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ORIGINAL ARTICLE

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Effect of postcure conditions on the dynamic mechanical behavior of water-based polymer–isocyanate adhesive for wood

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Abstract To study the effect of postcure conditions on the viscoelastic behavior of water-based polymer isocyanate adhesives for wood (API adhesive), dynamic mechanical analysis (DMA) was performed for a simplified model of API adhesives under various postcure conditions. These conditions were achieved by storing the samples at room temperature or by heating them in an oven. Fourier transform infrared (FT-IR) spectroscopy was performed to test for residual isocyanate groups (NCO) and isocyanate derivatives to elucidate the reaction mechanism under the postcure conditions. DMA revealed that the postcure conditions led to wide variations in the viscoelastic behaviors of API films. FT-IR analysis confirmed the decrease of residual isocyanate during postcure treatments. However, the complete consumption of isocyanate could not be achieved under the postcure conditions. A good correlation was found between the DMA result and the chemical changes in the API samples heated above 140°C. However, no correlation was observed in the case of the samples heated at temperatures less than 140°C. This implies that postcure conditions led to a difference in the reaction chemistry of API.

Key words Water based · Isocyanate adhesive · Postcure · Dynamic mechanical analysis

Introduction

Water-based polymer–isocyanate adhesives, also referred to as aqueous polymer isocyanate (API) adhesives, are widely used in timber processing and plywood manufacturing.[1–4] These adhesives are composed of a water-based polymer mixture and an isocyanate crosslinker. The isocyanate group (NCO) of the crosslinker allows reaction with the components of the water-based polymer mixture and a wood substrate during API preparation and application.[5] Many studies have been conducted on the fundamental reactions and operating performance of these adhesives and on the possible improvements in the adhesive properties.[6–9] It is known that the major NCO reactions in this adhesive system are those with water or a hydroxyl group to form urea or urethane. Allophanate and biuret groups are possible by-products; however, such reactions are rare.[7,8]

It has been established that the complete consumption of the isocyanate group in the API takes a long time in practical applications. The consumption of these residual isocyanate groups occurs during certain postcuring treatments such as storage and heat treatment.[7–10] The changes in the properties of API during the postcuring treatment have been the focus of many investigations conducted over the past several years, because it is important to design the treatment conditions in order to optimize the mechanical properties of the API adhesives.[7–12] However, in these investigations, (1) the effect of the heat treatment has not been taken into account; (2) because relatively simple types of API samples were considered, the postcuring mechanism of these adhesives has not been completely understood; and (3) the data obtained is not sufficient to reveal the correlation between the adhesive properties and the details of the reaction mechanism in a solid state. In order to obtain some insight into the reaction mechanism and the formation of a crosslinking structure during postcure, a systematic study is necessary.

Dynamic mechanical analysis (DMA) is a useful method for evaluating the viscoelastic behavior of polymer materials. In the study of API adhesives, DMA is mainly used to investigate density changes in the crosslinking structure.[13,14] Taki et al.[15] reported correlation between the DMA results and the strength of an API sample. Umemura et al.[16] performed the DMA measurement of a reaction product of emulsion isocyanate (EMDI) and water to study the post-

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curing process of isocyanate and water. The purpose of the present study was to investigate the effect of the postcuring conditions on the DMA spectra of a simplified model of API. Because the dispersion of the crosslinker in the API and the curing process are strongly related to the species and properties of the base mixture, we selected a model compound similar to practical applications for understanding the postcuring process of the API adhesives. Fourier transform infrared (FT-IR) spectroscopy was employed to investigate the change in the chemical structure of the API films.

Experimental

Materials

Poly(vinyl alcohol) (PVOH; Sigma-Aldrich, Tokyo, Japan) used in this experiment was 99+% hydrolyzed, and its molecular weight was in the range of 89 000–98 000. It was gradually added to water and stirred at 80°C for 1 h to obtain a 15% (w/w) solution and subsequently was stored at room temperature and stirred for 1 day.

Styrene–butadiene copolymer latex (SBR) was specially synthesized by Nippon A&L (Osaka, Japan) and was used as received. It had a solid content of 51.9%, viscosity of 180 mPa·s (at 25°C), pH of 6.4, and styrene/butadiene ratio of 60/40 (by weight).

Polymeric diphenylmethane diisocyanate (pMDI), referred to as Milionate MR200 (Nippon Polyurethane Industry, Tokyo, Japan), was used as received. It was mainly composed of 4,4′-MDI oligomers and did not contain solvents such as toluene or xylene. It had a viscosity of 163 mPa·s (at 25°C), an isocyanate molar concentration of 7.27 mmol/g (i.e., an isocyanate content of 31.0% w/w), and a specific gravity of 1.23 (at 25°C).

Water used in the experiment was purified by using an Elix 5 water purification system (Millipore Japan, Tokyo, Japan) and its specific electrical conductivity was maintained to be less than 0.5 μS/cm.

Sample preparation

A water-based polymer mixture was prepared by mixing the PVOH solution and SBR with the same weight ratio. It was mixed for 1 min and degassed for 20 s using a HM-500 hybrid mixer (Keyence, Tokyo, Japan). Fifteen parts of pMDI was added to the base mixture, and they were mixed together for 1 min and degassed for 30 s. The mixed glue (simplified API) was cast onto a smooth Teflon sheet and stored at 23°C and 50% relative humidity for 4 days to yield films. The obtained films averaged ca. 0.15 mm in thickness. Thereafter, the films were subjected to the following three different postcuring conditions: (1) storage at room temperature for various periods, (2) storage at room temperature for 4 days and heating at various temperatures up to 200°C for 2 h, and (3) storage at room temperature for 4 days and heating at various temperatures for 10 min. For comparison, PVOH and SBR films were also prepared by casting and were stored at room temperature for 4 days and annealed at 100°C for 2 h before the measurements.

Measurements

DMA was performed on a DVA-200 dynamic viscoelastometer (ITK, Kyoto, Japan). The tests were performed using extension mode at a frequency of 5 Hz and a heating rate of 2°C/min with the temperature ranging from –50° to 250°C under a nitrogen atmosphere.

FT-IR spectra were measured with a Magna-IR 860 spectrometer (Nicolet, Tokyo, Japan) using the KBr tablet method. Each sample was scanned 128 times with a resolution of 4 cm^{-1} between 400 and 4000 cm^{-1}. The obtained spectra were normalized with the peak height of the C-H stretching band at approximately 2920 cm^{-1}.

Results and discussion

DMA results

Figure 1 illustrates the temperature dependence of the storage modulus (E') and loss factor ($\tan\delta$) of the API, SBR, and PVOH films. The API film was stored for 4 days without heating. E' is a measurement of the material stiffness. The loss tangent $\tan\delta$ represents the ratio of energy dissipated to the energy stored per cycle. The SBR and PVOH films clearly exhibit a $\tan\delta$ peak at around 30° and 70°C, respectively, that are attributed to the relaxations due to their glass transitions. Meanwhile, in the $\tan\delta$ curve of the API film, four peaks are observed at around 30°, 70°, 110°, and 170°C. The peaks at 30° and 70°C are attributed to the glass transitions of the SBR and PVOH films, respectively, that are smaller than the peaks observed in the SBR and PVOH spectra. This is because their relative concentration is low in the film, and because the molecular motion in the main chain is restricted by a crosslinking structure produced by an isocyanate reaction.

The E' spectrum of the API adhesive exhibits two drops starting at 30° and 110°C and also a small peak at approximately 170°C. The relaxation at 170°C could be attributed to a residual isocyanate reaction during the DMA measurement. A possible reason is that the crosslinking structures produced by the isocyanate reaction could lead to an increase in the E' value. Thereafter, E' decreases again with an increase in the measurement temperature. The peak of E' has also been observed by other researchers in the DMA spectra for incompletely cured API adhesives.[14] The IR spectroscopy of the films will provide further evidence for the interpretation of this observation.

Figure 2 shows the DMA spectra of the API films stored for different periods at room temperature. As aforementioned, the $\tan\delta$ curve of the film stored for 4 days exhibits four peaks at 30°, 70°, 110°, and 170°C. The former two peaks are due to the glass transitions of SBR and PVOH,

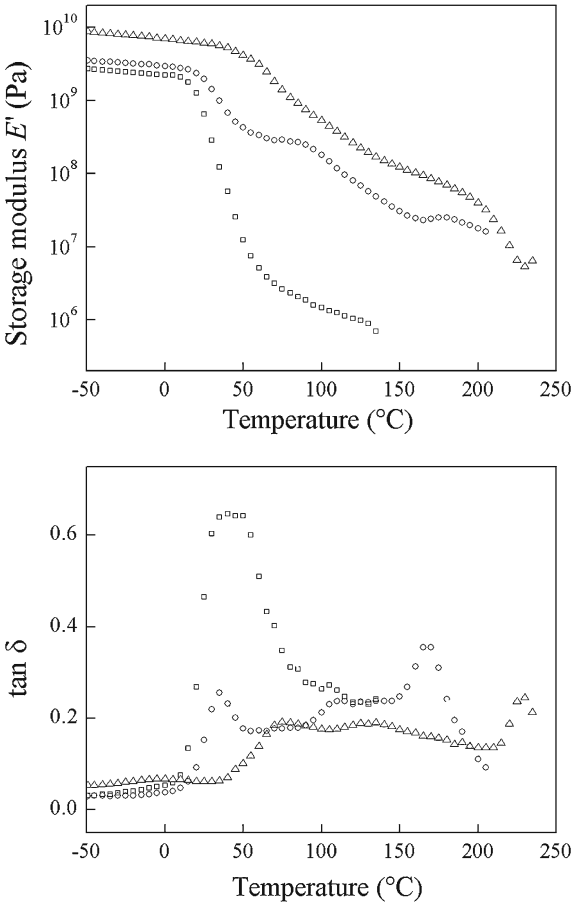

Fig. 1. Dynamic mechanical analysis (DMA) plots of styrene–butadiene copolymer latex (SBR), aqueous polymer isocyanate (API), and poly(vinyl alcohol) (PVOH) films (100°C, 2 h). *Upper*, storage modulus E'; *lower*, loss factor tan δ; *squares*, SBR latex; *open circles*, API; *triangles*, PVOH

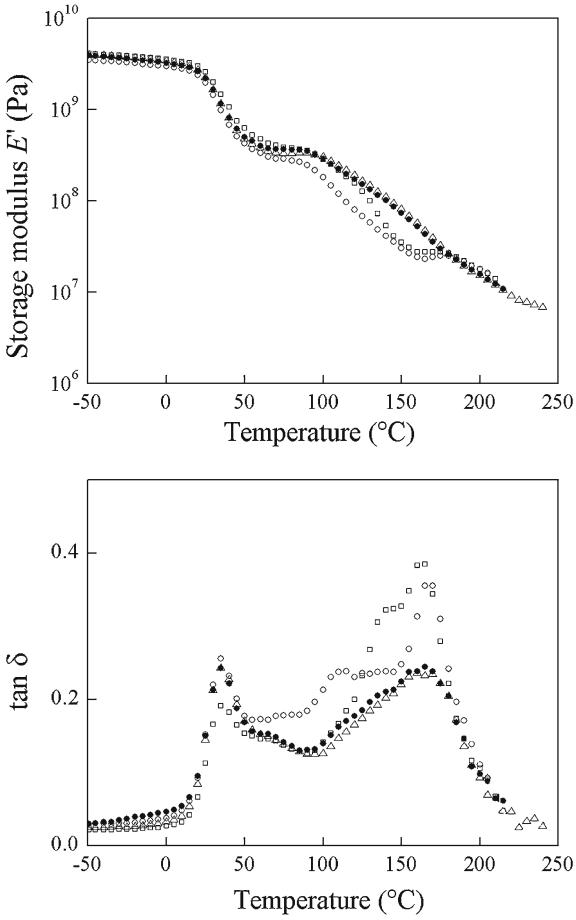

Fig. 2. DMA plots of API for different conditioning durations. *Upper*, storage modulus E'; *lower*, loss factor tan δ; *open circles*, stored 4 days; *squares*, stored 12 days; *filled circles*, stored 25 days; *triangles*, stored 60 days

and the peak at 170°C is related to the reaction of the residual isocyanate. The peak at 110°C cannot be explained. This peak shifts to 140°C for the film stored for 12 days. For the films stored for 25 and 60 days, this peak disappears or converges with the peak related to the residual isocyanate reaction and forms a single peak at 170°C. A corresponding increase in E' in the range of 100° to 150°C is observed simultaneously. Several studies reported that the predominant postcuring process of an API adhesive for storing at room temperature is due to the forming of a urea linkage, while urethane, allophanate, and biuret will also permit.[7,8] The increase in these chemical linkages can enhance the properties of the API adhesives, such as strength, modulus, and thermal stability. Here, we have assumed that the shift in the tan δ peak at 110°C is mainly due to the increase in the number of chemical structures produced during the storage process.

As the isocyanate groups were consumed and the number of chemical structures increased during the storage process, the films became stable in both mechanical and chemical properties. As a result, no significant difference in the E' of the samples stored for 25 and 60 days was observed. Correspondingly, only one transition of tan δ was observed in the high-temperature region above 100°C, and no significant changes in the peak shape could be observed. This data also indicated that API was not stable at storage times less than 25 days at ambient temperature.

Figure 3 illustrates the DMA spectra of the API films heated at various temperatures for 2 h. The most distinguished feature of the DMA spectra is that for the samples treated at 140°C, the E' peak at 170°C attributed to the residual isocyanate reaction disappears. This indicates that the corresponding reaction can be promoted by a heat treatment at 140°C. For the samples heated below 140°C, the value of E' increases with the temperature in the range of 100° to 150°C. This behavior is similar to that observed in the spectra of the samples stored at room temperature for less than 25 days (Fig. 2). During the heat treatment, the reaction between the water-based polymer mixture and the residual isocyanate may easily occur because of the increase in the molecular motion. Referring to the abovementioned discussion, the increase in E' could be due to the chemical structures produced during the heat treatment. The E' value for the samples treated at 180°C was higher than that of samples treated at 140°C in the high-temperature region above 100°C. This indicates that the heat treatment at 180°C

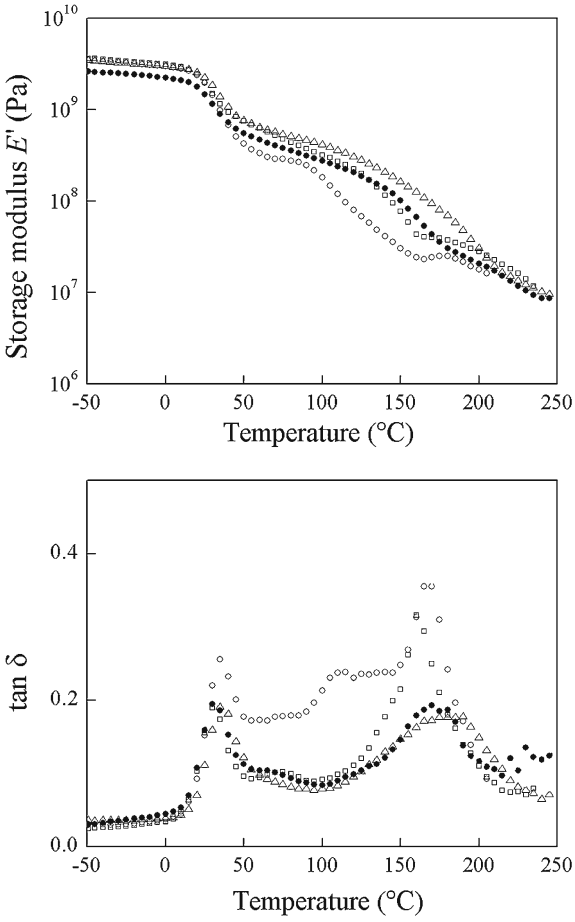

Fig. 3. DMA plots of API for different treatment temperatures with duration of 2 h. *Upper*, storage modulus E'; *lower*, loss factor tan δ; *open circles*, not heated (4 days, same sample as in Fig. 2); *squares*, 120°C; *filled circles*, 140°C; *triangles*, 180°C

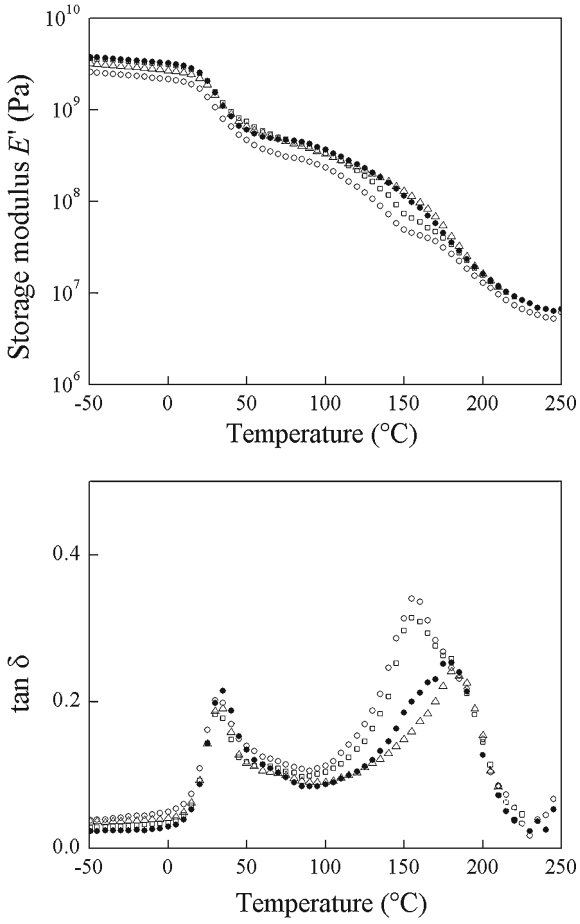

Fig. 4. DMA plots of API for thermal treatment for 10 min. *Upper*, storage modulus E'; *lower*, loss factor tan δ; *open circles*, 100°C; *squares*, 120°C; *filled circles*, 140°C; *triangles*, 180°C

promotes further isocyanate consumption from that consumed at 140°C.

In order to elucidate the temperature dependence of the viscoelastic behavior of the API adhesives, it is necessary to consider the influence of heating time. Figure 4 presents the DMA spectra of the API adhesive heated at various temperatures for 10 min. Observing in the temperature range between 100° and 150°C, E' increases with the curing temperature for samples treated below 140°C. Simultaneously, the E' peak at 170°C observed for the samples treated at 100° and 120°C disappears for the samples treated at 140° and 180°C. This result indicates that the heat treatment at 140°C is effective in promoting the isocyanate reaction and increasing E'. In contrast, it should be noted that no significant increase in E' can be observed in the samples heated in an oven at 180°C for 2 h (Fig. 3). This difference indicates that the change in E' depends not only on the heating temperature but also on the heating time.

FT-IR spectra

FT-IR analysis was employed to investigate the change in the chemical structure of the API films under the different postcuring conditions. In the previous studies of the FT-IR spectra of isocyanate adhesives, the curing degree was evaluated from the intensity of the band at 2270 cm^{-1} that was assigned to an asymmetric isocyanate stretching; the presence of the isocyanate derivatives has been usually detected due to the presence of absorption bands in the C=O stretching region from 1740 to 1620 cm^{-1}.[7,8]

In the present API sample, quantitative analysis of the NCO derivatives is challenging because of the overlapping of the C=O groups of urea, urethane, and various secondary products. Therefore, we discuss only the change in the relative intensity of the bands in the C=O region.

Figure 5 illustrates the FT-IR spectra of the API films stored for different periods at room temperature. The intensity of the isocyanate band at 2270 cm^{-1} decreased gradually with an increase in the storage period, indicating that the residual isocyanate reacted continuously during storage. The band of the isocyanate absorption at 2270 cm^{-1} was still detected in the spectrum of a sample stored for 60 days. This indicated that complete consumption of the residual isocyanate in the API samples was difficult when stored at room temperature. This result agrees with those of previous studies.[7,8] It is believed that the isocyanate group can react quickly with water molecules in the atmosphere

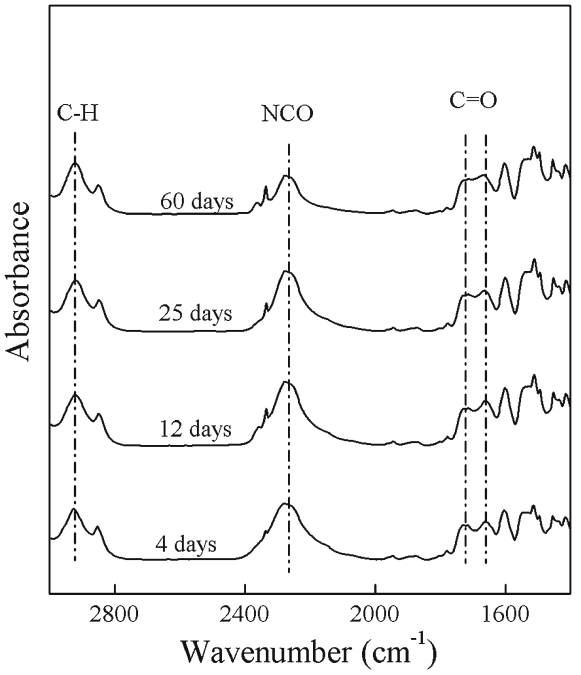

Fig. 5. Fourier transform infrared (FT-IR) spectra of API for different conditioning times

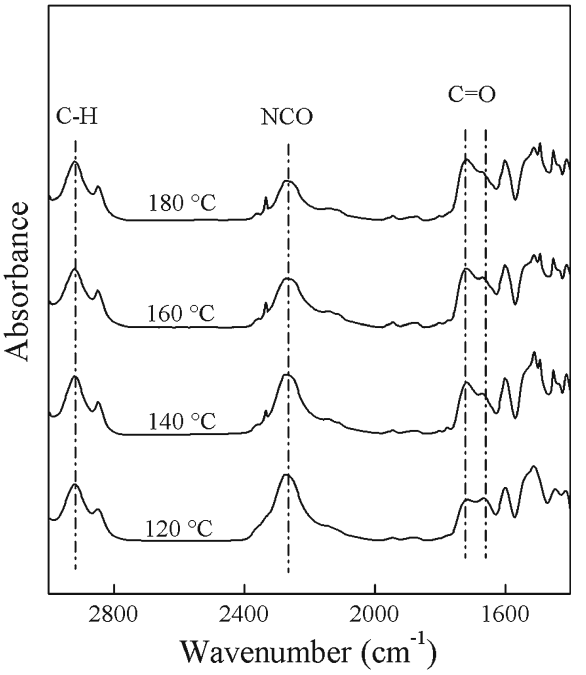

Fig. 6. FT-IR spectra of API for different treatment temperatures with duration of 2 h

to form an amine structure. This amine can then react with another isocyanate group to yield a urea linkage. The incomplete consumption of the residual isocyanate indicated that water vapor from the atmosphere could not easily react with the residual isocyanate group. It could have been because water vapor diffusion was obstructed due to the increase in the number of chemical structures in the film. In other words, the residual isocyanate reaction in the film depends on the diffusion of water vapor into the film. This reaction mechanism can be observed in the moisture curing of polyurethane adhesive.[17] In this case, the film thickness and the humidity in the environment might play an important role in the curing process. Taki[12] has reported that the consumption of the residual isocyanate in an adhesive applied to a wood sample is faster than that in a film. This could also be due to the difference in the reaction environments of the residual isocyanate.

In the C=O region, two major peaks were observed at 1660 and 1720 cm^{-1}. These peaks exhibited a slight change in shape with an increase in the storage period. This change is insignificant for discussion of the relationship between chemical change and storage time.

The effect of the heating temperature on the FT-IR spectra of the API film is shown in Fig. 6. A decrease in the characteristic absorption peak of the isocyanate groups at 2270 cm^{-1} was observed with an increase in the treatment temperature, supporting the observation that the increase in temperature promotes the residual isocyanate reaction. This peak was still detected after heating the sample at 180°C for 2 h. This result indicates that the complete consumption of the residual isocyanate in the API sample could not be achieved easily even at high temperature. This phenomenon observed in the case of API adhesives has not been thoroughly discussed in other studies. The reason for this is similar to the crosslinking reaction of thermoset systems such as epoxy and phenolic resin.[18,19] An increase in the temperature causes the film to soften and promotes a continuous reaction between the residual isocyanate and the functional groups in the adhesive system. As the reaction proceeds, the resulting chemical structures can lead to an increase in the viscosity of the film; thus, the reactions are highly restricted. In this situation, the reaction is governed by a reduction in molecular mobility. For a continuous reaction, additional thermal energy is required to soften the chemical structures.

Inspection of the C=O stretching regions reveals a difference between the spectra of the samples treated at 140° and 120°C. In the FT-IR spectrum of the sample treated at 120°C, the intensity of the band at 1720 cm^{-1} is weaker than that of the band at 1660 cm^{-1}. In contrast, for samples treated above 140°C, the intensity of the band at 1720 cm^{-1} is stronger than that of the band at 1660 cm^{-1}, indicating that a specific chemical change had occurred. The change in the C=O region of this API sample is mainly related to the isocyanate derivatives. Although the details of the chemical structure cannot be comprehended, this result indicates that a specific reaction of the residual isocyanate did occur in the case of the samples treated above 140°C. The products of this reaction might have caused the significant increase in E' of the films treated above 140°C.

Figure 7 shows the FT-IR spectra of the API film heated at various temperatures for 10 min. In the samples treated at temperatures above 140°C, the intensity of the band at 1720 cm^{-1} is stronger than that of the band at 1660 cm^{-1}. This tendency is similar to that for the samples heated for 2 h (Fig. 6), indicating that a corresponding chemical change

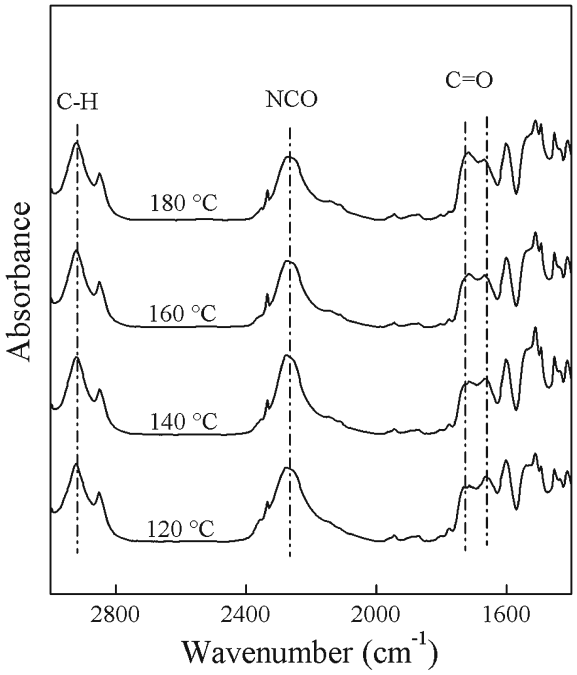

Fig. 7. FT-IR spectra of API after thermal treatment for 10 min at different temperatures

had rapidly occurred in the API films when the temperature exceeded 140°C. These results indicate that this chemical change is dependent on the temperature. This temperature dependency corresponds to that of the increase in E' from 100° to 150°C for API films treated above 140°C (Fig. 4). Therefore, this proves that the increase in E' of the API films treated at high temperatures (above 140°C) is related to the change in their chemical structures. Although the mechanism responsible for the reactions above 140°C is not fully understood, it is possible that phase transfer of the base polymer leads to softening of the system and promotion of the reaction.

These results support the observation that various postcuring conditions can lead to different reaction mechanisms and products. Therefore, when conducting DMA of API adhesives, the influence of reaction degree and postcure conditions must be taken into consideration.

Conclusions

The effect of different postcuring conditions on the dynamic mechanical behavior of API samples has been investigated. The results indicate that the complete consumption of the residual isocyanate is difficult to achieve even under high-temperature conditions. Various treatment conditions lead to different reaction mechanisms and produce different crosslinking structures. The change in the DMA spectra is related to the residual isocyanate reaction in the film. When the treatment temperature exceeds 140°C, the samples exhibit a rapid increase in E' in the high-temperature region, with a corresponding significant change in their chemical structures.

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