Distribution Analysis of Epoxy Groups in Polymers by Derivatization–Electron Probe X-ray Microanalysis

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An analytical method, referred to as "derivatization–electron probe X-ray micro-analysis (XMA)", has been developed to determine the distribution of a small amount of the functional groups in a polymer. The suitable conditions for the derivatization reaction with epoxy groups, which contribute to the hardening reactions of polymers, were investigated. It was found that epoxy groups in polymers were derivatized selectively using gas-phase esterification with hydrochloric acid (HCl). The most suitable amount of HCl in a 50 ml vial was 300 μl. After setting a sample in the vessel without directly contacting the reagent, by reacting the reagent and the sample at 25°C for 1 h, the highest reaction yield and selectivity were obtained. By derivatization-XMA using this reaction condition, the measurement of the distribution of epoxy groups in the polymer became feasible. Actual applications to a depth analysis of epoxy groups in the hardened acrylic coating and epoxy resin proved that this method is useful for the characterization of polymers and for the study of the hardening reaction of polymers.

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An analytical method, referred to as "derivatization–electron probe X-ray micro-analysis (XMA)", has been developed to determine the distribution of small amounts of functional groups in polymers with a lateral resolution of μm order using equipment available generally. The suitable conditions for the derivatization reaction with the vinyl group, the carbonyl group, the carboxyl group and the hydroxyl group formed by the oxidation and the hydrolysis of polymers were investigated.[1-4] This present method is useful for the characterization of polymers and the study of the polymer degradation. Also, this method can be used for the study of the hardening mechanism and the evaluation of the hardening degree, because the above-mentioned functional groups contribute to the hardening of polymers. The epoxy group also contributes to the hardening of the adhesive and of the coating, as well as the above-mentioned functional groups. The neutralization titration method and the potentiometric titration method, among others, have been reported as methods for measuring the quantity of epoxy groups. However, these methods can only measure the average of functional groups, and can not measure the distribution of functional groups in the polymer. Therefore, in this study, a suitable condition for the derivatization reaction of epoxy groups in polymers was investigated in order to use this method effectively. Also, the utility of this method in the study of the hardening mechanism and in the evaluation of the hardening degree was confirmed by applying this method to the distribution analysis of epoxy groups in the adhesive and the coating.

Experimental

Choice of derivatization reagent
  Hydrochloric acid (HCl), trifluoroacetic anhydride ($(CF_3CO)_2O$), sodium thiosulfate ($Na_2S_2O_3$) and sodium sulfide (Na_2S) are known as representative derivatization reagents which react to the epoxy group.[5-7] These reagents are used for the color reaction and for the improvement of the detection sensitivity in XPS. Among these reagents, hydrochloric acid has the following advantages. This reagent has a Cl element which is sensitive to XMA. The reactivity of this reagent is high at room temperature and the damage to the sample by this reagent is small, because the reaction that uses this reagent is a gas-phase reaction. Therefore, the optimal derivatization condition was investigated using hydrochloric acid.

Samples and reagents
  As polymers with epoxy groups in their structure, an acrylic coating (acryl-coating, butyl methacrylate:glycidyl methacrylate:hydroxyl ethyl methacrylate:N,N',N''-tris-(hexamethylene isocyanate) buret = 3:4:3:1 mole ratio, concentration of epoxy groups: 9 wt%, 50 μm thickness), which was cured at 120°C for 20 min and an epoxy resin (epoxy, 44 wt% maleic acid anhydride/Epikot 828, 3 mm thickness), which was cured at 120°C for 17 h were prepared.
  Films or pellets of the following polymers which have functional groups except for an epoxy group were prepared to confirm the selectivity of the reaction: polymethyl methacrylate (PMMA, General Science Co. Ltd.), which has ester groups; ethylene-vinyl alcohol copolymer (EVA, Kurare Co. Ltd., concentration of ethylene monomers: 47 mol%), which has hydroxyl groups to the main chain; poly-2-hydroxylethyl methacrylate (HEMA, General Science Co. Ltd), which has hydroxyl groups to the side chain; polyacrylic acid (PAA, Sumitomo Chemistry Co. Ltd.), which has carboxyl groups; ethylene-carbon monoxide copolymer (E-CO, Japan Yunika Co. Ltd., concentration of carbonyl groups: 3 wt%, 50 μm thickness), which has carbonyl groups; acrylonitrile-butadiene-
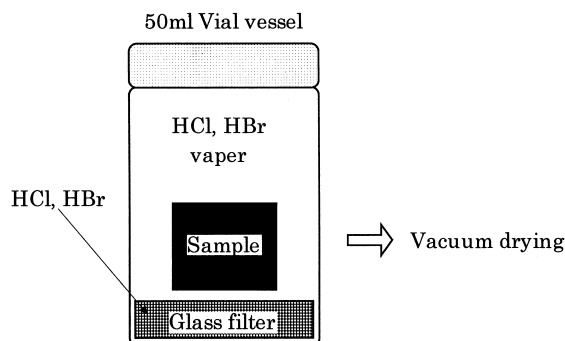
Fig. 1 Schematic illustration of a reaction instrument for derivatization of epoxy groups in polymers.

Fig. 2 Relationship between amounts of the reaction reagent and the concentration of Cl obtained by XMA after derivatization.

styrene copolymer (ABS, Nihon Gousei Gomu Co. Ltd., concentration of butadiene monomers: 23%), which has vinyl groups; and nylon-66 (Ny-66, General Science Co. Ltd.), which has amide groups.

As the derivatization reagent, hydrochloric acid (HCl, Wako Pure Chemical Ind. Ltd.) was used.

Derivatization of epoxy group

The outline of the derivatization is shown in Fig. 1. The sample was put on the glass filter in the 50 ml vial and the reaction reagent was poured into the glass filter without directly contacting the sample. After reacting at 25°C for 1 h, the sample was vacuum dried at 80°C for 15 h to exclude any reaction reagent that had penetrated the sample.

Measurement condition

The line analysis by XMA was performed under conditions, which were the same as those in the previous report.[4] However, as the detection X-ray, K_α-ray (0.4728 nm) was used for the Cl element and L_α-ray (0.8375 nm) was used for the Br element. The line analysis by micro-IR was also performed under conditions, which were the same as those in the previous report.[4]

Results and Discussion

Derivatization condition of epoxy group

The optimal quantity of hydrochloric acid as the derivatization reagent was investigated by fixing the temperature and the time of the derivatization reaction at 25°C and 1 h, respectively. Acryl-coating and epoxy resin were used as polymers with epoxy groups. The relationship between the quantity of hydrochloric acid in the 50 ml vial and the Cl concentration (∝ the reaction yield) obtained by the XMA measurement after the reaction is shown in Fig. 2. For both acryl-coating and epoxy resin, the reaction yield increased with increasing the quantity of hydrochloric acid and became constant at approximately 300 μl. Therefore, the quantity of hydrochloric acid was fixed at 300 μl in the 50 ml vial.

The optimal reaction time was also investigated by fixing the quantity of hydrochloric acid at 300 μl in the 50 ml vial and the temperature of the derivatization reaction at 25°C. The relationship between the reaction time and the Cl concentration obtained by the XMA measurement after the reaction is shown in Fig. 3. For both acryl-coating and epoxy resin, the reaction yield increased with increasing reaction time and became constant after approximately 1 h. Therefore, the reaction time
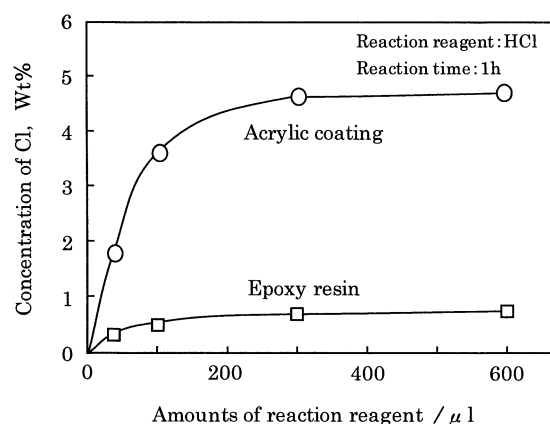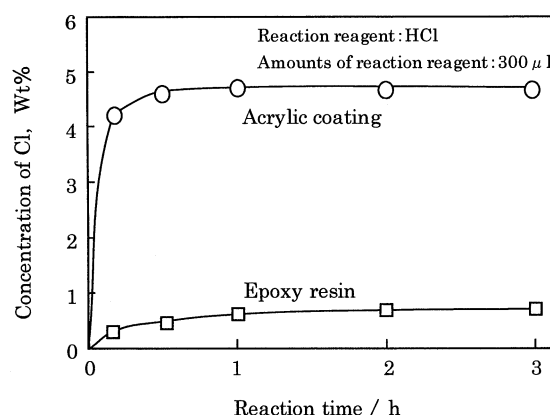

Fig. 3 Relationship between the reaction time and the concentration of Cl obtained by XMA after derivatization.

was fixed at 1 h.

Performances of derivatization-XMA

To measure functional groups with maximum sensitivity in the derivatization-XMA method, it is necessary for the derivatization reaction to progress to the detection depth of XMA. Therefore, the reaction depth of acryl-coating samples was examined using the diagonal-cutting method described previously.[1] The distribution of Cl elements obtained by XMA and the distribution of epoxy groups obtained by micro-IR are shown in the lower section of Fig. 4. The depth from the reaction surface, the Cl concentration measured by XMA and the absorbance of the epoxy groups (907 cm⁻¹) measured by micro-IR are shown in the horizontal axis, in the left vertical axis and in the right vertical axis, respectively. From these results, it was confirmed that the reaction reached 15 μm depth, because the depth with decreasing Cl element and the depth with increasing the absorbance of epoxy groups agreed. This is deeper than the detection depth (10 μm)[1] of XMA in a polymer.

The IR spectra of the surface and the inside are shown in the upper section of Fig. 4. From these spectra, the derivatization reaction was proven to advance, because the absorbance of epoxy groups (907 cm⁻¹) at the surface (the reaction part) was decreased more than that at the inside (the non-reaction part). Moreover, the reaction yield was 92%, because the absorbance
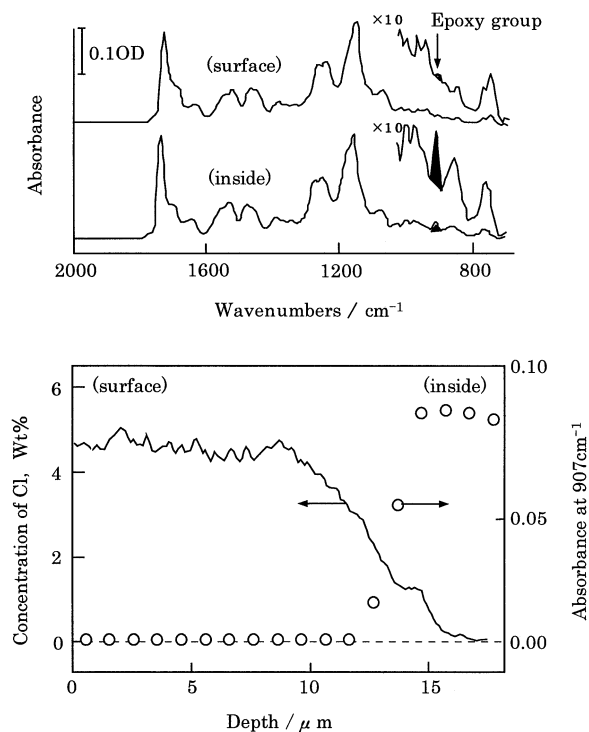
Fig. 4   Depth profiles of epoxy groups in derivatized acrylic coating for the measurement of derivatization reaction depth (lower) and IR spectra of derivatized acryl coating (upper).

Table 1   Selectivity of derivatization reaction in polymers that have various functional groups

Polymer	Functional group	Reaction yield, %
Acryl coating	Hydroxyl group	65
PMMA	Ester group	<1
HEMA	Hydroxyl group	3
EVA	Hydroxyl group	<1
PAA	Carboxyl group	<1
E-CO	Carbonyl group	1
ABS	Vinyl group	2
Ny-66	Amide group	12

of epoxy groups at the inside was 0.012 and the absorbance of epoxy groups at the surface (the reaction part) was 0.001 in these spectra.

On the other hand, when one analyzes functional groups using this method, it is important that only the functional group under analysis is derivatized (selectivity of the reaction). The results when derivatizing polymers, which have various functional groups, are shown in Table 1.   Acryl-coating (with epoxy groups) was derivatized. PMMA (with ester group), HEMA (with ester group and hydroxyl group), EVA (with hydroxyl group), PAA (with carboxyl group), E-CO (with carbonyl group) and ABS (with vinyl group) were not derivatized. However, Ny-6 (with amide group) was derivatized. Therefore, the measurement of epoxy groups in polymers, which have amide groups (*e.g.* nylon) can not be performed using this method.

Confirmation of the effectivity

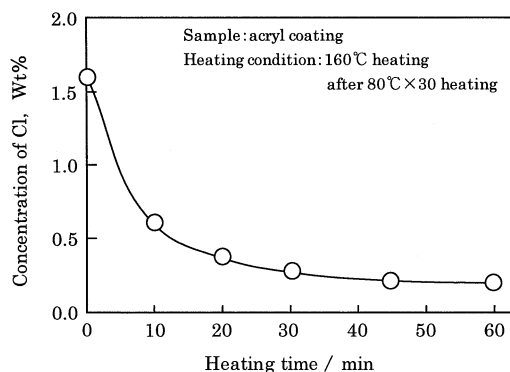The epoxy group is convenient for the study of the hardening

Fig. 5   Relationship between the heating time and the concentration of Cl obtained by XMA after derivatization on acrylic coating.
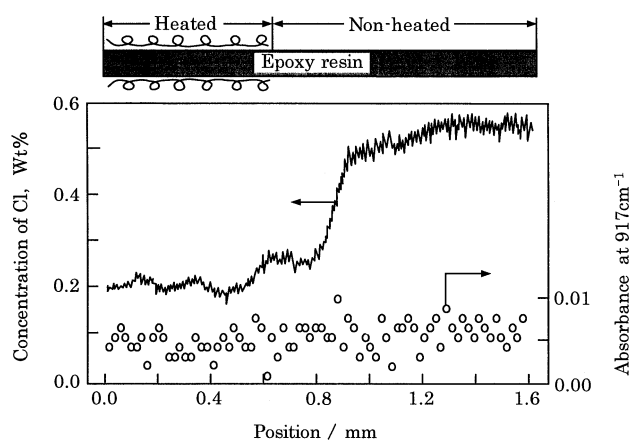

Fig. 6   Distributions of epoxy groups in epoxy resin that was heated as shown in the upper figure, by derivatization-EPMA (upper) and micro-IR (lower).

mechanism and the evaluation of the hardening degree, because the epoxy group reacts to the amine and acid anhydride in the adhesive and the coating. Therefore, the effectivity of this method was confirmed by a distribution analysis of epoxy groups remaining in actual polymer materials.

1) Change of the epoxy group quantity by the hardening of the acrylic coating.   In recent years, the use of acrylic coatings on automobiles has increased, because this coating, in which the epoxy group and acid anhydride harden, offers strong protection against acid rain.[8-10]   Here, the change of the epoxy group quantity in acrylic-coating by the hardening was measured. After acrylic-coating was coated on the glass plate, it preheated at 80°C for 30 min. The epoxy group quantity when hardening the preheated coating at 160°C was determined using this method. The results are shown in Fig. 5.   That the remaining epoxy group quantity decreases as the heating time increases was clearly determined.   The effectivity of this method was confirmed to the evaluation of the hardening degree.

2) Determination of the distribution of epoxy groups in the hardened epoxy resin.   A specimen was made by preheating bisphenol A-type epoxy resin for 17 h at 120°C in a mold (size: $50 \times 10 \times 1$ mm) after mixing maleic anhydride at 44 wt%. The distribution of the remaining epoxy groups when heating one side of the specimen for 30 min at 250°C was determined using this method and micro-IR. The results are shown in Fig. 6. The position near the boundary in the heating part and the non-

heating part is shown in the horizontal axis.   The Cl concentration determined by this method and the absorbance of 917 cm^{-1} (epoxy groups) determined by micro-IR are shown in the left vertical axis and in the right vertical axis, respectively. The results found in this method show that the quantity of epoxy groups in the heating part was decreased to 1/3 of the quantity of epoxy groups in the non-heating part.   The sensitivity of this method was also confirmed, because epoxy groups were not detected in the determination of micro-IR.

From the above examinations, the distribution of epoxy groups in the polymer could be measured by derivatization-XMA with hydrochloric acid as the derivatization reagent. Also, by applying this present method to the distribution analysis of epoxy groups in acrylic coating and epoxy resin, the utility of this method in the study of the hardening mechanism and in the evaluation of the hardening degree was confirmed.

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