Research Report

Distribution Analysis of Functional Groups in Polymeric Materials by X-ray Microanalysis Utilizing Their Derivatization

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誘導体化を併用するX線マイクロアナリシスによる高分子材料中の官能基の分布分析

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Abstract

A new analytical method, referred to as "Derivatization-Electron Probe X-ray Microanalysis (Derivatization-XMA)", has been developed to determine the distribution of 0.1 % order functional groups in polymers with μm level lateral resolution. Also, the optimal reaction conditions that make it possible to selectively derivatize the vinyl groups, carboxyl groups, carbonyl groups, hydroxyl groups and epoxy groups have been found. This method first derivatizes the functional groups in a polymer using a reagent with an indicator element highly sensitive to XMA, and moreover, with high selectivity to the functional group, and then measures the distribution of the indicator elemens by XMA, thus obtaining the distribution of the original functional groups. The fundamental performance of XMA in analyzing derivatized polymers has been investigated. The results showed that the detection limit was 0.05 % and the lateral resolution was 3 μm. In addition, the depth profile of the vinyl groups in an amine-degraded polyvinylchloride sheet was analyzed using this method. Since the depth profiles agreed well with those obtained by micro-IR spectroscopy, the reliability of measuring the distribution of functional groups by this method was confirmed. By this method, the sensitivity was 30 times higher, and the lateral resolution was 4 times higher than those obtained by micro-IR spectroscopy. Actual application to the depth analysis of degraded polymers has proved that this method is useful for the characterization of polymers and the study of polymer degradation.

Keywords
Depth profiling analysis, Functional group, Polymer, Chemical derivatization, Electron probe X-ray microanalysis, Polyamide-6, Polyvinylchloride, Ethylene-carbon monoxide copolymer

要　旨

高分子材料中に存在する0.1%オーダーの官能基の分布をμmオーダーの位置分解能で測定できる新しい分析法として，"誘導体化ー電子線プローブマイクロアナリシス（誘導体化ーXMA）"が有効であることを見出した。また，官能基であるビニル基，カルボキシル基，カルボニル基，水酸基およびエポキシ基について，本法のキーとなる誘導体化が選択的に行える最適反応条件を見出した。本法はXMAに高感度な標識元素を持つ反応試薬で官能基を誘導体化した後，この標識元素の分布をXMAで測定することにより，元の官能基の分布を得るものであり，検出感度0.05%，位置分解能3μmであった。本法をアミンで劣化させた塩化ビニル樹脂中のビニル基の分布測定に適用したところ，本法による分布は顕微IR法による分布と良く一致し，本法による官能基の分布測定の信頼性が確認された。また，本法は顕微IR法に比べて検出感度が30倍，位置分解能が4倍高いことも分かった。さらに，劣化させた高分子材料に適用し，高分子材料の劣化機構の解析や劣化状態の評価に有効であることを示した。

キーワード
深さ方向分析，官能基，ポリマー，化学修飾，誘導体化，電子線プローブマイクロアナリシス，ポリアミドー6，塩化ビニル樹脂，エチレンー一酸化炭素共重合体

1. Introduction

Polymeric materials such as plastics, rubbers and coatings, have many advantages over other materials. For example, plastics are light, cheap and easy to mold. Therefore, the use of polymeric materials is increasing. However, they have disadvantages as well. It is well known that polymeric materials degrade under environmental conditions, being affected by light, heat and other conditions, thus losing their properties. Therefore, it is important to study the degradation mechanism of the polymers and also to develop a method for estimating the degradation degree of the polymers. In order to estimate their degradation, both chemical and physical points of view are necessary. Estimation from a chemical point of view is achieved by measuring changes in the chemical structure and composition in the materials induced during degradation, either on the surface or in the bulk. Almost all methods of polymer analysis are utilized for the estimation of chemical changes in polymeric materials.

Because infrared absorption spectroscopy (IR) provides very valuable information about the chemical structure among these methods, and microscopic IR (micro-IR) has been developed, the use of IR for depth analysis of compositions and functional groups in polymeric materials is increasing.1-3) In particular, because the microscope IR method has depth resolution as low as 1-μm order, it has often been used for the estimation of degraded polymeric materials.4) However, changes which involve less than a few percent of the components are difficult to evaluate by conventional IR. Therefore, in order to study the degradation mechanism of polymeric materials and estimate their degradation degree, test samples exposed for a prolonged time must be examined. For example, exposure tests over a few years are often necessary in outdoor tests to enhance the deterioration of polymeric materials.

In this study, a new analysis method to measure the depth profile of small amounts of functional groups such as vinyl groups, carboxyl groups, carbonyl groups, hydroxyl groups and epoxy groups generated in the degraded polymeric materials with a lateral resolution of μm order was investigated. During this study, a new microanalysis method, "derivatization-electron probe X-ray microanalysis (derivatization-XMA)", was developed, in which chemical derivatization of the functional groups in the polymeric materials to enhance the detection sensitivity of XMA was effectively utilized. The optimal conditions for the derivatization reaction with vinyl groups, carboxyl groups, carbonyl groups, hydroxyl groups and epoxy groups in polymers and the applications of the developed method for the degradation of the polymers have been investigated. It was found that this method is definitely useful for the estimation of the degraded polymers and the study of the degradation mechanism of the polymers.

2. Experimental

2. 1 Principles

An outline of the derivatization-XMA is shown in **Fig. 1**. This method first derivatizes the functional groups in a polymer using a reagent with an indicator element highly sensitive to XMA, and moreover, with high selectivity to the functional group, and then measures the distribution of the indicator elements by XMA, thus obtaining the distribution of the original functional groups. It was designed to increase the sensitivity and the lateral resolution by the use of chemical derivatization and XMA, respectively.

2. 2 Line analysis by XMA

In the line analysis, a Shimadzu EPM-810Q electron micro-analyzer was used for the XMA analysis, and the beam diameter, acceleration voltage, sample electric current and scan speed were set to 1 μm, 20 kV, 20 nA and 50 μm/min, respectively. The thickness of the gold coating was 5 nm. For the detection of the Cl element and the Br element, $K\alpha$-rays (0.4728 nm) and $L\alpha$-rays (0.8375 nm), respectively, were used. The concentration (C) of elements was obtained from Eq. (1) by the ZAF revision method generally used in XMA.

$$C = G(k) \cdot k \quad \cdots\cdots\cdots\cdots\cdots (1)$$

Here, $G(k)$ is a revision coefficient and k is an X-ray intensity ratio between the sample and a standard substance. KCl and KBr were used as the standard substances.

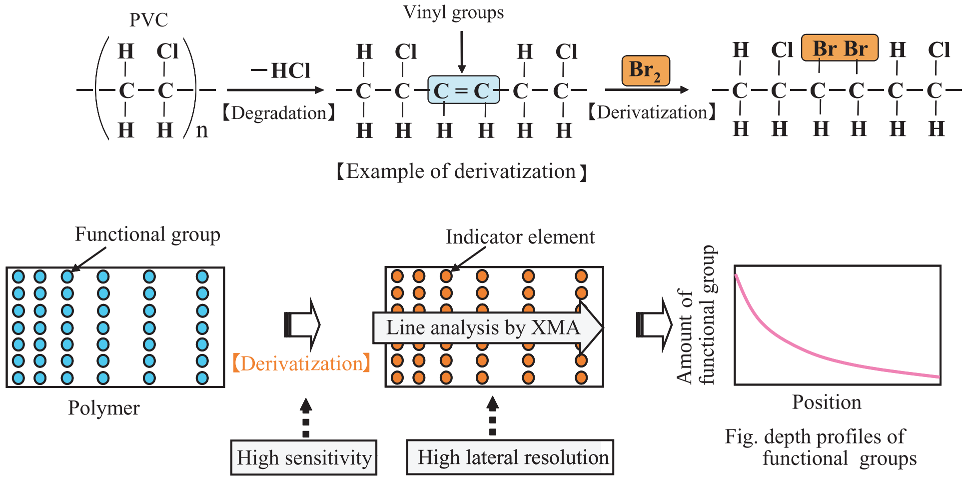


Fig. 1 Scheme for Derivatization-XMA.

2. 3 Line analysis by micro-IR

In the line analysis, a JEOL JIR-100 type Fourier transform infrared spectrometer with a MAU110 type micro-IR unit was used for micro-IR analysis, and the slit size and stepping width were set to 20 μm × 50 μm and 20 μm, respectively.

2. 4 Derivatization of the functional groups

The successful use of derivatization-XMA requires optimal derivatization conditions. Therefore, optimal conditions for derivatization of the vinyl groups, carboxyl groups, carbonyl groups, hydroxyl groups and epoxy groups were investigated. The vinyl groups were generated by dehydrochlorination in PVC. The carboxyl groups, carbonyl groups and hydroxyl groups were generated by oxidation degradation in the polymer. The carboxyl groups and hydroxyl groups were also generated by hydrolysis of the polymer itself. The epoxy groups contribute to the hardening reactions of polymers.

3. Results and discussion

3. 1 Fundamental performances of XMA in analyzing polymers

3. 1. 1 Detection sensitivity of Cl and Br elements in the polymer

The detection limits (S/N=2) of the Cl and Br elements in polymers were examined using PVC and Br-Epoxy (brominated epoxy resin), of which the element concentrations were known. As a result, the detection limit concentrations of both elements were found to be 0.05 %. When converting this concentration to the concentration of vinyl groups generated in PVC, this concentration was equal to two vinyl groups per 10,000 vinyl chloride monomer units.

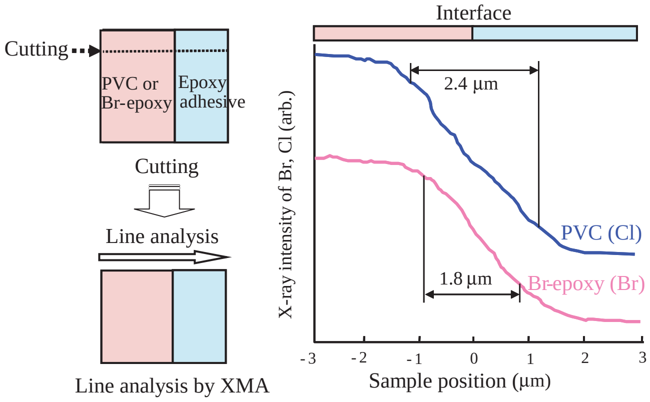


Fig. 2 Scheme for the measurement of lateral resolution (left) and X-ray intensity profiles of two polymers for the measure-ment of lateral resolution (right).

3. 1. 2 Lateral resolution of XMA in the case of the polymers

After cutting perpendicular to the gluing phase boundary of PVC glued to an epoxy adhesive using a microtome, the cut surface was line analyzed perpendicular to the gluing phase boundary by XMA as shown in **Fig. 2** (reft). The obtained profiles of

X-ray intensity are shown in Fig. 2 (right). As a result, the lateral resolution of PVC and Br-Epoxy are found to be 2.4 μm and 1.8 μm, respectively. This lateral resolution is 4 times higher than that of micro-IR (the lateral resolution of micro-IR is about 10 μm).

3. 2 Derivatization of the functional groups

3. 2. 1 Optimal derivatization conditions for the functional groups

The optimal conditions for derivatization of the vinyl groups, carboxyl groups, carbonyl groups, hydroxyl groups and epoxy groups were investigated. As a result, the five different functional groups were derivatized as shown in **Table 1**. Also, the optimal reaction conditions that make it possible to selectively derivatize the five different functional groups have been confirmed.

3. 2. 2 Reaction depth of the derivatization

To obtain maximum sensitivity in this method, it is necessary that the reaction depth of the derivatization is above 8 μm (the detection depth of XMA). Therefore, the reaction depth of the carbonyl groups in the ethylene-carbon monoxide copolymer (E-CO polymer) was examined as follows. After cutting a sample with a microtome as shown in **Fig. 3**, the cutting surface was derivatized and then the reacted surface was cut diagonally. The cut film of 1-μm thickness and the cut surface were line analyzed by micro-IR and derivatization-XMA, respectively, in the depth direction.

The depth profiles of the carbonyl groups and Cl elements obtained by both methods are shown in **Fig. 4** (lower). Since the depth at which the carbonyl groups increase coincides with the depth at which Cl elements decrease, we can conclude that the reaction depth of derivatization is 15 μm. Also, since the absorption of the carbonyl groups (1720 cm^{-1}) seen in the IR spectrum of the bulk decrease in the IR spectrum of the surface in Fig. 4 (upper), it is proven that the derivatization reaction has advanced. The results apparently indicate that the reaction depth of derivatization under optimum conditions advanced with in the detection depth of XMA.

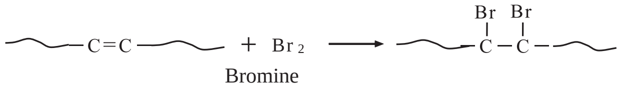
3. 3 Confirmation of the derivatization-XMA effectiveness

It is known that the amine promotes the dehydrochlorination of PVC and generates vinyl

Table 1 Optimal derivatization conditions for the functional groups.

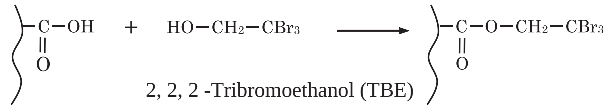
Double bonds

	(ABS)	(PVC)
Reaction reagent :	Br_2	Br_2
Solvent :	Methanol	Acetone / methanol (2/1)
Concentration of Br_2 :	3 %	3 %
Reaction temp. :	0 ℃	0℃
Reaction time :	10 min	30 min
Washing :	5 min × 3 times washing	
Drying :	Vacuum drying (R.T., overnight)	



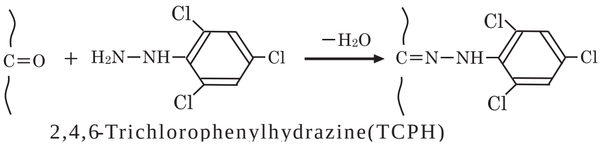
Carboxyl groups

Reaction reagent : 2, 2, 2 - tribromoethanol (TBE)
Catalyst : Pyridine
Dehydration agent : Dicyclohexyl carbodiimide(DCC)
Reagent component : TBE 70mg / Pyridine 70 µl / DCC 50 mg (in 50ml vial vessel)
Reaction temp. : 110 ℃
Reaction time : 2 h
Drying : Vacuum drying (110℃, overnight)



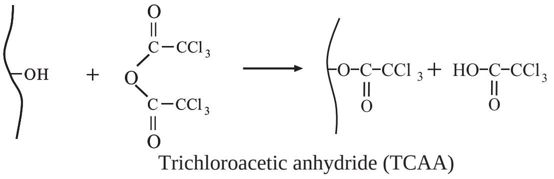
Ketone groups

Reaction reagent : 2, 4, 6 -Trichlorophenylhydrazine(TCPH)
Solvent • Catalyst : Acetic acid
Conc. of reagent : 2.5% (Wt/Vol)
Reaction temp. : 90℃
Reaction time : 30 min
Washing : 5 min (R.T.) dipping
Drying : Vacuum drying (R.T., overnight)



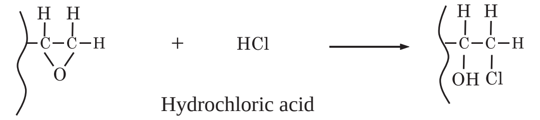
Hydroxyl groups

Reaction reagent : Trichloroacetic anhydride
Amounts of regent reaction : 50μl (in 50ml vial vessel)
Temp. : 60 ℃
Reaction time : 90 min
Drying : Vacuum drying (60℃, 30h)



Epoxy groups

Reaction reagent : Hydrochloric acid
Amounts of reagent : 300μm (in 50ml vial vessel)
Reaction temp. : Room temp. (25℃)
Reaction time : 60 min
Drying : Vacuum drying (80℃, 15h)



groups in PVC.[5)] Therefore, the effectiveness of derivatization-XMA was proven by measuring the actual distribution of the vinyl groups in amine-degraded soft PVC. A soft PVC sheet of 3-mm thickness was placed in the inner lid part of a vial into which N, N, N', N'-tetramethyl-1, 6-hexanediamine was poured and then the vial was heated at 80°C and 110°C for 5 hrs and 20 hrs, respectively. The treated sheet was cut perpendicularly to the surface with a microtome. The cut film of 1-μm thickness and the cut surface were line analyzed by micro-IR and derivatization-XMA, respectively in the depth direction.

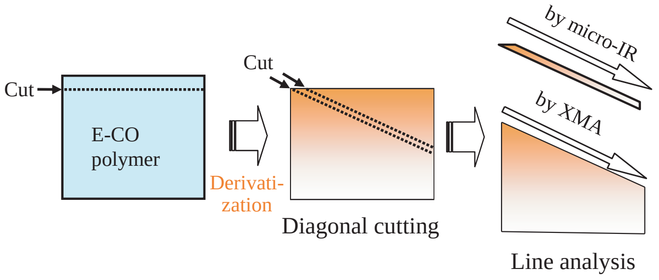


Fig. 3 Scheme for the depth measurement of derivatization reaction.

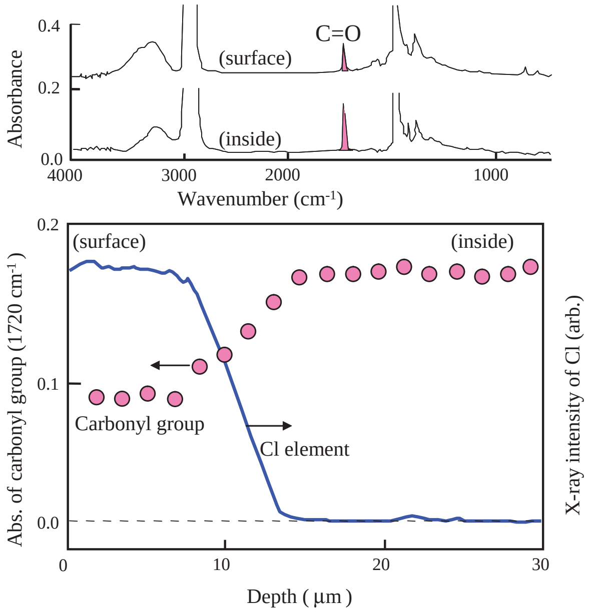


Fig. 4 IR spectra of derivatized E-CO polymer (upper) and depth profiles of the carbonyl groups and Cl elements in derivatized E-CO polymer (lower).

The depth profiles of the vinyl groups and Br elements obtained by both methods are showed in **Fig. 5**. As can be seen in Fig. 5, the tendencies of the distribution of vinyl groups and the distribution of Br elements clearly agree after heating at 110°C for 5 hrs. This result indicates that the distribution of the vinyl groups is correctly measured by derivatization-XMA. Furthermore, in the case of the sample treated at 80°C for 20 hrs, the distribution of vinyl groups is clearly measured by derivatization-XMA, while it is not measured at all by micro-IR. The results reveal that the sensitivity of derivatization-XMA was higher than that of micro-IR by approximately 30 times.

4. Applications

4. 1 Depth analysis of the carboxyl groups in polyamide-6

It is well known that polyamide-6 degrades due to hydrolysis of the amide bond under environmental

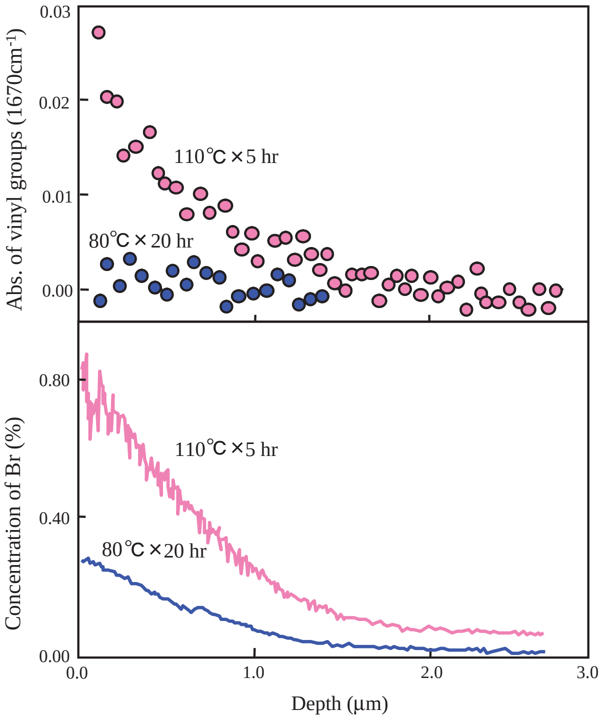


Fig. 5 Depth profiles of vinyl groups in amine-degraded PVC obtained by micro-IR (upper) and derivatization-XMA (lower).

conditions, being affected by water, heat and light. During the degradation of polyamide-6, carboxyl groups and amino groups generate at the end of the polymers. Generally, measurement of the molecular weight distribution, quantitative analysis of the end groups and other methods are used to estimate the degradation of the polymer. However, these methods show only averaged information and do not show distribution in the depth direction. Therefore, the depth profile of carboxyl groups generated in degraded polyamide-6 was measured by derivatization-XMA. Polyamide-6 (thickness: 3 mm) was degraded by an accelerated weathering device (Sunshine weather meter: SWM).

The depth profiles of the carboxyl groups in the degraded and undegraded polyamide-6 are shown in **Fig. 6** (lower). The formation of carboxyl groups is observed from the surface and gradually decreases until ca. 300-μm depth, at which it levels. These results suggest that hydrolysis occurred during the weathering of the polymer. The number average molecular weights of polyamide-6 were also measured from the surface to ca. 100-μm depth. As a result, the average molecular weights of undegraded and degraded polyamide-6 were found to be 11,000 and 5,800, respectively. Since the molecular weight of degraded polyamide-6 decreased to approximately half of the undegraded polyamide-6, the carboxyl groups detected by this method are the end groups generated by hydrolysis of the amide bonds.

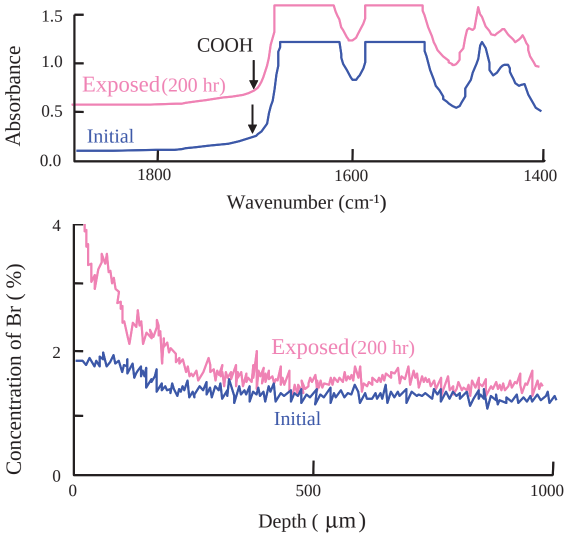


Fig. 6 IR spectra of polyamide-6 exposed to SWM at ca. 20-μm depth (upper) and depth profiles of the carboxyl groups in polyamide-6 exposed to SWM obtained by derivatization-XMA (lower).

IR spectra at ca. 20-μm depth in the same samples are shown in Fig. 6 (upper). Since the absorptions of the carboxyl groups overlap with the left side of the large absorption of the amide groups, it is certainly difficult to estimate the extent of the degradation of polyamide-6 by IR. Therefore, the derivatization-XMA method developed in this paper is especially powerful for degradation studies of polyamides and polyesters.

4. 2 Depth analysis of the carbonyl groups in E-CO polymer

Photodegradable E-CO polymer film has been used in agriculture. It is known that this polymer undergoes Norrish -I and -II type photolysis by the 290-nm light absorption of carbonyl groups.[6, 7] Therefore, the changes in quantity of carbonyl groups were investigated in the E-CO polymer films (thickness: 50 μm) with different initial carbonyl group concentrations (1 and 3 %) exposed to xenon light. A Shimadzu SUNTESTER XF-180 (light strength: 11 mW/cm^2 at 300 ~ 400 nm) was used as the xenon light source.

The relationship between irradiation time and elongation at the breaks is shown in **Fig. 7** (upper) and the relationship between irradiation time and the concentration of carbonyl groups (equal to Cl concentration) is shown in Fig. 7 (lower). As can be seen in Fig. 7, for the copolymer with the higher initial concentration of carbonyl groups, the decrease in elongation at the breaks is faster and the increase in carbonyl groups is also faster. The depth profiles of the carbonyl groups in the degraded E-CO polymer are shown in **Fig. 8**. The carbonyl groups increased in both the exposed surface and the back surface due to exposure of xenon light. The tendency of these distributions is similar to that of usual transparent polymers degraded due to oxidation.

4. 3 Depth analysis of the vinyl groups in the soft PVC sheet backing polyurethane foam (PUF)

The soft PVC sheet backing PUF has been used as an interior material in cars. It is well known that heat and light promotes the dehydrochlorination of PVC and generates vinyl groups in PVC. Therefore, the depth profile of the vinyl groups generated in heat-degraded soft PVC was measured by derivatization-XMA. The soft PVC sheet was heated at 100°C for 400 hrs or exposed to xenon light at 110°C for 400 hrs.

The depth profiles of the vinyl groups in the degraded soft PVC are shown in **Fig. 9**. As a result, the degradation mechanism of the PVC sheet backing PUF was clearly elucidated as follows. In the heat test, the vinyl groups in the PVC layer increased at the interface of the two layers rather than at the surface. The results showed that amine catalyst originally contained in the PUF layer moved to the PVC layer and promoted dehydrochlorination of the PVC layer.

5. Conclusions

The "derivatization-XMA" method, which can measure the distribution of 0.05 % functional groups in a polymer with a 3-μm lateral resolution, was established. This method was successfully applied to evaluate the deterioration of actual polymeric materials in use such as polyamide-6, E-CO polymer and the soft PVC sheet backing PUF. This method definitely proved to be useful for the study of the degradation mechanism and the evaluation of the degradation degree.

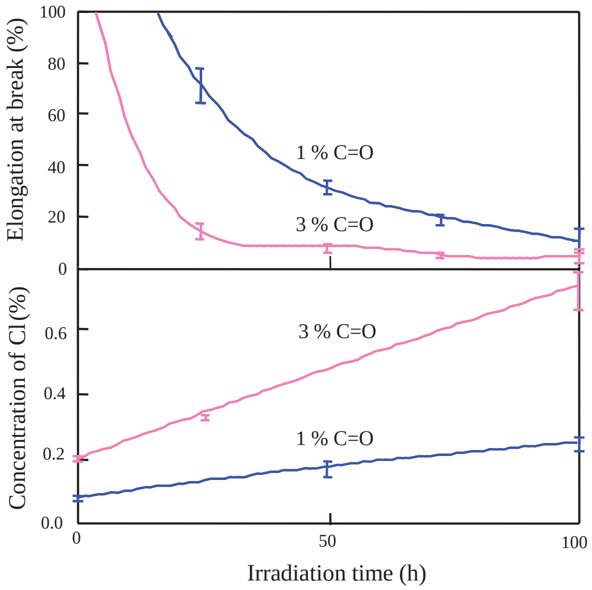


Fig. 7 Relationship between irradiation time and elongation at break (upper) and relationship between irradiation time and concentration of Cl of the carbonyl groups (lower) in E-CO copolymer exposed to xenon light.

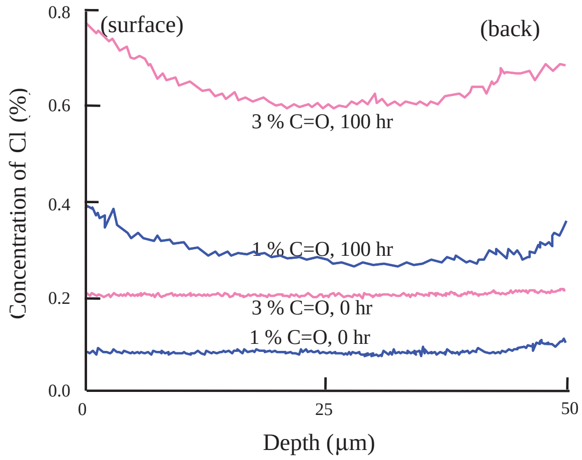


Fig. 8 Depth profiles of the carbonyl groups in E-CO copolymer films exposed to xenon light.

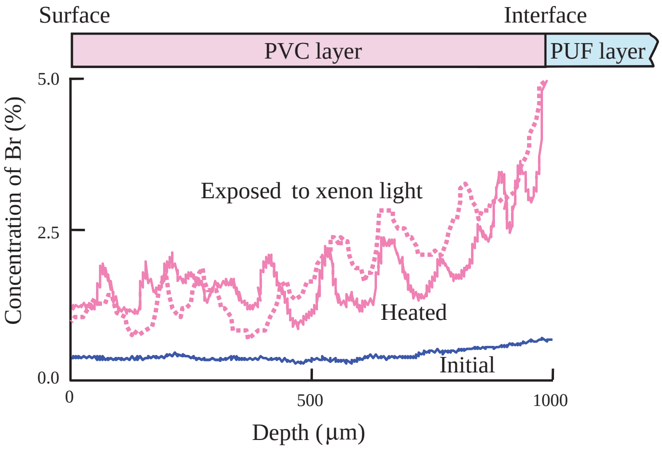


Fig. 9 Depth profiles of the vinyl groups in the degraded soft PVC backing polyurethane form (left).

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