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TOF SIMS and XPS study of the interaction of silanized E-glass with epoxy resin

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The interaction of a silanized E-glass plate surface with the diglycidyl ether of bisphenol S (DGEBS) has been studied using time-of-flight secondary ion mass spectrometry (TOF SIMS) and X-ray photoelectron spectroscopy (XPS). In the TOF SIMS spectra, in addition to a series of ion fragments readily assigned to the parent DGEBS epoxy resin, some new ion fragments attributable to the reaction product of DGEBS with the polymeric hydrolysed γ-aminopropyl triethoxysilane (HAPS) precoating have been observed. In the XPS spectra a mixed coating of HAPS and DGEBS was demonstrated by the presence of intense N1s and S2p peaks. With the previous demonstration that the HAPS deposit is strongly bound to the E-glass plate surface, direct confirmation of the formation of chemical bonds at the E-glass–silane–resin interfaces has been obtained. These conclusions were complicated by the presence of polydimethylsiloxane (PDMS) and the incorporation of aluminium and calcium ions from the HAPS silanized glass plate into the mixed coating of HAPS and DGEBS epoxy resin.

1. Introduction

Efficient load transfer between fibre and matrix in a composite material is essential to the optimization of mechanical performance. In the case of glass fibres in polymeric resins, silane adhesion promoters called coupling agents are used to improve the fibre–matrix bond. Because the improvements observed could not be readily attributed to a chemical bonding mechanism, several studies were initiated to explore these interactions [1–12]. Much of this work has examined the interaction of epoxy resins and/or silane coupling agents with glass surfaces. Fourier transform infra-red spectroscopy (FTIR) [1–8] and nuclear magnetic resonance NMR [9–12] are the principal techniques which have been used to study the interaction of hydrolysed γ-aminopropyl triethoxysilane (HAPS) with glass surfaces and with the diglycidyl ether of Bisphenol A (DGEBA). These studies have provided the basic knowledge of the interfacial chemistry operating in glass fibre-reinforced plastics, but attempts to identify surface chemical reactions have been largely unsuccessful because of limitations in surface sensitivity. The work of Jenneskens *et al.* [13] has come closest to this aim.

With the recognition that full understanding can provide engineering benefits, we have used the extremely surface-sensitive technique of time-of-flight secondary ion mass spectrometry (TOF SIMS) in combination with X-ray photoelectron spectroscopy (XPS) to study the interaction of fresh HAPS with the glass surfaces [14–16]. In this paper, therefore, we have extended our study to the interaction of the HAPS silanized E-glass plate surface with the diglycidyl ether of bisphenol S (DGEBS). DGEBS was chosen for this study since the sulphur can be readily detected by XPS. Attempts to apply this technique to commercially coated fibres have proved more difficult because of the presence of contaminants [17].

2. Experimental procedure

The preparation of the glass plate and its silanization have been described in our previous studies [14, 15]. The coatings were deposited from HAPS aqueous solution at the natural pH of 10.6 at a concentration of 1.5%. In this paper, the abbreviation HAPS refers to the hydrolysed oligo-polymeric aminosilane deposit. For simulation of an interface between the HAPS silane and epoxy resin in an E-glass fibre composite, the HAPS as-coated glass plates were immersed in refluxing dried distilled toluene (at the boiling point ~ 119 °C) containing 1% DGEBS for 1 h. The excess reagent was removed by thorough rinsing with three fresh batches of toluene at room temperature. Care was taken to ensure that additional contaminants did not arise from the coating procedures. The samples were dried in an air-circulating oven at 130 °C for 1 h. The heat-cleaned glass plates were treated with DGEBS similarly.

The TOF SIMS analysis was conducted on a VG IX23S instrument at a vacuum of $< 10^{-10}$ torr with a microfocused liquid Ga ion beam at 30 kV and 1.4 nA using a charge-compensating electron flood gun. The iris was half-closed. The mass calibration procedure for the TOF SIMS spectra has been described elsewhere [15].

For XPS analysis, the samples were examined with a VG Microtech CLAM 100 XPS spectrometer

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operating at a vacuum of $< 10^{-8}$ torr. An AlK_α X-ray source (1486.6 eV) was used at a power of 10 kV × 10 mA. Narrow scans for individual elements were obtained at 15, 30 and 45° relative to the plate surface in order to estimate the sampling depth.

3. Results and discussion

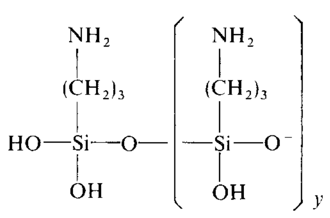
3.1. Interaction of E-glass plate surface with HAPS silane

TOF SIMS and XPS studies [14, 15, 18] have well identified that the major surface components on the heat-cleaned glass surface are aluminium, calcium, silicon and their oxides as well as some hydrocarbon contaminants.

For the interaction between the E-glass plate surface and fresh HAPS silane solution the XPS results indicated that a uniform HAPS silane coating with a thickness of about 6 nm on the glass surface was formed [18]. Moreover, TOF SIMS analyses demonstrated that a gradation in the degree of polymerization of HAPS from a physisorbed oligomeric component to a three-dimensional network existed, but they were complicated by the presence of polydimethysiloxane (PDMS) [14, 15, 19]. Another indication from this study is that hot water extraction led to an interfacial HAPS monolayer of high crosslink density left on the immediate glass surface. The structural assignments for these differing components, based on the chemical shift from the N1s peaks observed by XPS and the size of the ion mass obtained by TOF SIMS, have also been discussed in these studies with a view to understanding the nature of the interface between the HAPS molecules and the glass surface. TOF SIMS fragmentation patterns are presented in Table I.

Since we have employed a hot toluene solution of the epoxy resin to simulate reaction of the silanized glass surface, we have also examined the silanized glass surface after extraction with hot toluene. The

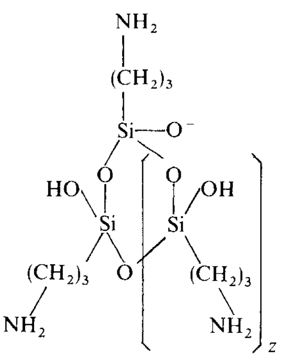
TABLE I Negative and positive ions from HAPS-coated E-glass plate



$$\mathrm{HO{-}\overset{\overset{\displaystyle NH_2}{|}\atop \displaystyle (CH_2)_3}{Si}(OH){-}O{-}\left[\overset{\overset{\displaystyle NH_2}{|}\atop \displaystyle (CH_2)_3}{Si}(OH){-}O^-\right]_y}$$

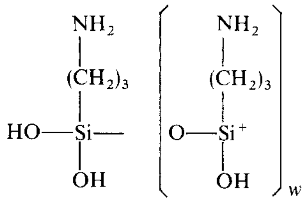
Fragments from HAPS in linear form

a.m.u.	136	255	374
y	0	1	2



Fragments from HAPS in cyclic form

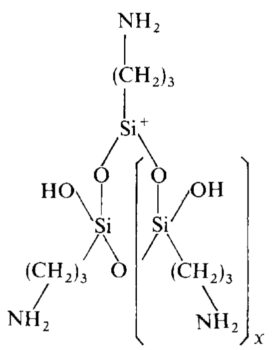
a.m.u.	237	356	475
z	0	1	2



$$\mathrm{HO{-}\overset{\overset{\displaystyle NH_2}{|}\atop \displaystyle (CH_2)_3}{Si}(OH){-}\left[O{-}\overset{\overset{\displaystyle NH_2}{|}\atop \displaystyle (CH_2)_3}{Si^+}(OH)\right]_w}$$

Fragments from HAPS in linear form

a.m.u.	120	239	358	477
w	0	1	2	3



Fragments from HAPS in cyclic form

a.m.u.	221	340	459
x	0	1	2

XPS results obtained from the silanized glass surface after extraction with hot toluene are tabulated in Table II. They are similar to those from the silanized glass surface after extraction with hot water. The largest secondary ions from these samples are presented in Table III. Following the arguments presented elsewhere [14, 15, 20], since the largest secondary ion sputtered from this interfacial layer is at 340 a.m.u., the implication is that an interfacial HAPS monolayer with an apparently higher crosslink density is left on the glass surface after extraction with hot toluene.

Toluene is a good solvent for the HAPS oligomers. However, since it is generally considered that hot water extraction also involves the hydrolytic removal of network ends and the less well cross-linked network chains [14, 15] it follows that toluene, largely in the absence of water, has the same effect. It is known that siloxanes depolymerize by a "back-biting" mechanism and that at these concentrations a net tendency to reequilibrate to a high oligomer concentration exists [21]. Applied to a chemisorbed layer, the net result is the removal of network ends and an apparent reduction in the largest secondary ion.

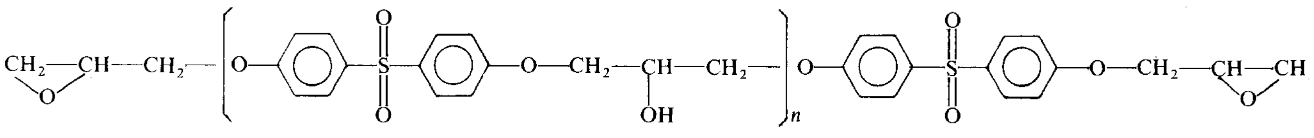
3.2. Interaction of E-glass plate surface with DGEBS epoxy resin

3.2.1. XPS analysis

The presence of a significant concentration of sulphur on the DGEBS-coated surface as shown in Table IV confirms its deposition on to the heat-cleaned glass surface. The surface oxygen concentration also increased proportionally in line with the molecular structure of DGEBS. The surface concentrations of silicon, aluminium and calcium also decreased, demonstrating the presence of a relative thick resin overlayer. These results are completely consistent with the TOF SIMS peak intensities given in Table V. Taken together, the XPS and TOF SIMS results indicate that in contrast to the aqueous HAPS solution, the aluminium and calcium species have not migrated from the glass substrate into the DGEBS coating in this case.

3.2.2. TOF SIMS analysis

From Fig. 1 it can be seen that treatment of the heat-cleaned E-glass surface with DGEBS in organic solution gave rise to a series of negative ion fragments from 64 to 397 a.m.u. The nominal formula (I) for DGEBS is



(I)

where $n = 0$.

TABLE II Variation in relative atomic surface composition (%) for extracted HAPS-coated E-glass plates obtained by angle-resolved XPS

Element	Without extraction			With hot water			With hot toluene		
	15°	30°	45°	15°	30°	45°	15°	30°	45°
Si	22.2	22.1	22.3	17.5	18.2	19.1	17.3	18.8	20.0
Al	6.5	6.0	5.5	10.1	8.1	7.5	9.7	8.3	6.5
Ca	3.8	3.0	2.8	3.5	3.9	4.5	3.4	4.8	5.5
O	41.5	44.4	45.2	47.1	50.0	51.2	47.5	50.2	51.5
C	17.1	16.4	16.5	17.3	16.7	15.7	17.5	14.6	14.0
N	8.9	8.1	7.7	4.5	3.1	2.0	4.6	3.3	2.5

TABLE III Effect of extraction on the largest HAPS secondary ion fragments sputtered from HAPS-coated E-glass plates

Surface	Positive ions (a.m.u.)		Negative ions (a.m.u.)	
	Linear	Cyclic	Linear	Cyclic
HAPS-coated	477 ($w = 3$)	459 ($x = 2$)	374 ($y = 2$)	475 ($z = 2$)
Extracted with warm water	596 ($w = 4$)	578 ($x = 3$)	493 ($y = 3$)	356 ($z = 1$)
Extracted with hot water	477 ($w = 3$)	459 ($x = 2$)	374 ($y = 2$)	356 ($z = 1$)
Extracted with hot toluene	239 ($w = 1$)	340 ($x = 1$)	255 ($y = 1$)	237 ($z = 0$)

The type of synthesis employed could lead to the presence of molecules of $n = 1$ and more. However, as shown in Table VI, most of these negative ion fragments could be assigned to the parent DGEBS molecule [22] and ions with more than one repeat unit were not observed.

The positive ion fragments (Fig. 2) were also readily attributable to DGEBS as shown in Table VII, but the spectrum was complicated by the presence of Na^+ and related ions and a series of ion fragments of $C_nH^+_{2n-3}$, $C_nH^+_{2n-1}$ and $C_nH^+_{2n+1}$ up to mass 788 a.m.u. of a fatty acid impurity $C_{53}H_{107}COOH$. For the following discussion, it is important to stress the absence of PDMS fragments in these spectra.

3.3. Interaction of HAPS-silanized E-glass plate surface with DGEBS epoxy resin

In order to simulate the reactions which occur during the cure of an epoxy resin at an elevated temperature, the HAPS as-coated glass plates were immersed in 1% DGEBS solution in hot toluene for 1 h.

3.3.1. *XPS analysis*

The results obtained by the XPS technique from the silanized glass plate surface after treatment with DGEBS are tabulated in Table IV. The striking result of this experiment is the decreasing trend in sulphur concentration and increasing trend in nitrogen concentration with increasing analysis angle. Thus only the extreme surface is dominated by a thin DGEBS overlayer. The increase in nitrogen concentration with analysis depth indicates that the HAPS is directly below the surface resin. In this case the sulphur concentration is lower than for the control without HAPS, indicating that the DGEBS is thinner in this case. The calcium concentration changes with analysis angle in a manner indicative of a significant substrate contribution to the overall results presented in Table IV. It is also noted that extraction with toluene (Table II) also leads to dissolution of some of the HAPS deposit. As a consequence, it appears that the coating is either patchy and/or of a thickness for which the substrate contributes significantly to the analysis. We would not expect the calcium concentration to increase with analysis angle if a patchy film existed but to remain constant; therefore we conclude that a very thin layer of DGEBS is over the monomolecular layer of HAPS on the glass surface. On the other hand the aluminium concentration is unaffected by varying the analysis depth but is at a lower concentration than the control (Table II). Since the aluminium concentration remains constant then Al ions are uniform throughout the sampling depth. Therefore, the DGEBS overlayer appears to be inconsistent with the aluminized component of the siloxane deposit present on the glass surface, and therefore must be bonded through the siloxane. A similar conclusion can be drawn from the intensity of the 27 + peak in Table V.

TABLE IV Relative atomic surface composition (%) from differing E-glass plate surfaces by angle-resolved XPS

Element	Uncoated with DGEBS			HAPS as-coated with DGEBS		
	15°	30°	45°	15°	30°	45°
Si	3.1	5.0	7.0	8.3	11.2	14.1
Al	0.6	1.6	2.5	7.0	6.9	6.7
Ca	0.4	0.7	1.4	1.4	2.6	2.8
O	56.2	57.0	58.4	51.4	51.1	51.5
C	29.4	27.4	24.2	22.1	19.6	17.1
N	0.0	0.0	0.0	1.5	2.6	3.7
S	10.3	8.3	6.5	8.3	6.0	4.1

3.3.2. *TOF SIMS analysis*

Fig. 3 shows that deposition of DGEBS on to the silanized glass plate surface occurred. A series of negative ion fragments from 64 to 381 a.m.u., originated from the DGEBS deposit (see Table VI), was observed. The negative ion fragments which could be attributed to the HAPS fragmentation patterns for both the linear (y) and cyclic (z) forms (Table I) were not observed. This could imply that the HAPS deposit could have been desorbed by the hot toluene solvent; however, the XPS studies (Table IV) confirmed the presence of both components, with significant N1s and S2p intensities. Therefore, the source of the HAPS secondary ion fragments had been removed either by extraction of oligomers, overcoating or reaction. The most likely reason for the absence of HAPS fragments is that a continuous resin overlayer had been formed.

In addition, four unique ion fragments (R) at 182, 214, 228 and 338 a.m.u. could be identified. We consider that these ions can only be introduced by the

TABLE V Relative intensities of various secondary positive ions, as a fraction of the total ion count from 0–150 a.m.u. for variously treated E-glass surfaces

Treatment	Fragment a.m.u.					
	27 (Al^+)	28 (Si^+)	40 (Ca^+)	59 (DGEBS)	73 (PDMS)	120 (HAPS)
Uncoated	0.26	0.23	0.28	0.00	0.00	0.00
HAPS-coated	0.12	0.19	0.06	0.00	0.04	0.02
DGEBS	0.06	0.02	0.05	0.05	0.00	0.00
HAPS + DGEBS	0.11	0.15	0.05	0.02	0.01	0.00

The 59, 73 and 120 mass fragments are the most intense of the peaks attributable to DGEBS, PDMS and HAPS, respectively.

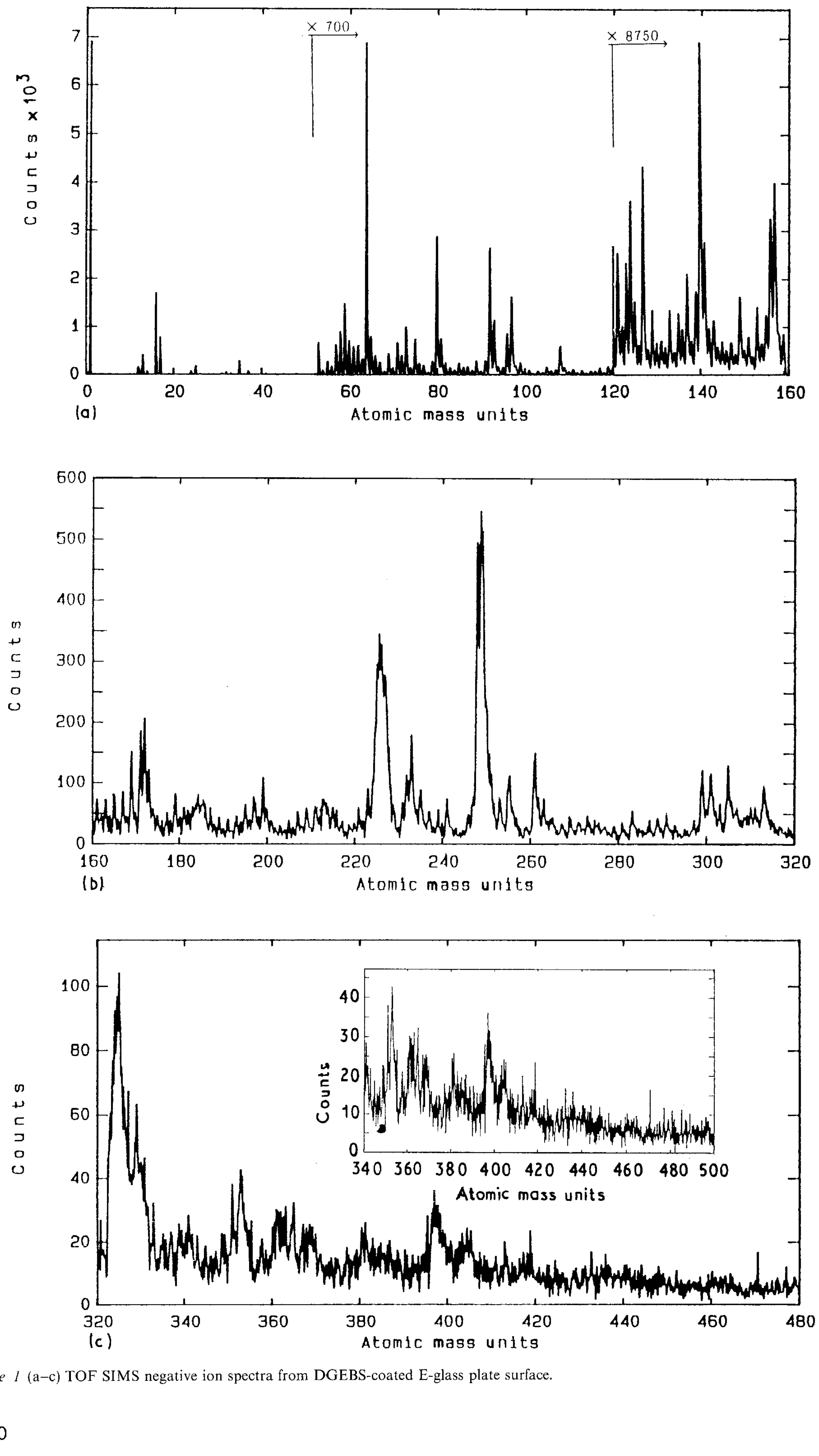
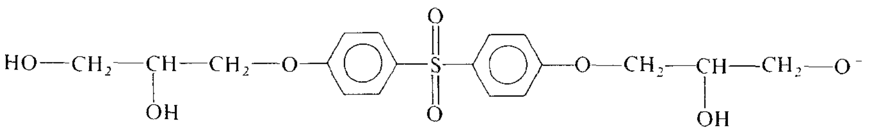
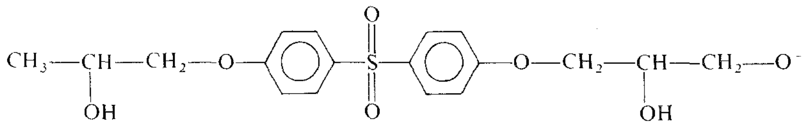
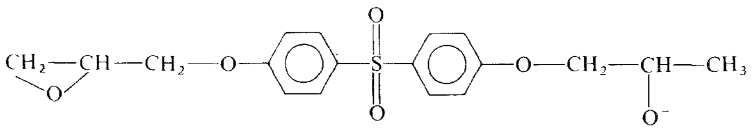
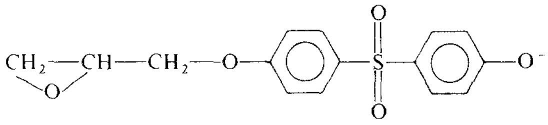
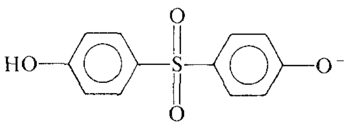
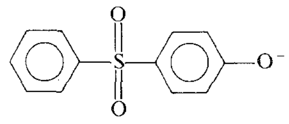
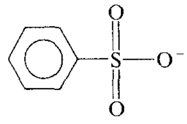
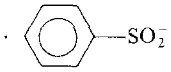
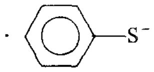
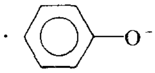
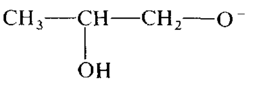
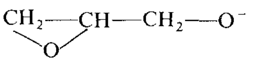
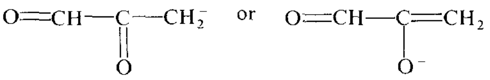


Figure 1 (a–c) TOF SIMS negative ion spectra from DGEBS-coated E-glass plate surface.

TABLE VI Negative ions from DGEBS-coated E-glass plate

a.m.u.	Fragment
397	
381	
363	
305	
249	
233	
157	
140	
108	
92	
97	HSO_4^-
96	SO_4^-
80	SO_3^-
64	SO_2^-
75	 $CH_3{-}CH(OH){-}CH_2{-}O^-$
73	
71	 $O{=}CH{-}C({=}O){-}CH_2^-$ or $O{=}CH{-}C(O^-){=}CH_2$

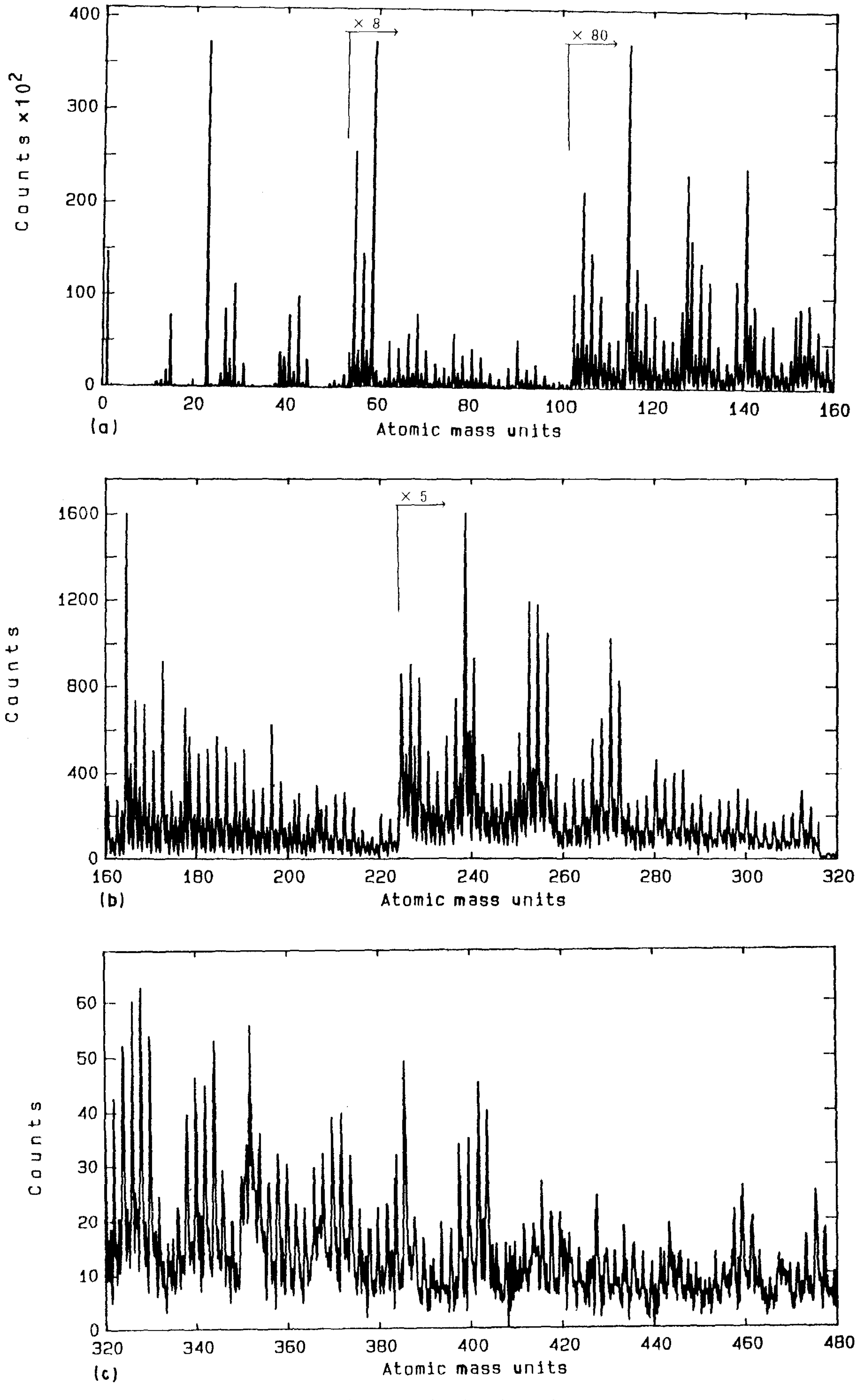


Figure 2 (a–e) TOF SIMS positive ion spectra from DGEBS-coated E-glass plate surface.

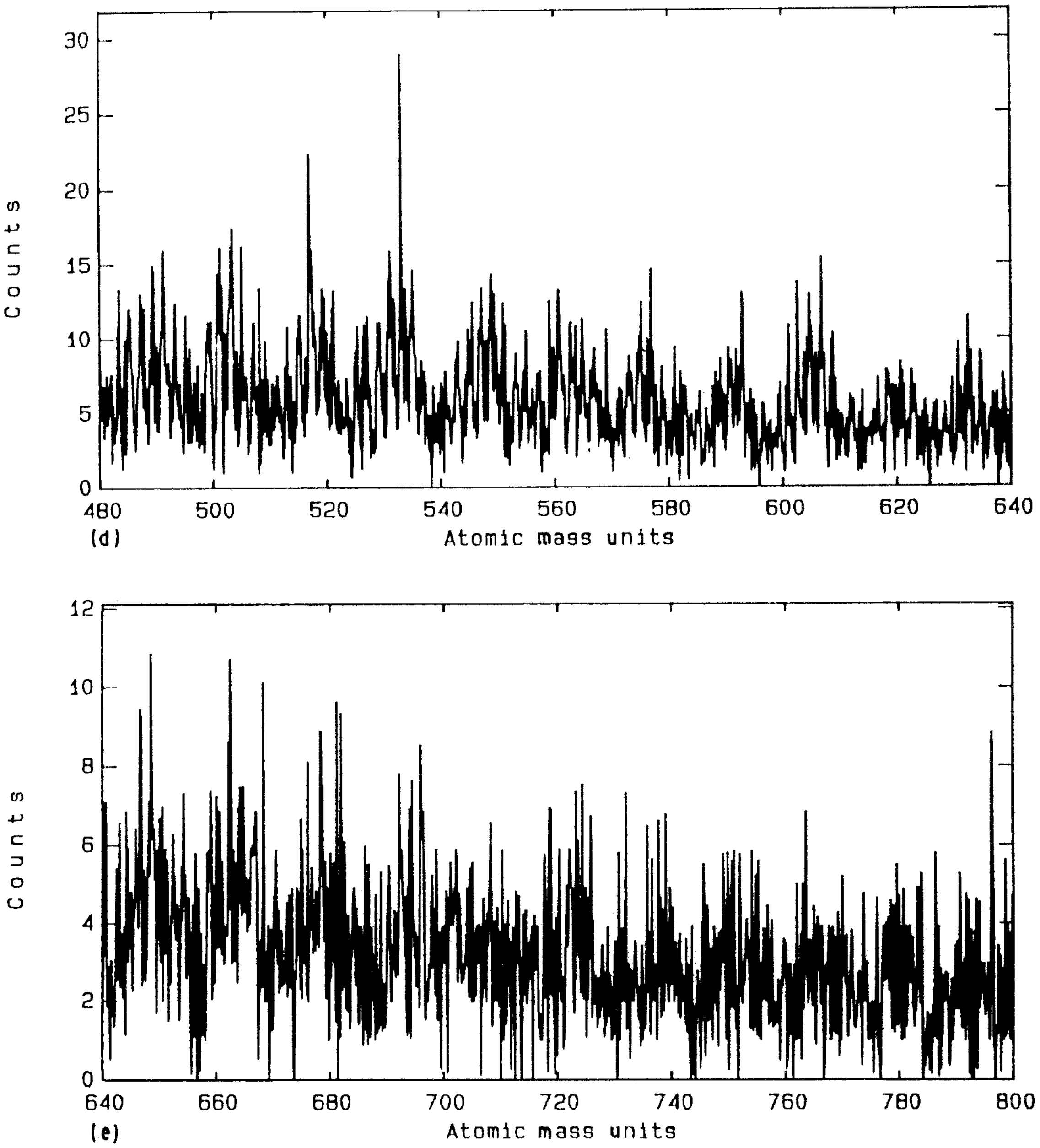


Figure 2 Continued.

TABLE VII Positive ions from DGEBS-coated E-glass plate

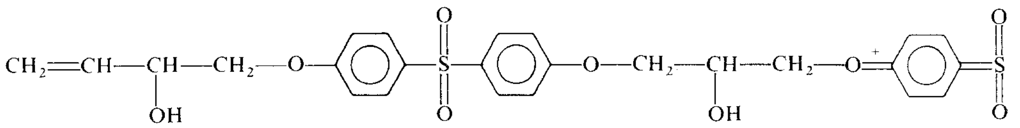
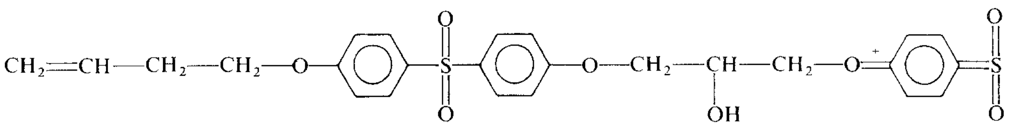
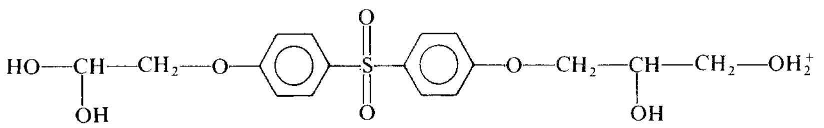
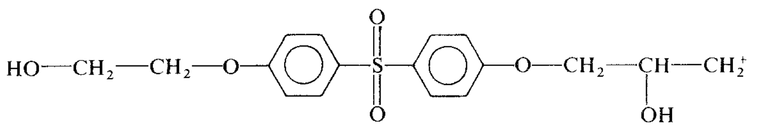
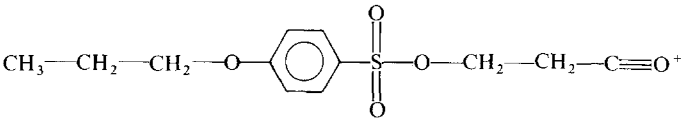
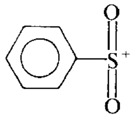
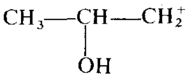
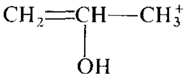
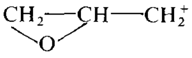
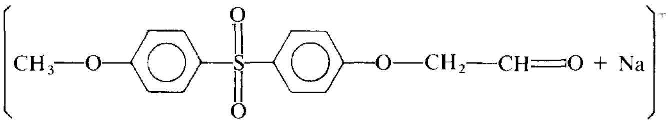
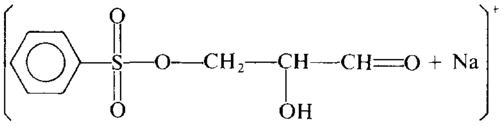
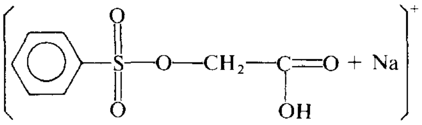
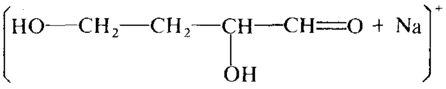
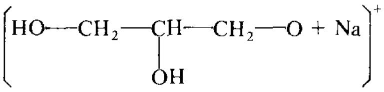
a.m.u.	Fragment
533	
517	
385	
351	

TABLE VII (continued)

271	
141	
59	 $\mathrm{CH_3{-}\underset{OH}{CH}{-}CH_2^+}$ or $\mathrm{CH_3{-}CH_2{-}CH{=}OH^+}$
58	 $\mathrm{CH_2{=}\underset{OH}{CH}{-}CH_3^+}$
57	
329	
253	
239	
127	 $[\mathrm{HO{-}CH_2{-}CH_2{-}\underset{OH}{CH}{-}CH{=}O + Na}]^+$
114	 $[\mathrm{HO{-}CH_2{-}\underset{OH}{CH}{-}CH_2{-}O + Na}]^+$
165	$[Na_3SO_4]^+$
23	Na^+

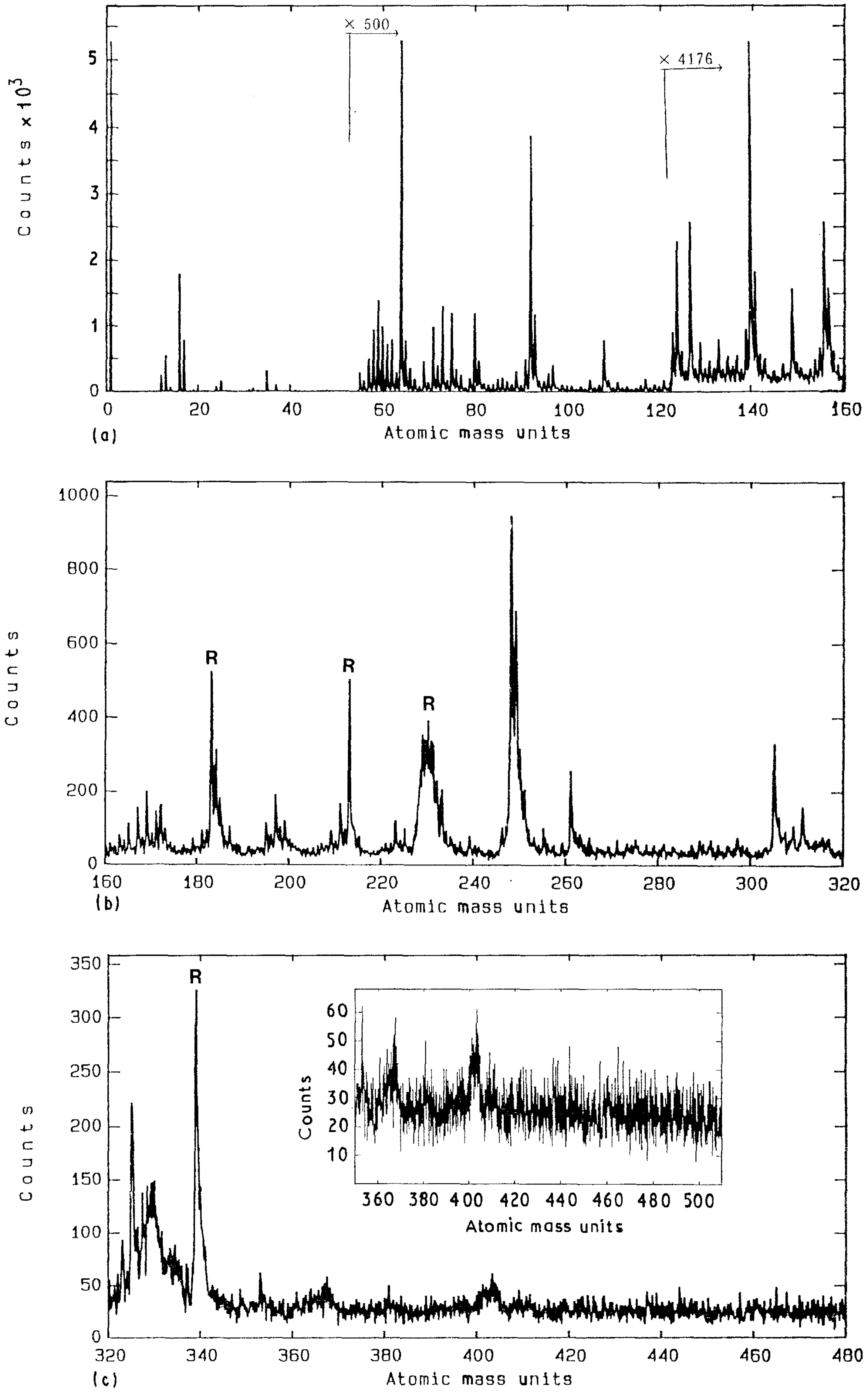
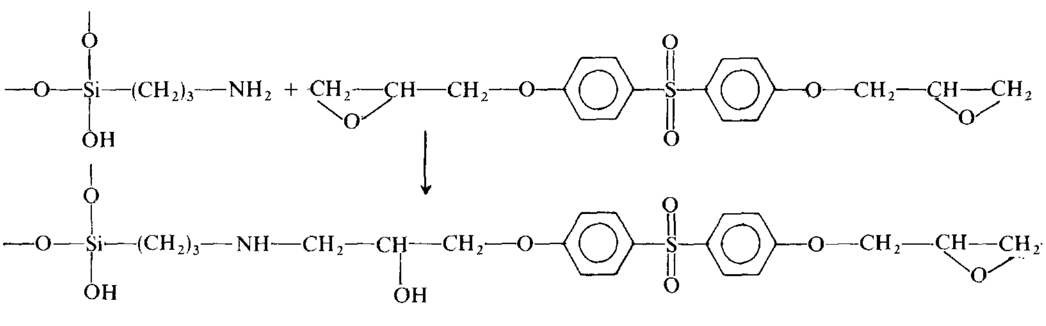
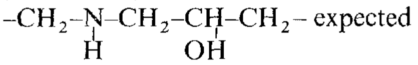


Figure 3 (a–c) TOF SIMS negative ion spectra from HAPS-silanized E-glass plate surface after re-dosing with DGEBS.

formation of a chemical reaction product (II) between HAPS with DGEBS,



(II)

Thus, the proposed structures for these fragments (Table VIII) all involve the molecular structure  $-CH_2-\underset{H}{N}-CH_2-\underset{OH}{CH}-CH_2-$ expected from the formation of a chemical covalent bond between the amino group in the HAPS deposit and the epoxy group of DGEBS.

In the positive-ion spectra (Fig. 4) some ion fragments associated with DGEBS at 57, 58, 59, 141 and 271 a.m.u. were also observed, but high-mass peaks at 351 and 385 a.m.u. disappeared. Another observation is that all the fragments associated with the sodium cationized DGEBS ion other than sodium itself were absent. The fatty acid impurity was also removed by the treatment. However, the features typical of PDMS were present at 73, 147, 221 a.m.u. for the linear (n) and 133, 207, 281 a.m.u. for cyclic (m) ions [19]. These must have arisen from the original HAPS coating, indicating the mobility and high ion yield of the PDMS contaminant. Its lack of reaction with epoxides and/or presence as an HAPS network chain end is also implied by this result.

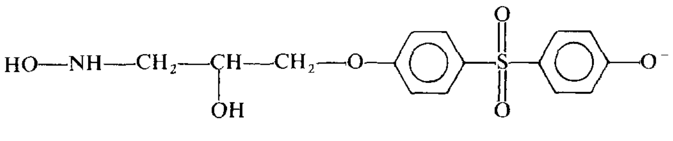
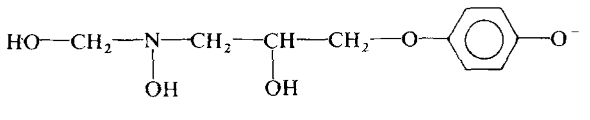
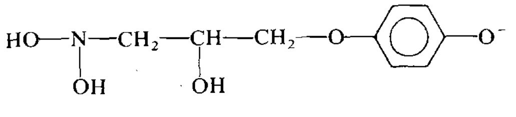
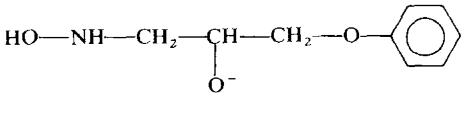
Moreover, the treatment also introduced two unique positive ion peaks (R) at 356 and 376 a.m.u. which could be attributed to the chemical reaction product (II) of HAPS with DGEBS. Possible structures are given in Table IX.

3.4. Interface between HAPS silane and DGEBS epoxy resin

It is known from Table II that extraction with hot toluene leaves a strongly chemisorbed HAPS monolayer on the immediate glass plate surface. Thus, we can consider that when a HAPS as-coated glass plate was put into hot toluene containing 1% DGEBS, the oligomeric components would be removed to expose the amino group of the chemisorbed monolayer for reaction with the epoxy group of DGEBS. Thus, the reactive species of aminosilane on the glass plate surface is most likely to be the chemisorbed monolayer. Together with the structural assignments given in Tables VI to IX, a model of the chemical interactions at the glass–silane–resin interfaces is proposed in Fig. 5, showing siloxane bonds with the glass surface and chemical covalent bonds between the HAPS deposit and the DGEBS epoxy resin through their functional amino and epoxy groups.

With reference to the formation of a strong interfacial bond between the fibre and matrix in a composite material, it is clear that dissolution of non-cross-linked hydrolysed siloxane to expose the

TABLE VIII Negative ions from HAPS as-coated E-glass plate after treatment with DGEBS

a.m.u.	Fragment
338	
228	
214	
182	

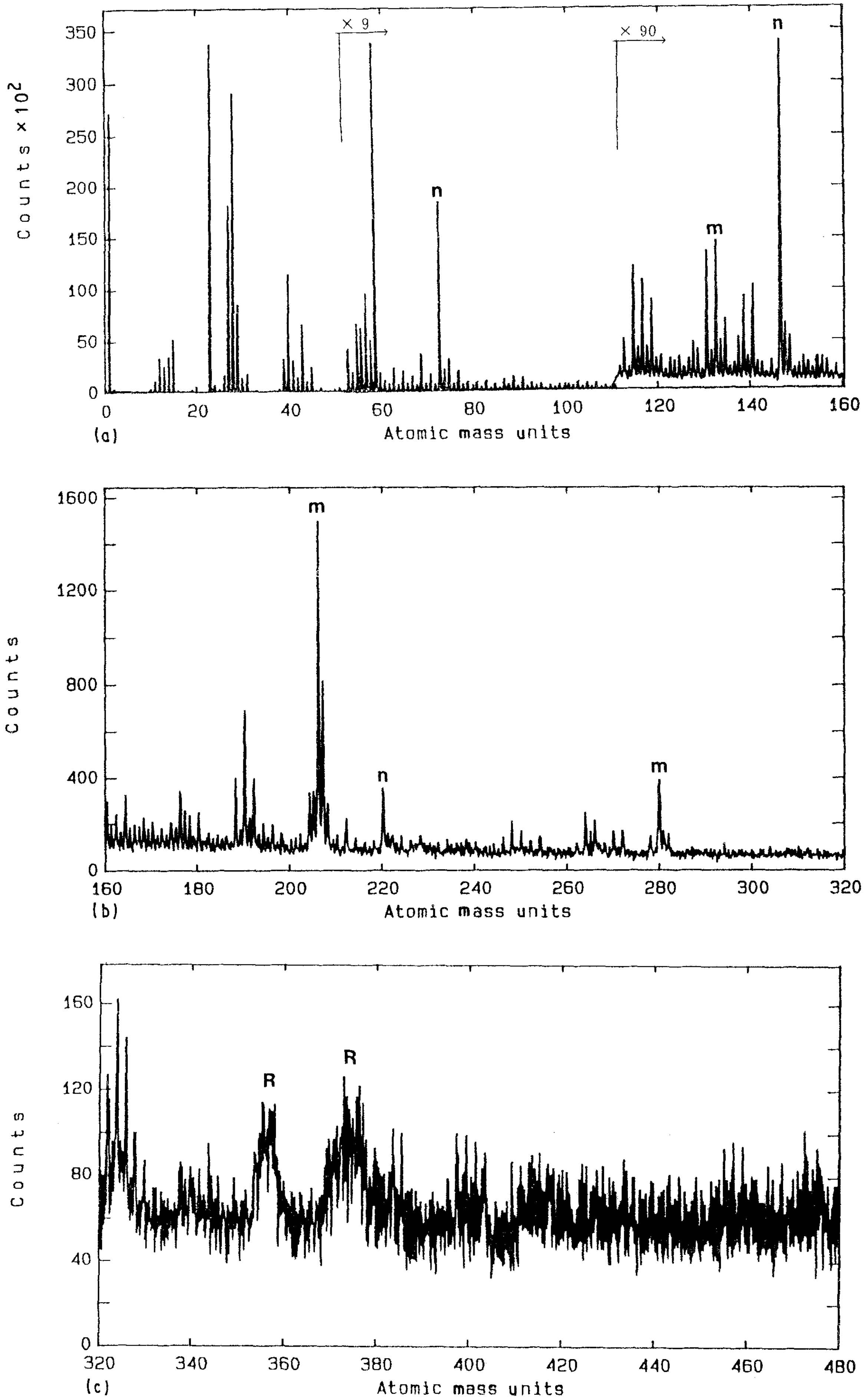
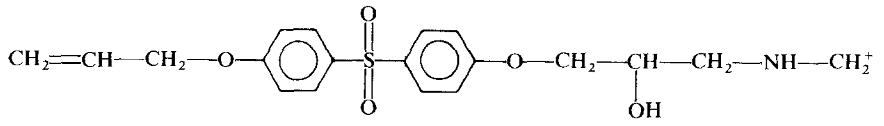
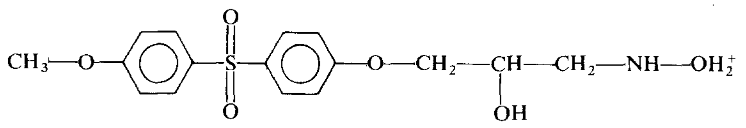


Figure 4 (a–c) TOF SIMS positive ion spectra from HAPS-silanized E-glass plate surface after re-dosing with DGEBS.

TABLE IX Positive ions from HAPS as-coated E-glass plate after treatment with DGEBS

a.m.u.	Fragment
376	
356	

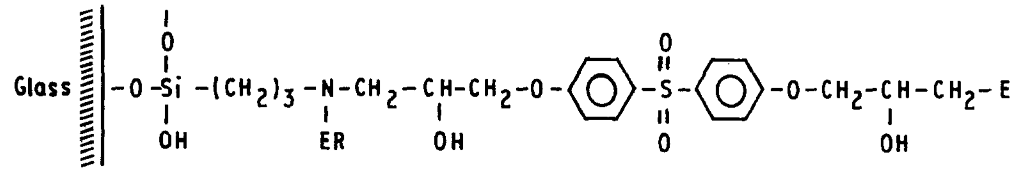


Figure 5 A model of chemical interactions at the glass–silane–resin interfaces: E = unreacted or reacted epoxy group, ER = H or reacted epoxy group.

reactable silane functional groups is probably very apparent. This would explain why the interfacial shear strength of a composite can be improved by pre-extraction of the fibres [23, 24]. In addition, the aluminium sites of the siloxane deposit do not appear to be involved in the coupling reaction (see Table V).

4. Conclusions

The formation of chemical bonds between an E-glass surface and poly(aminosiloxane) deposit has been confirmed. Furthermore, a monomolecular layer of bonded epoxy resin deposited from toluene solution on to the silanized glass surface has been demonstrated. Distinct chemical covalent bonds between the HAPS deposit and a DGEBS epoxy resin have also been demonstrated. Aluminium appears to be incorporated into the silane deposit from aqueous solution. However, the DGEBS deposit appears to be uniformly coated over the "silane" and "aluminoxane" areas of the silane deposit on the molecular scale.

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