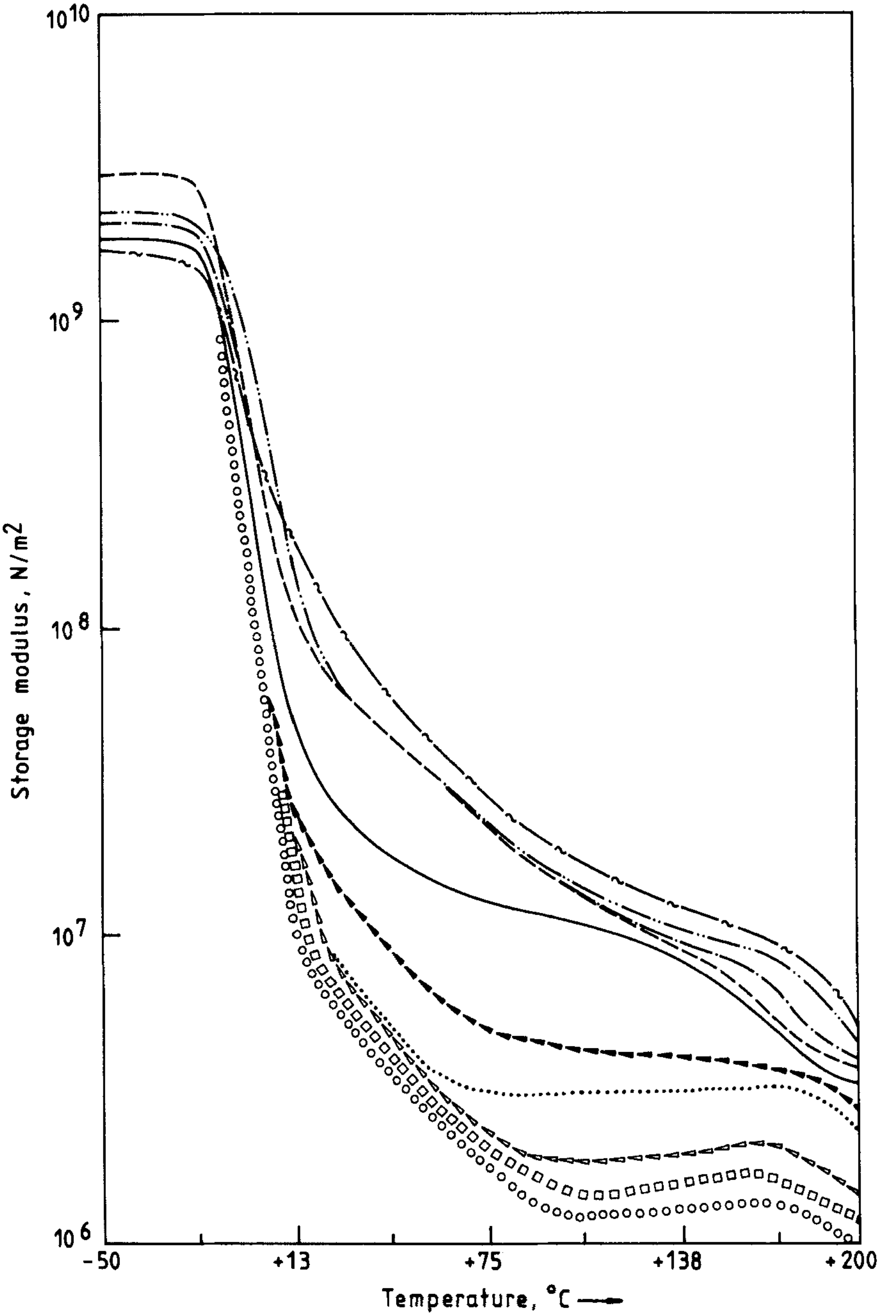

FIGURE 3 Storage modulus *versus* temperature plots of silica filled 50/50 PAA/ENR blends and their composites: (a) (○ ○ ○ ○) blend with 0 phr silica; (b) (□ □ □) blend with 2 phr silica; (c) (◁ ◁ ◁) blend with 5 phr silica; (d) (· · · ·) blend with 7 phr silica; (e) (◀ ◀ ◀) blend with 10 phr silica; (f) (————) composite with 0 phr silica; (g) (— — — —) composite with 2 phr silica; (h) (— · — · —) composite with 5 phr silica; (i) (—— · · ——) composite with 7 phr silica; (j) (— ~ — — ~ —) composite with 10 phr silica.

TABLE III
Storage modulus (E′) values at 100°C of blends and the corresponding sandwich composites

Blend designation	Filler loading, phr	E′, N/m^2 of blend × 10^{-6}	E′, N/m^2 of composite × 10^{-7}
A	0	2.84	1.02
B	2	3.52	1.58
C	5	4.53	2.35
D	7	5.09	2.76
E	10	5.70	2.93

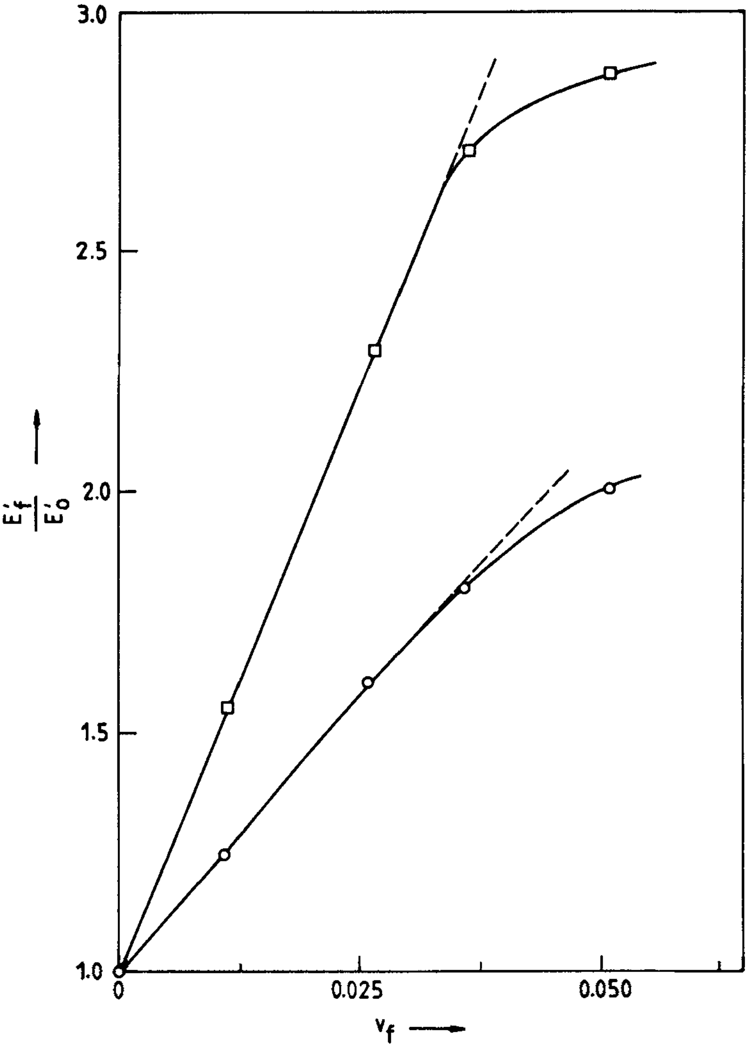

FIGURE 4 Plots of storage moduli *versus* volume fraction of filler of silica-filled 50/50 PAA/ENR blend and its composite: (a) (—○—○—) blend; (b) (—□—) composite.

nature of the plots for both the blend and the sandwich composite is similar. The plots follow the empirical equation:

$$\frac{E_f'}{E_o'} = 1 + K\,v_f^n \tag{3}$$

where E_f' is the storage modulus of the filled system (blend or composite) at 100°C, E_o' is the storage modulus of the unfilled system (blend or composite) at 100°C, v_f is the volume fraction of filler, and K and n are constants. It is evident that for the blend, up to 7 phr filler loading, the plot is linear with a slope of 23 and $n = 1$. For the sandwich composite, the plot is also linear up to 7 phr filler loading, the slope of the plot is 50 and $n = 1$. The higher slope in the case of the composite indicates that, at a fixed silica filler concentration, attachment of Al foil to the surface of the blend causes an increase in the storage modulus. Figure 3 also shows that the curve is a straight line up to 7 phr filler loading. That means that the effect of the filler changes uniformly upon addition of filler up to 7 phr, but then the curve deviates downward (*i.e.*, $n<1$) upon further addition of filler, implying that the effect of silica filler on the PAA/ENR blend tends to reach a saturation point. Thus, the constant n signifies the change in effect of the silica filler on the PAA/ENR blend with the increase in filler content.

Figures 5(a) and (b) show the loss tangent *versus* temperature plots of the 50/50 PAA/ENR blend and their dependence on Al-attachment to the blend surface as in the sandwich composites. The loss peak around 0°C is due to the α-transition of ENR.[16–17] The two broad peaks around 50°C and 160°C are believed to be due to β- and α-transitions of PAA,[18–19] respectively. It is evident from Figure 5(a) that as the filler loading increases the loss peak values decrease. Also at 10 phr filler loading a slight shift in the α-transition temperature of ENR was observed. This decrease in loss peak value and shift in the α-transition temperature of ENR can be ascribed to the polymer-filler interaction.[13–15]

In Figure 5(b), in the case of the sandwich composites, the loss peaks due to PAA increase at low loadings of silica filler (up to 5 phr), though the loss peak due to ENR showed an expected decrease. At higher filler loading (7–10 phr), however, all the loss peaks (both due to PAA and ENR) showed the expected decrease. It is known that ENR can act as an adhesive in Al-Al bonding.[4] Also, it has been shown earlier that high temperature can cause crosslinking of ENR with PAA.[1] In the present case, it is believed that, in the presence of Al, the bonding of Al with the ENR phase dominates over the participation of ENR in crosslinking with PAA. As a result of this, the ENR is not totally available for crosslinking with PAA. Furthermore, the adhesion between Al and the ENR phase increases on incorporation of silica filler (up to 5 phr) in the blend. This results in an increase in free PAA (that is not crosslinked) in the blend which causes an increase in the loss peak value due to the PAA phase. It is known that crosslinking causes lowering of the loss peak.[8,9]

At a filler loading of 7 phr or above, adhesion decreases sharply as discussed later (Table IV), thereby facilitating crosslinking between PAA and ENR. Accordingly, the loss peaks due to the PAA phase show the expected decrease at high filler loading. The loss peak due to ENR behaves differently. It decreases gradually with an increase in filler loading. At low filler loading, the decrease in the loss peak due

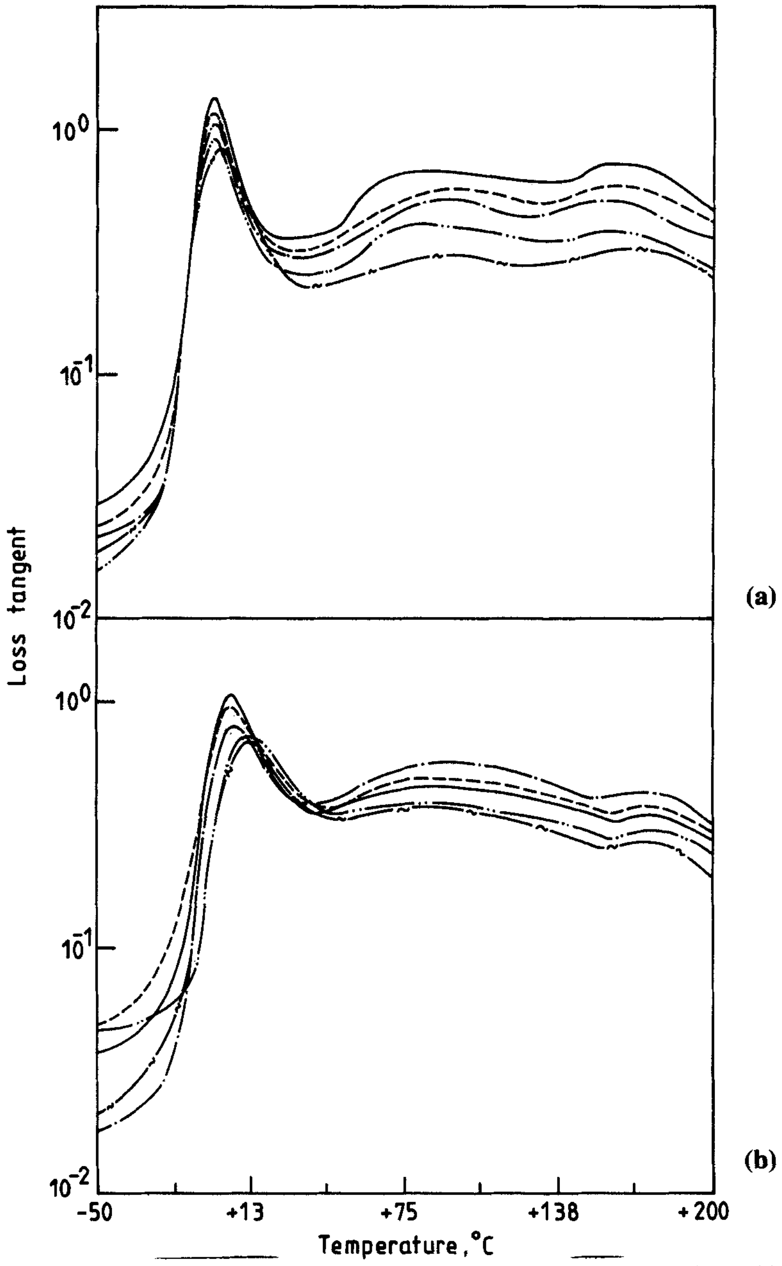

FIGURE 5 (a) Plots of loss tangent *versus* temperature of silica-filled 50/50 PAA/ENR blends: (i) (————) 0 phr silica; (ii) (— — — —) 2 phr silica; (iii) (—·—) 5 phr silica; (iv) (—··—) 7 phr silica; (v) (—~—) 10 phr silica: (b) Plots of loss tangent *versus* temperature of silica-filled Al/blend/Al composites; (i) (————) 0 phr silica; (ii) (— — —) 2 phr silica; (iii) (—·—) 5 phr silica; (iv) (—··—) 7 phr silica; (v) (—~—) 10 phr silica.

TABLE IV
Loss tangent peak values corresponding to the ENR phase and the peel strength of Al/adhesive/Al joints. Samples moulded at 190°C for 120 mins

Blend designation	Silica filler loading	$\tan\delta_{max}$ of blend	$\tan\delta_{max}$ of composite	$\Delta\tan\delta_{max}$[a]	peel strength[b] N/m	$\frac{W_f}{W_o}$[c]
A	0	1.32	1.06	0.26	4000	1.0
B	2	1.27	0.98	0.29	5280	1.32
C	5	1.14	0.78	0.36	7200	1.80
D	7	0.95	0.75	0.20	2240	0.56
E	10	0.86	0.72	0.14	1360	0.34

[a] $\Delta\tan\delta_{max} = (\tan\delta_{max})_{blend} - (\tan\delta_{max})_{composite}$.
[b] peel strength of Al/adhesive/Al joints.
[c] W_f, peel strength for filled adhesive (blend); W_o, peel strength for unfilled adhesive (blend).

to ENR is believed to be due to Al-ENR adhesion. It is known that adhesion of rubber with metal foil can cause a decrease in the loss tangent values.[2] At high filler loading, however, the decrease in loss peak due to ENR is ascribed to the crosslinking with PAA as well. Figure 6 shows the plot of the ratio of the loss peaks of the ENR phase *versus* volume fraction of the silica filler. At 7 phr silica filler or above, the ratio of loss peaks for both the blend and the composite is almost the same but, at low filler loading, this ratio for the composite is much smaller than that for the

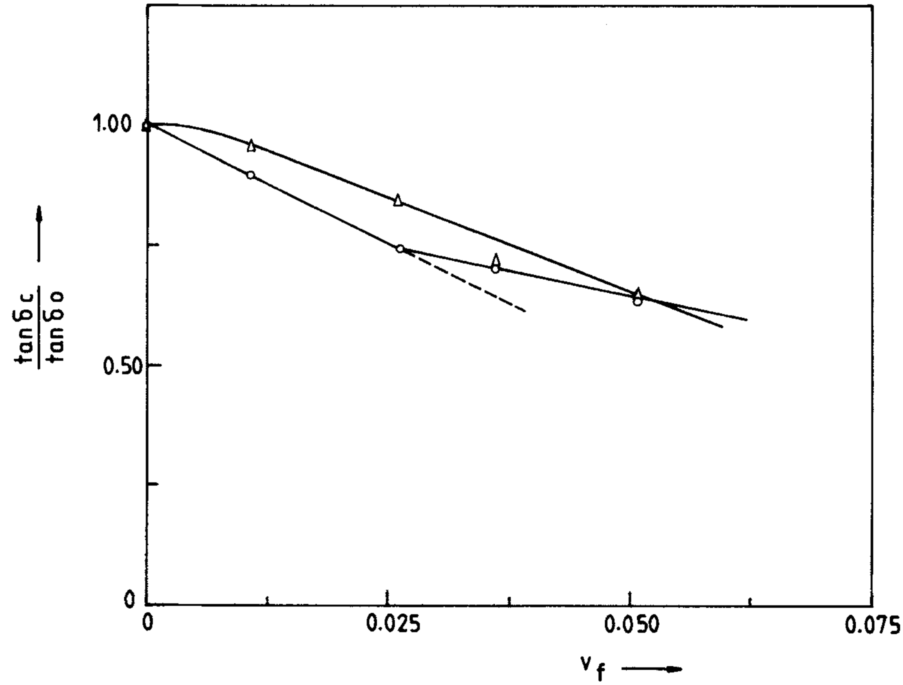

FIGURE 6 Plots of ratio of loss peak of ENR of unfilled blend to that of filled blend *versus* volume fraction of filler of the 50/50 PAA/ENR blend and its composite, (i) (—△—) blend; (ii) (—O—) composite. $\tan\delta_c$, loss peak due to ENR in the filled blend or composite; $\tan\delta_o$, loss peak due to ENR in the unfilled blend or composite.

blend. It may be concluded that adhesion between Al and ENR increases up to 5 phr filler loading and that at higher filler loading adhesion decreases sharply and, thus, its role in lowering loss peak is insignificant.

Table IV shows that the peel strength of Al-Al joints increases up to 5 phr silica filler loading. At a filler loading of 7 phr, and beyond, the peel strength decreases. It has been discussed earlier, in the case of dynamic mechanical studies, that the Al-rubber adhesion increases up to 5 phr silica filler loading, beyond which the adhesion decreases at the cost of crosslinking with PAA. Accordingly, it is believed that the results of dynamic mechanical studies could be correlated with the peel strength results. Since the ENR seems to be the dominant phase in adhesion with the Al and its loss peak is sharp, the ENR–loss peak was chosen to correlate with the peel strength results. Table IV shows the loss peaks of ENR in the blend and the sandwich composites. The difference in loss peak values at a particular silica filler loading (that is, $\Delta\tan\delta_{max}$ = the $\tan\delta_{max}$ of the blend less the $\tan\delta_{max}$ of the corresponding composite) are listed in Table IV. At a particular filler loading, the higher the $\tan_{max}$, the higher is the peel strength of the blend with Al foil. Table IV also shows the peel strength values of Al-Al joints with both the unfilled and the filled adhesive. The ratios of the peel strength values of the filled adhesive to those of the unfilled adhesive are also shown in the same table. Figure 7 shows the variation of the peel strength ratio, W_f/W_o, with the $\Delta(\tan_{max})$. A linear plot was obtained and the results fit an equation of the following type:

$$\Delta\tan\delta_{max}=0.12+0.125\ (W_f/W_o) \tag{4}$$

Accordingly, it can be inferred that the peel strength and the dynamic mechanical test results were correlated.

ESCA was performed in order to understand the mechanism of adhesion of Al with the blend. The ESCA scans are shown in Figure 8 and the results are summarised in Table V. The Al surface from which the gum adhesive system was leached registered the C1s peak at 288.5 eV and the O1s peak at 536.5 eV. For the epoxy group, the binding energies of the C1s and the O1s have been reported to be 286.8 eV and 533.6 eV, respectively.[20] It was reported that the binding energy of the C1s shifts 1.5 eV for each C—O bond.[21,22] Again, the binding energy of the C1s of the carbonyl group of PAA has been reported to be 289.5 eV.[23,24] For the leached Al-gum adhesive surface, the singlet C1s peak observed at 288.5 eV indicates that the carbonyl group of PAA is absent from the Al surface. Furthermore, the O1s peak of the carbonyl group of PAA has been reported to be 533.4 eV,[23,24] but in the ESCA scan no peak at 533.4 eV was observed. The singlet O1s peak at 536.5 eV indicates that the carbonyl group is absent from the Al surface. Accordingly, it is believed that the adhesion between the Al and the blend occurs *via* the ENR and a probable mechanism is shown in Figure 9.

It is known that the presence of a highly electropositive element or an electronegative atom/group shifts the binding energy of the neighbouring atom to a higher level.[25] In the above mechanism, Al is directly attached to the oxygen. Since Al is strongly electropositive with respect to oxygen, its bonding with Al increases the binding energy of the O1s from 533.6 eV to 536.5 eV.

Figure 8 also shows the scan of leached Al surface from which the silica-filled adhesive system had been leached. The C1s peak was observed at 288.5 eV and the

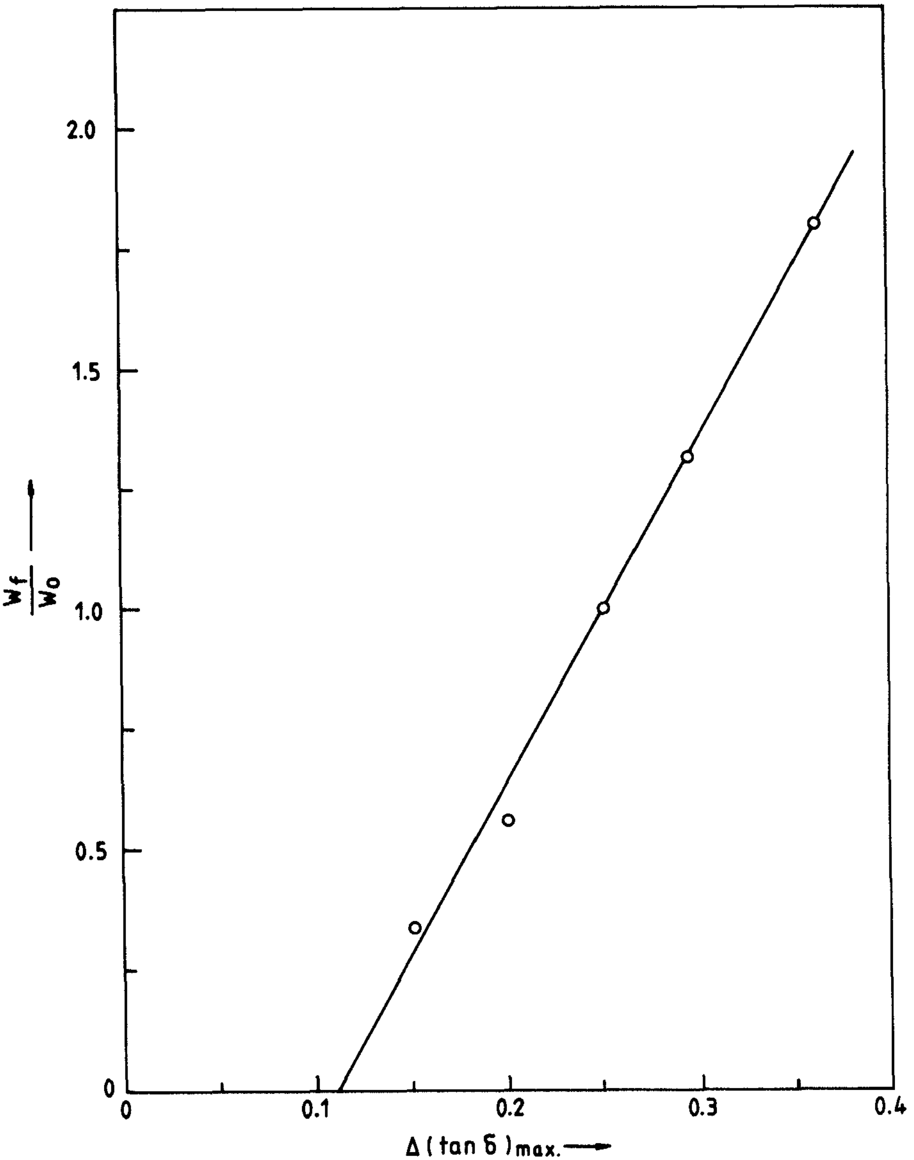

FIGURE 7 Ratio of peel strength (W_f/W_o) *versus* difference in loss tangent peak of ENR phase. W_f = peel strength of the filled composite and W_o = peel strength of the unfilled composite.

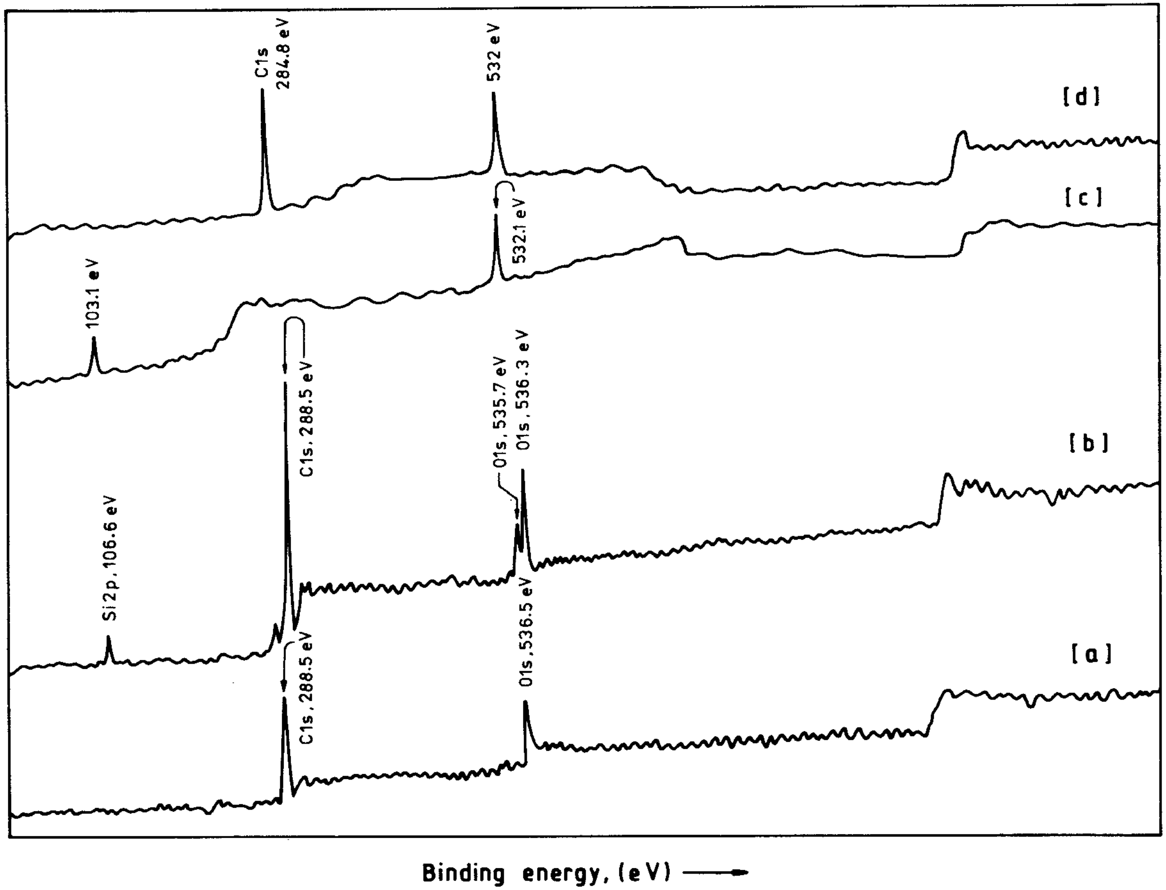

FIGURE 8 (a) ESCA scan of composite with 0 phr silica filler; (b) ESCA scan of composite with 5 phr silica filler; (c) ESCA scan of composite with 7 phr silica filler; (d) ESCA scan of Al foil only.

TABLE V
ESCA results for the adhesive-coated aluminium foil

Photo-peak	Binding energy (eV)
(i) Aluminium surface, leached from gum adhesive:	
Al2p	No peak
C1s	288.5
O1s	536.5
(ii) Aluminium surface, leached from silica-filled (5 phr) adhesive:	
Al2p	No peak
C1s	288.5
O1s	535.7, 536.3
Si2p	106.6
(iii) Aluminium surface, leached from silica-filled (7 phr) adhesive:	
O1s	532.1
Si2p	103.1
(iv) Aluminium foil:	
Al2p	No peak
C1s	284.8
O1s	532.0

O1s peak was found at 536.3 eV and 535.7 eV. Another peak was found at 106.6 eV, which is ascribed to the Si2p. It has been reported that the binding energy of the Si2p in SiO_2/SiO_3^{2-} is 103.6 eV.[26–27] This large shift of the binding energy indicates the presence of a strong electron-deficient environment surrounding the Si atom. The doublet of the oxygen peak indicates that the oxygen is present in two different types of bonds. Again, no peak due to the O1s of the carbonyl oxygen was found, indicating no participation of PAA in adhesion with the Al. In case of 7 phr silica-filled adhesive, two peaks were found, (a) at 532.1 eV, due to the O1s and (b) at 103.1 eV, due to the Si2p of SiO_3^{2-}. This indicates that at 7 phr silica filler loading, Al silicate was formed. In the case of the silica-filled adhesive, a probable mechanism of adhesion with Al is shown in Figure 10. Two different types of bonding, Si—O—Al and C—O—Al, causes a doublet in the O1s peak. As silicon is less electronegative than carbon, the 536.3 eV peak is believed to be due to the O1s of C—O—Al.

In the Si—O—Al system, the binding energy of the Si2p is shifted to a higher level due to the presence of oxygen and Al. In the C—O—Al system also, the binding energy of the C1s is shifted to a higher level for the same reason. The ESCA spectrum of Al foil shows two peaks, (a) at 532 eV due to the O1s of Al_2O_3 and (b) at 284.8 eV, due to the C1s. This indicates that Al remains in a tripositive state on its surface. Accordingly, attachment of oxygen to the aluminium surface results in a shift in the binding energy of the O1s. According to the proposed mechanism, both the silicon and the carbon are attached to the aluminium surface through the oxygen atom and, hence, the binding energies of the Si2p and the C1s are shifted to higher values. Al_2O_3 also forms Al silicate in the presence of SiO_2. In conclusion, at low silica filler loading the adhesion dominates over the Al silicate formation and the crosslinking of PAA with ENR becomes restricted. At high silica filler loading, the Al silicate formation restricts the adhesion, and the crosslinking between PAA and ENR occurs freely. Thus, ESCA results are in conformity with the findings of dynamic mechanical analyses.

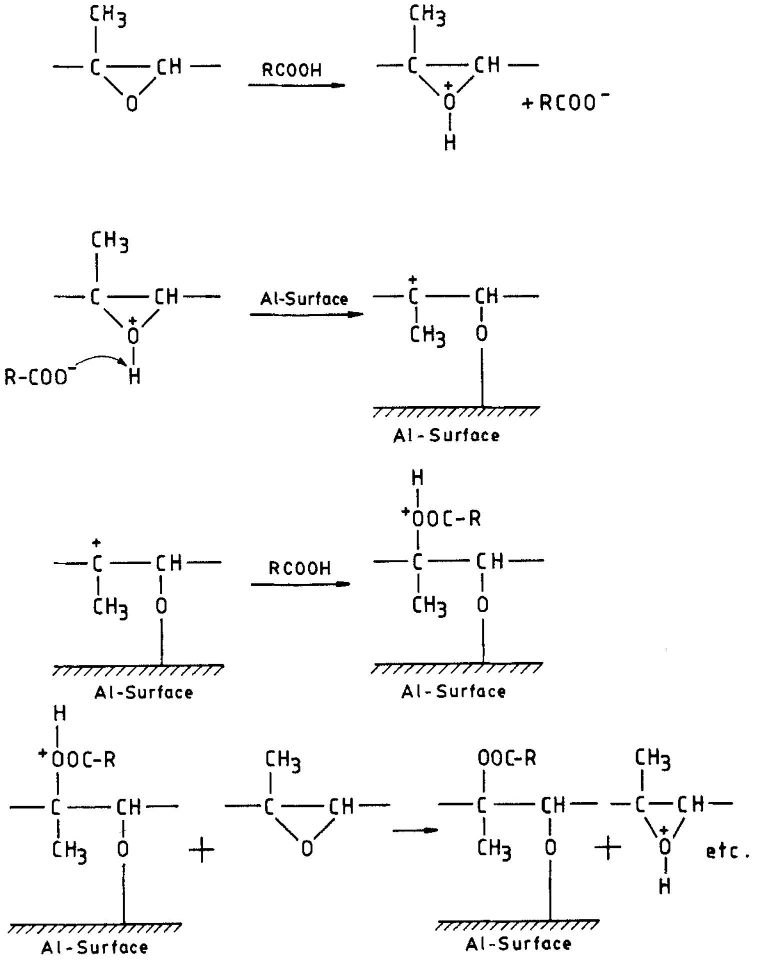

FIGURE 9 Probable mechanism of adhesion between unfilled blend and aluminium surface.

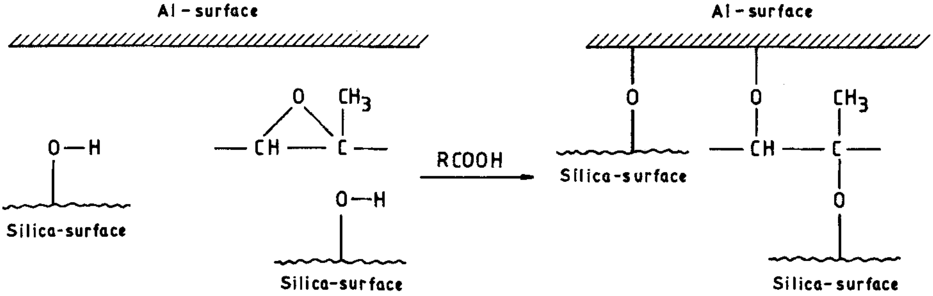

FIGURE 10 Probable mechanism of adhesion between silica-filled blend and aluminium surface.

CONCLUSIONS

Thermally-induced crosslinking occurs in the blend of polyacrylic acid and epoxidised natural rubber during high temperature moulding and such a blend can act as an adhesive for Al-Al bonding. Studies of the peel strength of Al-Al joints show that the incorporation of silica filler (up to 5 phr) increases the peel strength of the blend with Al. However, at high silica filler loading, the peel strength decreases. Dynamic mechanical analysis results indicate that at low silica filler concentration in the blend, the adhesion of the rubber blend with Al foil occurs presumably through the ENR phase at the cost of its crosslinking with PAA. However, at high filler loading the peel strength with Al decreases. There exists a correlation between the peel strength and the dynamic mechanical test results. The results of dynamic mechanical studies are corroborated by the ESCA results on the solvent-leached Al surface.

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