

A thermal oxidative degradation study of triallyl isocyanurate crosslinking moiety in fluorinated rubber by two-dimensional infrared correlation spectroscopy

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ABSTRACT

Thermal degradation of crosslinking moiety in fluorinated rubbers was studied with a new method using spatial-dependent infrared (IR) microscopy and two-dimensional (2D) IR correlation spectroscopy. Upon heating the fluorinated rubber, initially the amount of crosslinker decreased followed by generating another chemical species with carbonyl substituent with IR absorption at around 1730 cm⁻¹, implying generation of carboxylic acids forming intermolecular hydrogen bonding. Furthermore, projection 2D IR correlation analysis revealed that another chemical species with IR absorption at around 1755 cm⁻¹ generates, indicating that further degradation progresses upon heating and intermolecular hydrogen bonding were broken. As a result, the multi-step degradation process of the crosslinker in the fluorinated rubber could be detected by combination of spatial-dependent IR microscopy and projection 2D IR correlation spectroscopy.

1. Introduction

Here we describe a method for characterizing degradation of small amount of crosslinkers used for fluorinated rubbers (FRs) by taking advantages of infrared (IR) spectroscopy. In the FRs, the adjacent polymer chains are tied together by crosslinker to develop three-dimensional network of fluorinated chains, which improves their elastic properties. Importantly, the crosslinker essentially affects the long-term stability of the materials. For example, the crosslinker spontaneously undergoes thermally induced degradation under an aerobic condition. In the cases of FRs, the degradation of crosslinker is significant since main chain of polymer has a lot of thermally stable C–F bonds [1]. The degradation often induces cleavage of the crosslinking and eventually deteriorates the mechanical properties, while the quantity of the crosslinker in the FR is usually very small. Consequently, by probing the variation of the crosslinker, it may become possible to elucidate an onset of the degradation of the FR.

A general concept of the proposed method is shown in Fig. 1. At first, an FR sample is subjected to degradation by applying heating treatment to one side of it. A set of IR spectra is then collected under

varying spatial position. The crosslinkers in the FR sample go through thermal degradation depending on the distance from the heating source. The carbonyl group, which is often included in crosslinker, shows strong IR absorption. This preferable feature is especially suitable for the detection of small amount of crosslinker in FR sample. In sort, the variation of molecular structure, such as cleavage and subsequent extraction of H atom caused by the thermal degradation, may result in different IR spectral feature depending on the progress of the alteration. Consequently, the detailed analysis of spatially induced variation of the IR spectra provides an interesting opportunity to examine the progress of degradation by circumventing the need of measuring multiple samples each degraded at different degradation level.

Spatially dependent change in the IR spectral feature is readily captured when the thermal treatment is applied to an FR sample including isocyanurate crosslinker. The IR spectra is then subjected to two-dimensional (2D) correlation spectroscopy [3,4] coupled with projection treatment [5–7]. 2D correlation spectrum derived from the IR spectra revealed the presence of multiple reaction products developed by the degradation of the crosslinker.

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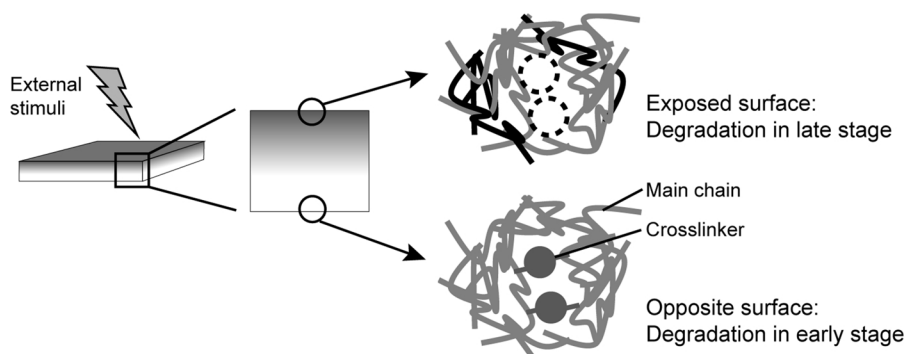
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One sample provides information about degradation process.

Fig. 1. A schematic illustration of the degradation study method proposed in this study.

2. Theory

2.1. Projection treatment

Projection operation aims to selectively remove the specific signal contribution from spectra by sorting out original spectra \mathbf{A} into two separate sets \mathbf{A}_p and \mathbf{A}_n , where \mathbf{A}_p is fully aligned with a chosen projecting vector and \mathbf{A}_n is orthogonal to the same vector. The projection matrix \mathbf{R}_y is defined as

$$\mathbf{R}_y = \mathbf{y}(\mathbf{y}^T \mathbf{y})^{-1} \mathbf{y} \quad (1)$$

where \mathbf{y} is a projection vector \mathbf{y} and the superscript T denotes the transpose operation of the matrix. The m -by- m matrix \mathbf{R}_y works as a projector for the space spanned by \mathbf{y} . The projected data matrix \mathbf{A}_p is obtained as

$$\mathbf{A}_p = \mathbf{R}_y \mathbf{A} \quad (2)$$

The projected data \mathbf{A}_p represents the projection of \mathbf{A} onto the abstract space spanned by \mathbf{y} . The portion of \mathbf{A} projected onto the space spanned by \mathbf{y} will have the same trend of \mathbf{y} . In other words, all signals contained in \mathbf{A}_p are fully synchronized.

The corresponding null-space projection is carried out as

$$\mathbf{A}_n = (\mathbf{I} - \mathbf{R}_y) \mathbf{A} = \mathbf{A} - \mathbf{A}_p \quad (3)$$

where \mathbf{I} means m -by- m identity matrix. \mathbf{A}_n is the residual after the removal of \mathbf{A}_p from \mathbf{A} by using the information contained within \mathbf{y} . Consequently, the null-space projection selectively eliminates the portion of dynamic spectra which is synchronized with \mathbf{y} .

By using a spectral intensity change at specific wavenumber where a peak is observed as the vector \mathbf{y} , \mathbf{A}_n becomes free from the signal contribution from the trend associated with \mathbf{y} . Such an ability is suitable for the elimination of specific trend from spectra. In fact, this advantageous feature becomes especially useful in selectively removing overwhelming feature appearing on 2D correlation spectra.

2.2. 2D correlation spectra

Given m -by- n spectral data matrix \mathbf{A} consisting m spectra with n spectral variables, we define a set of dynamic spectra $\tilde{\mathbf{A}}$ by subtracting a reference spectrum, typically the average spectrum. The synchronous and asynchronous correlation spectra, Φ and Ψ , are obtained as

$$\Phi = \frac{1}{m-1} \tilde{\mathbf{A}}^T \tilde{\mathbf{A}} \quad (4)$$

$$\Psi = \frac{1}{m-1} \tilde{\mathbf{A}}^T \mathbf{N} \tilde{\mathbf{A}} \quad (5)$$

where matrix \mathbf{N} is the so-called Hilbert-Noda transformation matrix defined by

$$N_{ij} = \begin{cases} 0 & \text{if } i = j \\ 1/\pi(j-i) & \text{otherwise} \end{cases} \quad (6)$$

The intensity of a synchronous correlation spectrum Φ_{ij} represents simultaneous changes of two spectral intensity variations measured at i th and j th spectral variables during the collection of the spectra. In contrast, an asynchronous correlation spectrum Ψ_{ij} means the out-of-phase or sequential changes of spectral intensities measured at i th and j th spectral variables.

3. Experiment

An FR was prepared with tetrafluoroethylene hexafluoropropylene vinylidene fluoride (Dai-El G912, Daikin Co. LTD.), 2 phr of triallyl isocyanurate (TAIC, Tokyo Gosei), and 0.75 phr of 2,5-dimethyl-2,5-di(*t*-butyl peroxy)hexane as an initiator (Fig. 2). After press molding of this mixture at 170 °C for 10 min, followed by curing at 180 °C for 4 h, a 1 mm thick FR was obtained. A schematic image for preparation of heated FR and samples for IR microscopy is shown in Fig. 3. The FR on glass plate was heated with a hot stage whose temperature was set at 250 °C. After heating for 5 h, the heated sample was cut and sliced against cross sectional direction using microtome. The sample thickness was set about 20 μm. Spatial-dependent IR spectra were taken using Thermo Nicolet Continuum. Spatial resolution is about 80 × 80 μm and 12 spectra were taken from the heated side to opposite side. The first 7 spectra from the heat side were used for the subsequent analysis.

4. Results and discussion

4.1. Spatial-dependent IR spectra

Fig. 4 illustrates the spatial-dependent IR spectra of the heated fluorinated rubber over 1850 – 1600 cm^{-1} region. Peaks observed at around 1700 cm^{-1} are specific to C=O vibrational modes of carboxyl

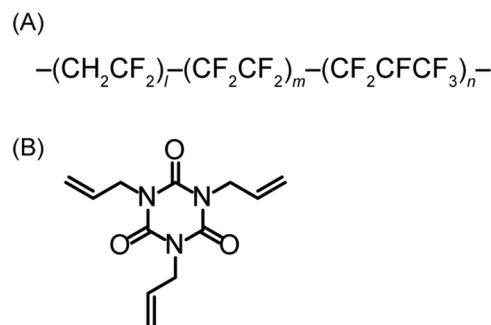


Fig. 2. A) Monomer structures of fluorinated rubber used in this study. (B) Molecular structure of triallyl isocyanurate (TAIC).

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