

ToF-sims Investigation of Epoxy Resin Curing Reaction at Different Resin to Hardener Ratios

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ABSTRACT: Time-of-flight secondary ion mass spectrometry (ToF-SIMS) and principal components analysis (PCA) were used to analyze diglycidyl ether of bisphenol A (DGEBA) and diglycidyl ether of bisphenol F (DGEBF) epoxy resin blend cured with isophorone diamine (IPD) hardener at different resin to hardener ratios. The aim was to establish correlations between the hardener concentration and the nature and progress of the crosslinking reaction. Insights into the cured resin structure revealed using ToF-SIMS are discussed. Three sets of significant secondary ions have been identified by PCA. Secondary ions such as $C_{14}H_7O^+$, CHO^+ , CH_3O^+ , and $C_{21}H_{24}O_4^+$

showed variance related to the completion of the curing reaction. Relative intensities of $C_xH_yN_z^+$ ions in the cured resin samples are indicative of the un-reacted and partially reacted hardener molecules, and are found to be proportional to the resin to hardener mixing ratio. The relative ion intensities of the aliphatic hydrocarbon ions are shown to relate to the cured resin crosslinking density. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2711–2717, 2008

Key words: ToF-SIMS; epoxy resin; PCA; crosslinking; secondary ions

INTRODUCTION

Epoxy resins are used in a wide range of application such as adhesives, coatings, paints, and composites.^{1–3} The chemical stoichiometry of the resin and hardener, reaction condition, and time control the curing reaction which is a complex process in molecular level.^{4,5} The localized concentration of the hardener and its mobility determine the curing reaction rate and the crosslinking density. Localized excess of hardener or resin results in un-reacted molecules in the polymer matrix, altering its molecular, thermal, and mechanical properties. Furthermore, the presence of localized un-reacted molecules results in weakness in the overall structure that may diminish the overall performance of the material under various environmental conditions. Shortage of hardener molecules will lead to an incomplete curing reaction.

Crosslinked epoxy resins are normally formed via the curing reaction of a bi-functional epoxide such as diglycidyl ether of bisphenol A (DGEBA) or diglycidyl ether of bisphenol F (DGEBF) with a multi-functional crosslinking/curing agent (hardener). Amine-type curing agents are widely used.

Each amino group is a difunctional in case of epoxy curing reaction that can react with two epoxide groups and as a result new carbon-nitrogen bonds and a hydroxyl functional group are produced.³ The tetra functionality of the crosslinking agent means that a single hardener molecule can react with four epoxide groups, which eventually results in a cross-linked structure. The final product is ideally a fully crosslinked network; effectively a single, giant molecule.

A significant number of researchers have attempted to explain the reaction chemistry and physics of the DGEBA/DGEBF diamine mixture.^{5–7} The curing behavior of DGEBA as a function of varying imide-amine and diamine hardener concentration using DSC has been reported previously.^{4,8} Pichaude et al.⁶ reported the effects of hydroxyl content on the curing kinetics of DGEBA with isophorone diamine (IPD) as a hardener. Lopez-Quintela et al.⁷ studied the cis/trans reactivity of the DGEBA epoxy/diamine blend. The morphology of the cured resin determines its properties; this is dependent on the nature and the rate of the crosslinking reaction between the resin and the hardener.⁹ Another study showed that the curing of the epoxy resin is dependent on the structure of the hardener and its concentration.⁸

Resin curing information from the literature and technical sources indicates that resin reacting with tetra-functional crosslinking agents such as diamine

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hardener exhibit four reaction steps: blocking, coupling, branching, and crosslinking.^{10–18} Blocking occurs when one DGEBA or DGEBF molecule reacts with one IPD molecule. The addition of another DGEBA or DGEBF molecule to the blocking element results in coupling. Branching occurs when more than two DGEBA or DGEBF molecules react with one IPD molecule. The crosslinking reaction step occurs when many DGEBA or DGEBF molecules react with many IPD molecules to form a network. The ultimate goal is to have one large network in which the IPD molecules are fully reacted and integrated into the final structure.

In this study, we introduce time of flight secondary ion mass spectrometry (ToF-SIMS) to provide molecular information on the DGEBA/DGEBF epoxy resin/IPD curing reaction at different mixing ratios (hardener concentrations). ToF-SIMS is sensitive to changes in composition and molecular structure at the surface. Variations in the intensities of ion peaks characteristic of the resin and hardener and their reaction products are compared using univariate and multivariate techniques.

Ion bombardment of surfaces creates a range of chemical and structural changes, and may often lead to implantation of the primary ions, and removal of material from the surface by sputtering and associated processes. Primary ion bombardment is an energetic process and may be characterized by three energy regions.^{10,19} In the first region or zone, violent fragmentation occurs in a narrow central area directly beneath the impacting primary ions. In the case of the DGEBA/IPD reaction system, aliphatic hydrocarbon ions are most likely to be the products of the primary ion interaction as a result of what is called a 'violent fragmentation'.^{10,19} Surrounding this central area is a second zone where the primary ion energy has been decreased, yielding fragmentation of neutral species. It is believed that fragmentation of these species leads to a degree of ionisation.¹⁰ Double and single ring ions are believed to be examples of fragments derived from this region for the DGEBA resin. The third zone, surrounding the first two, receives primary ions of even lower energy leading to the generation of larger, more structured fragments. Examples of which are the DGEBA molecule and its derivative ions.

ToF-SIMS has been used previously to investigate the molecular changes of thermosetting resin. For example, Coullerez et al.²⁰ used ToF-SIMS to inspect the surface of uncured and fully cured Melamine Formaldehyde (MF) resin, revealing information about the resin chemical structure. Rattana et al.²¹ reported on the adsorption kinetics and thermodynamics of DGEBA epoxy resin molecules on aluminum substrates treated with an organosilane, γ -glycidoxypropyltrimethoxysilane, and used ToF-

SIMS to establish the fractional monolayer coverage of DGEBA molecules.

ToF-SIMS data are complex but may be productively analyzed using multivariate techniques such as Principal Components Analysis (PCA). PCA has been used previously by many researchers in combination with ToF-SIMS to aid spectral interpretation.^{22,23} ToF-SIMS data are normally pretreated before PCA application, providing assurance that variance in the data is due to chemical differences between samples and not mathematical differences in relative peak intensities arising from variations in primary ion current or detector efficiency.^{22,23} Scaling is also a common pretreatment procedure in which data are normalized to the corrected total intensity of a given spectrum and by multiplication of the individual peak intensities by a scalar value.²²

EXPERIMENTAL

Materials

KINETIX R246TX epoxy resin (ATL Composites, Australia) was used in this study, consisting of a DGEBA/DGEBF resin blend with an aliphatic glycidylether functional diluent. Super fast hardener, KINETIX H126 (ATL Composites, Australia), manufactured to cure at room temperature is an aliphatic/cycloaliphatic amine, with isophorone diamine being the main ingredient. Figure 1 shows chemical names and structure of the resin and hardener materials. The resin (R) and hardener (H) are mixed for 10 min at a ratio of 2 (HR2), 3 (HR3), 4 (HR4), and 5 (HR5) resin parts to one hardener part by weight. The initial curing was conducted according to the manufacturer recommendations and at room temperature (22°C). The post cure procedure was continued curing at room temperature for a period of 2 weeks, prior to ToF-SIMS analysis. No heating treatments were used to facilitate curing. Mixing ratios indicate HR2 will have low crosslinking and high blocking or coupling reaction steps probability. The reactions steps' rate and significance are expected to change as a result of decreasing the hardener ratio (HR3–HR5).

ToF-SIMS

ToF-SIMS analyses were performed using a ToF-SIMS IV instrument (Ion-TOF GmbH, Germany) equipped with a reflectron time-of-flight mass analyzer, a Bi_3^+ cluster ion source (25 keV) and a pulsed electron flood source for charge compensation. The primary pulsed ion beam current was 1.1 pA and the primary ion dose density was below the static SIMS limit of 10^{13} ions cm^{-2} . Positive ion mass spectra were acquired from a minimum of five $100 \times 100 \mu\text{m}^2$

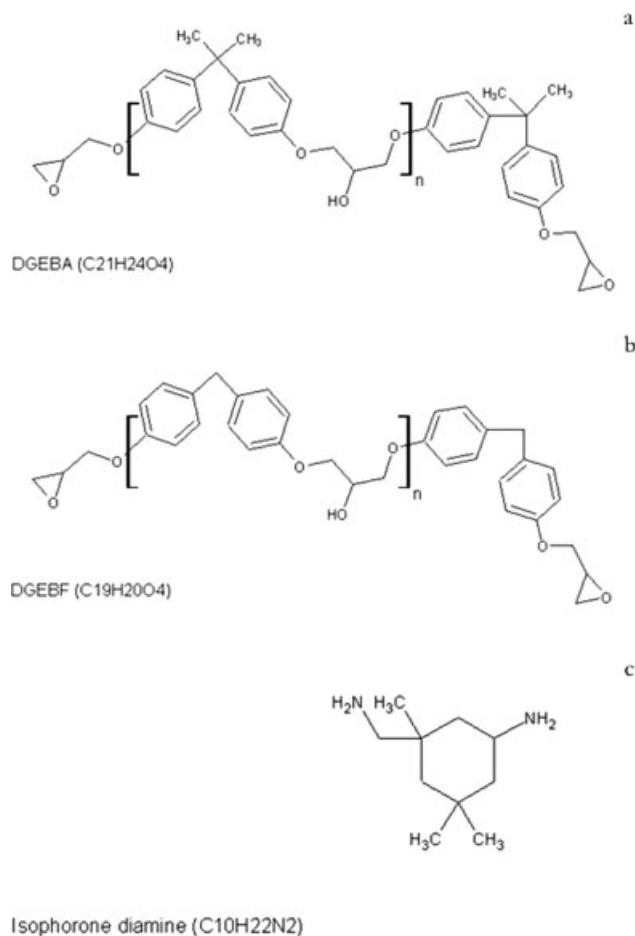


Figure 1 Molecular structures of the noncrosslinked poly DGEBA (C₂₁H₂₄O₄) $n = 0, 1, \dots$, DGEBF (C₁₉H₂₀O₄) $n = 0, 1, \dots$, resin and IPD (C₁₀H₂₂N₂) hardener molecule.

areas from each sample using a cycle time of 100 μ s. Mass resolution was greater than 7500 at $m/z = 29$.

Data analysis

The peaks for data analysis were selected initially based on reference libraries and previous assignments in the literature for DGEBA, DGEBF, and IPD molecules.^{20,21,24,25} Further, peaks were assigned using the library and the exact mass calculator tool incorporated in the Ionspec software package (IonTOF GmbH, Germany) to identify contaminant peaks, including the hydrocarbon peaks, and peaks that were likely to correspond to fragments of the resin/hardener not listed in the literature. All the significant peaks above baseline in the m/z range from 0 to 300 were selected. Significant peaks that could be resolved and related to the DGEBA, DGEBF and IPD molecules in the range of m/z 300–650 were also included. The mass spectra were calibrated using a series of hydrocarbon (C_{*x*}H_{*y*}) peaks up to $m/z = 105$.

The data were then grouped in a matrix and mean-centered. The columns in the matrix were normalized to the total intensity before mean centering. The mean-centered matrix was used for PCA. PCA is a multivariate technique used to assist the interpretation of large datasets such as those generated by ToF-SIMS, in particular, identifying meaningful variables describing the major physical phenomena in the system. It does so by compressing the large number of variables to a smaller number of principal components. The principal components are calculated statistically to group the main variance in the data and sorted them in order of magnitude utilizing the singular value decomposition of the data set. PCA was performed using code developed in-house and functions provided in the Stats package for R (V2.5.1), a language and environment for statistical computing and graphics, based on the covariance method algorithm described in detail by Martens and Naes.²⁶

RESULTS AND DISCUSSION

ToF-SIMS spectra for the resin, the hardener and the cured resin samples were collected and pretreated numerically before the application of PCA. PCA results are best discussed in terms of scores and loadings plots.^{23,26} Figure 2 shows the scores plots for the first four principal components, denoted PC1, PC2, PC3, and PC4. These account for 50.72, 43.11, 2.83, and 1.82% of the variance, respectively. Figure 3 shows the loadings plots for these principal components.

Multiple ions that appear significantly in PC1 are related to multiple physical phenomena in the system. Figure 2(a) shows that information contained in PC1 enables the discrimination between the hardener, the resin and the cured resin samples. The cured resin samples at different mixing ratios showed a trend, which decreases towards the high resin ratio sample HR5. This trend indicates that PC1 captures at least part of the changing physical and chemical character of the resin associated with changing the fraction of hardener in the resin mixture. Further, data from the hardener only sample H and the resin only sample R, are very well separated from the HR mixtures and each other, occurring at the positive end and negative end of the scores plot axis, respectively. Hence, PC1 captures the explicit variance of the hardener and resin molecular structure. All cured resin samples, however, are closer to the hardener sample than the resin sample. This indicates that the PCA score is sensitive to ion intensities resulting from the curing reaction with the hardener concentration as the curing reaction main variable. HR2 spectra are closer to H and HR5 is closer to R which indicates that the PCA picks up

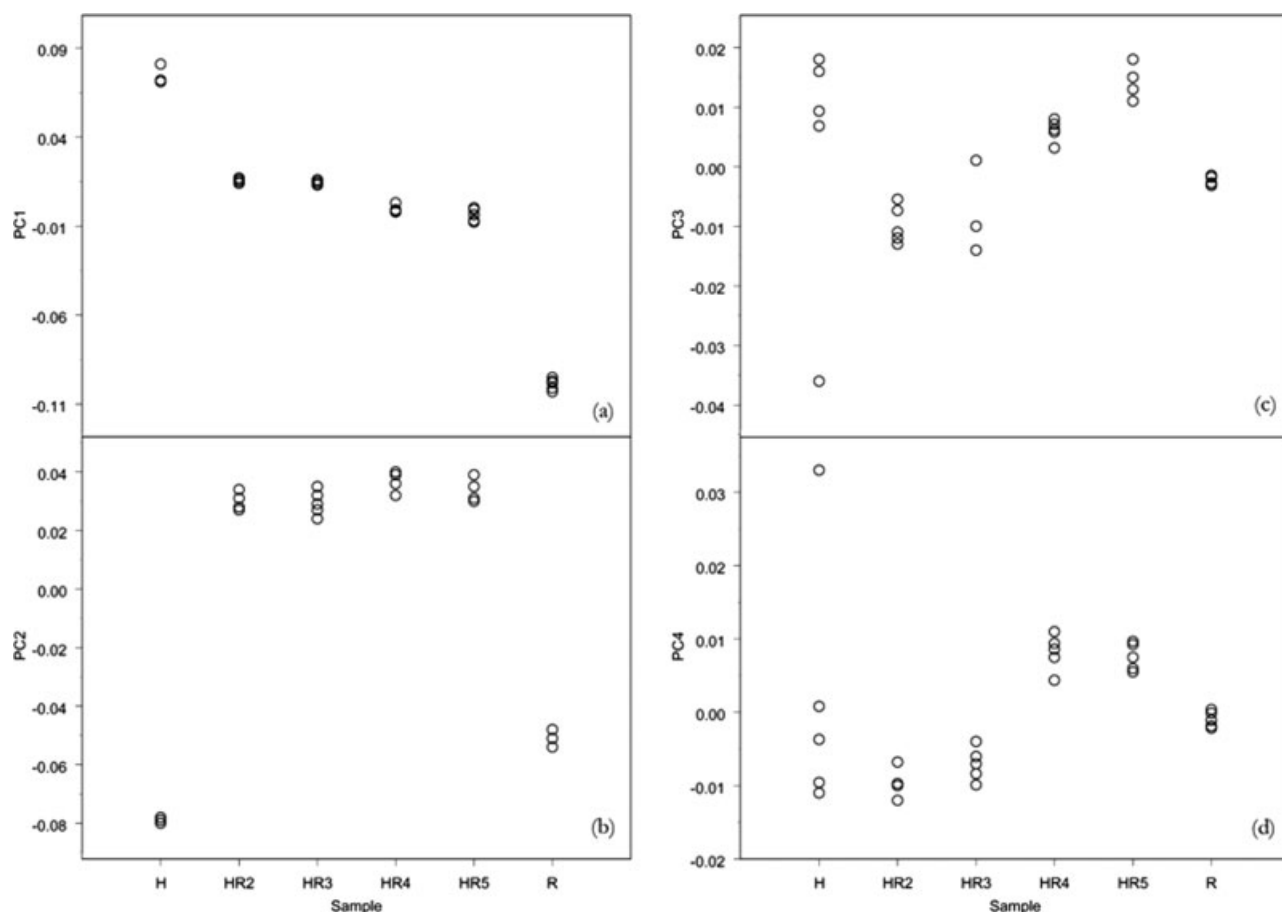


Figure 2 Principal components analysis score plots for (a) PC1 score (50.72%), (b) PC2 score (43.11%) and (c) PC3 score (2.83%) and (d) PC4 score (1.82%) using ToF-SIMS spectra for all samples. The percentage of total variance collected in each principal component is indicated in brackets.

the basic trend of the reaction which is the decrease in hardener concentration. The cured resin samples HR2 and HR3 have similar scores plot values, which appear somewhat higher than those for HR4 and HR5. This indicates that PC1 is sensitive to major changes in resin to hardener ratio, comparing HR2 with HR5, but less sensitive to smaller changes, comparing adjacent samples.

Figure 3(a) shows the loadings plot for PC1. The highest contribution comes from the $C_{14}H_7O^+$ ion, which corresponds to the double ring structure in the DGEBA and DGEBF molecules. Figure 4a shows the univariate plot of the ions that are related to the single and double ring in the DGEBA/DGEBF molecule, including $C_7H_7O^+$ and $C_{14}H_7O^+$. The $C_{14}H_7O^+$ ion, which appears in the resin material, has no significant counts in the cured resin samples. This suggests that the double ring ion is not detected when the curing reaction is complete, and its occurrence relates to the un-reacted DGEBA and DGEBF molecules. The dramatic reduction in relative intensity of this ion comparing the resin only sample with the cured resin samples, explains its high variance in

the PCA. This indicates that DGEBA molecules are consumed at any ratio in the resin/hardener mixture in the curing reaction after the application of post-cure process, as expected. At this point, however, there is no indication of the impact of network density or physical and chemical structure on the ToF-SIMS data. The single ring ion, $C_7H_7O^+$, was not significant in PC1, but appears in the resin and the hardener at a higher intensity and not changing significantly as function of the increase in resin ratio in the cured resin samples. This indicates that the crosslinking reaction conversion or network density does not affect the $C_7H_7O^+$ ion intensity significantly.

Significant contributions also arise from the CHO^+ and CH_3O^+ ions, corresponding to the epoxide functional group in the DGEBA and DGEBF molecules. Figure 4(a) shows that CH_3O^+ ion has significant intensity in the resin sample while this drops significantly in the cured resin samples. However, there is a slight increase in the ion count as the resin to hardener ratio increases. This indicates that the epoxide groups are consumed significantly in the

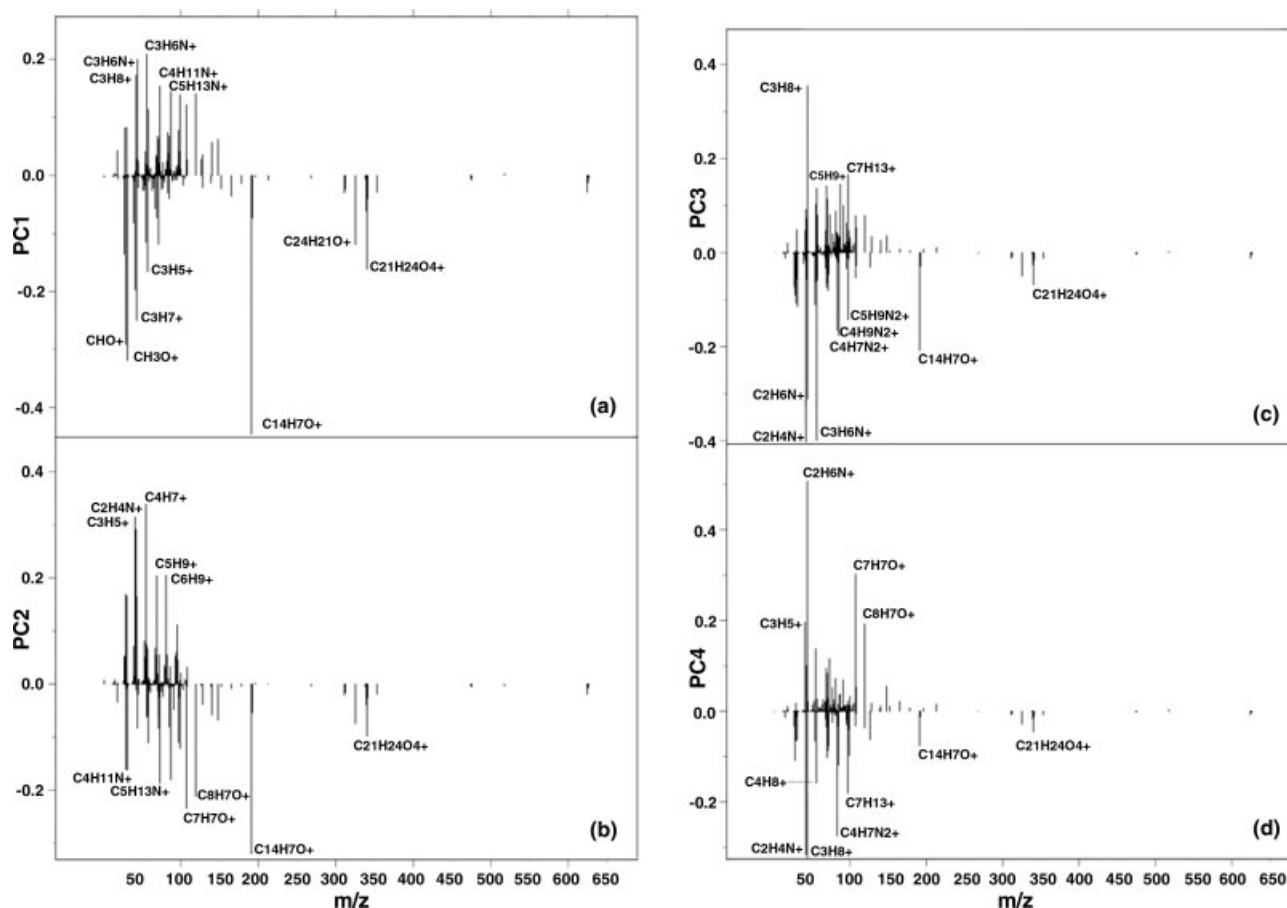


Figure 3 Principal components analysis loadings plots of (a) PC1, (b) PC2 (c) PC3 and PC4 using ToF-SIMS spectra for all time domains.

curing reaction of all samples. However, the rate of consumption is slightly reduced as the number of available hardener molecules drops in the increased resin to hardener ratio samples. CHO^+ ion, which show significant intensity in the resin sample, drop to an insignificant intensity in all cured resin samples. This slight proportional trend for these ions towards the increase of resin to hardener ratio is one of the factors directly related to the separation of the cured resin samples in the scores plot [Fig. 2(a)].

Another contribution appears in the $\text{C}_x\text{H}_y\text{N}_z^+$ ion fragments such as $\text{C}_2\text{H}_6\text{N}^+$, $\text{C}_3\text{H}_6\text{N}^+$, $\text{C}_4\text{H}_{11}\text{N}^+$, and $\text{C}_5\text{H}_{13}\text{N}^+$. Figure 4(b) shows that nitrogen-containing hydrocarbon ions are highest in the hardener sample, for which they originate. The $\text{C}_3\text{H}_6\text{N}^+$ ion has a higher intensity in the HR2 and HR3 samples than the HR4 and HR5 samples. The changes in relative ion intensity for this ion among the cured resin samples are one of the main factors that separate the samples in the scores plot [Fig. 2(a)]. This suggests that this ion is proportional to, or at least strongly related to, the IPD molecule concentration in the mixture. Relative intensity of the $\text{C}_2\text{H}_6\text{N}^+$ ion does not vary significantly across the cured resin samples. The $\text{C}_4\text{H}_{11}\text{N}^+$ and $\text{C}_5\text{H}_{13}\text{N}^+$ ions are not significant

in any of the cured resin samples, which suggest that these are characteristic of the un-reacted IPD molecule and could be indicative of the curing reaction conversion.

Contributions from the aliphatic hydrocarbon ions are represented by C_3H_7^+ , C_3H_5^+ , and C_3H_8^+ . Figure 4(c) shows that cured resin samples in general show a higher hydrocarbon ion intensity than the resin only R and hardener only H samples. The hydrocarbon ion intensities are higher in the HR4 and HR5 samples than in the HR2 and HR3 samples. The HR4 sample shows a higher relative ion intensity for the C_3H_7^+ and C_4H_7^+ ions than the rest of the cured resin samples, which may suggest a denser network. Further, both of these ions were identified to have correlation with polymers' molecular weight in a ToF-SIMS study on the determination of molecular weight of polymer surfaces by Galuska.²⁷ As evident from the primary ion bombardment scheme discussed in our earlier work,¹⁰ the aliphatic hydrocarbon ions relative intensity increases as the structural density increases and it becomes more difficult to fragment larger secondary ions. Consequently, the aliphatic hydrocarbon ions relative intensity is proportional to the sample network density.

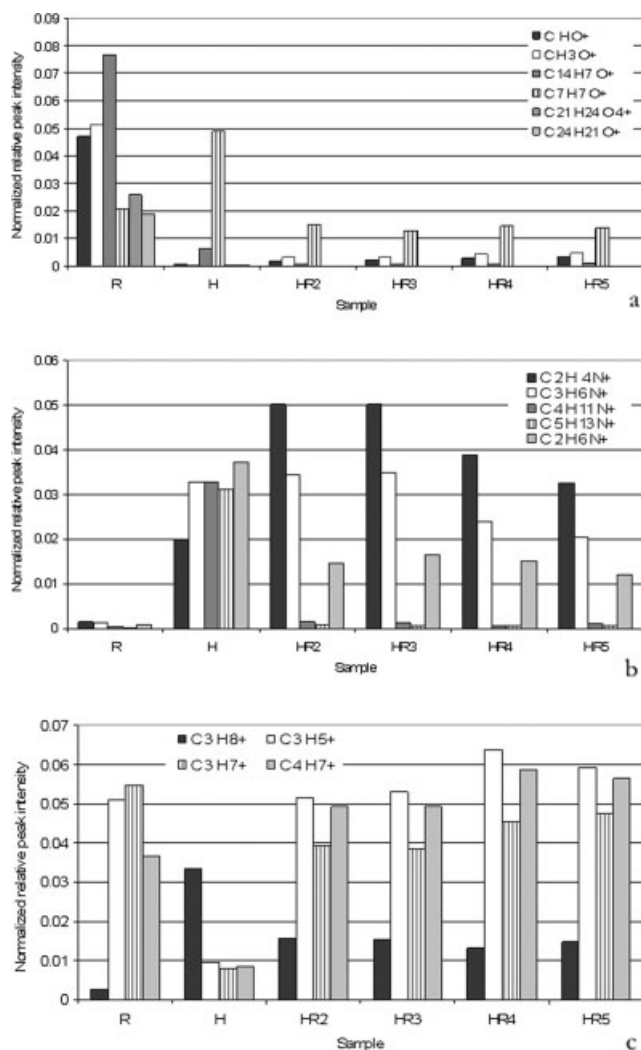


Figure 4 Variation in the intensity of secondary ion peaks of the samples that showed significant variance by PCA.

Further, there is a contribution from the ions that correspond to the DGEBA molecule and its derivative ion ($\text{C}_{21}\text{H}_{24}\text{O}_4^+$ and $\text{C}_{24}\text{H}_{21}\text{O}^+$). Figure 4(a) demonstrates that the $\text{C}_{21}\text{H}_{24}\text{O}_4^+$ and $\text{C}_{24}\text{H}_{21}\text{O}^+$ ions are related to the DGEBA molecule. $\text{C}_{21}\text{H}_{24}\text{O}_4^+$ and $\text{C}_{24}\text{H}_{21}\text{O}^+$ appear only in the resin sample and have no significant intensity in any of the other samples. This indicates that the DGEBA molecular ion is not detected during the curing reaction at any of the HR ratios. This finding is in line with observation made by Woerdeman et al.²⁵ that the DGEBA ion is not detected when the curing reaction is complete. Figure 3(a) also indicates that the $\text{C}_x\text{H}_y\text{N}^+$ ions and the C_3H_8^+ ion feature in the opposite direction (positive) to all other significant ions of $\text{C}_{14}\text{H}_7\text{O}^+$, CHO^+ , CH_3O^+ , C_3H_7^+ , C_3H_5^+ , and $\text{C}_{24}\text{H}_{21}\text{O}^+$. This indicates a discrete physical phenomenon in which the ions in the positive region correspond to the change in hardener concentration while the other ions are related to the change in the resin concentration in the data set.

The PC2 scores plot [Fig. 2(b)] shows that the hardener only H and resin only R samples are still separate while the cured resin samples overlap with each other. However, both the hardener and the resin samples appear in the negative region in close proximity, while the cured resin samples all appear in the distant positive region. This indicates a phenomenon that only occurs in the cured resin samples and is independent of HR ratio. The loadings plot, Figure 3(b), shows a significant contribution from the $\text{C}_{14}\text{H}_7\text{O}^+$, $\text{C}_7\text{H}_7\text{O}^+$, and $\text{C}_8\text{H}_7\text{O}^+$ ions that correspond to the double and single ring in the DGEBA molecule. A further contribution comes from the $\text{C}_x\text{H}_y\text{N}_z$ group of ions ($\text{C}_4\text{H}_{11}\text{N}^+$, $\text{C}_2\text{H}_4\text{N}^+$, $\text{C}_5\text{H}_{13}\text{N}^+$). The hydrocarbon contribution is from the ions C_3H_5^+ , C_4H_7^+ , C_5H_9^+ , and C_6H_9^+ . There is also significant contribution from the ion $\text{C}_{21}\text{H}_{24}\text{O}_4^+$, which corresponds to the DGEBA molecule. The changes of these ions are related to the occurrence of the blocking and coupling curing reaction steps which vary with the mixing ratios of resin and hardener, as mentioned in the material section [see Fig. 4(b)].

The PC3 scores plot [Fig. 2(c)] shows a trend among the cured resin samples in which the PC3 value increases as the resin to hardener ratio increases. HR2 and HR3, however, overlap with each other. Figure 3(c) shows that the major loading contribution for PC3 comes from the $\text{C}_x\text{H}_y\text{N}_z$ group, including $\text{C}_2\text{H}_6\text{N}^+$, $\text{C}_2\text{H}_4\text{N}^+$, $\text{C}_3\text{H}_6\text{N}^+$, $\text{C}_4\text{H}_7\text{N}_2^+$, $\text{C}_4\text{H}_9\text{N}_2^+$, and $\text{C}_5\text{H}_9\text{N}_2^+$. There is also another contribution from the hydrocarbon ions C_3H_8^+ , C_5H_9^+ , and $\text{C}_7\text{H}_{13}^+$. Comparison between Figures 2(c), 3(c), and 4(b,c) reveals that PC3 collected information related to the decrease in IPD hardener ratio in the cured resin samples. Figure 4(b) shows that the $\text{C}_2\text{H}_4\text{N}^+$, $\text{C}_2\text{H}_6\text{N}^+$, and $\text{C}_3\text{H}_6\text{N}^+$ ions significantly change in intensity relative to each other in the cured resin samples. The relative ion intensity of the $\text{C}_2\text{H}_4\text{N}^+$ ion increases significantly in HR2 and HR3 in comparison to the relative intensity of the hardener sample. HR4 and HR5 have a higher $\text{C}_2\text{H}_4\text{N}^+$ ion intensity than the hardener sample but lower than the HR2 and HR3 samples. The relative intensity for the $\text{C}_2\text{H}_6\text{N}^+$ ion is reduced in the cured resin samples in comparison with the hardener sample. The relative intensity of the $\text{C}_3\text{H}_6\text{N}^+$ ion increases slightly in the HR2 and HR3 cured resin samples and decreases in the HR4 and HR5 cured resin samples in comparison with its relative intensity in the hardener sample. The relative intensity of the C_3H_8^+ ion appears most significant in the hardener sample and reduces in intensity to almost half in the cured resin samples. Sample HR4 shows least intensity for this ion among the cured resin samples. Lesser contribution come from the double ring-associated ion $\text{C}_{14}\text{H}_7\text{O}^+$ and DGEBA-associated ion $\text{C}_{21}\text{H}_{24}\text{O}_4^+$.

The PC4 scores plot [Fig. 2(d)] shows a similar trend to PC3 for the cured resin samples; however, the HR2 and HR3 samples and HR4 and HR5 samples are segregated together. Figure 3(d) shows the loadings plot for PC4 in which the most significant contributions come from the $C_2H_6N^+$, $C_2H_4N^+$, and $C_4H_7N_2^+$ ions. The hydrocarbon contribution comes from the $C_3H_5^+$, $C_4H_8^+$, $C_3H_8^+$, and $C_7H_{13}^+$ ions. A lesser contribution is observed from the single ring ions $C_8H_7O^+$, and $C_7H_7O^+$, and the double ring ion $C_{14}H_7O^+$. Similar to PC3, PC4 collects information that relates to the change in IPD hardener concentration in the cured resin samples.

CONCLUSIONS

PCA analysis of ToF-SIMS data collected from cured and un-cured epoxy resin was successful in establishing correlations between a small number of secondary ions and the progress of the curing reaction. PCA showed that four components were sufficient to generate interpretations regarding the main reaction elements that separated the cured samples from the resin and hardener samples and between the cured resin samples themselves. The $C_{14}H_7O^+$ ion relative intensity is found to be indicative of the consumption of DGEBA/DGEBF molecules in the curing reaction and the reaction conversion. The relative intensity of the CHO^+ and the CH_3O^+ ions showed a slight proportional trend towards the increase of resin to hardener ratio. The relative intensity of the $C_xH_yN^+$ ions is the main factor that separates the cured resin samples in the PC1 score plot and it is proportional to the curing reaction conversion and the un-reacted IPD molecules. The relative intensity of the aliphatic hydrocarbon ions increased as the resin to hardener ratio increased with highest values is in the 4 : 1 ratio. The relative ion intensities of the aliphatic hydrocarbon ions are shown to be proportional to the cured resin crosslinking density.

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