# The Slip-Reducing Mechanism in Polypropylene-Laminated Films Studied by FTIR and XPS

T. NISHIOKA,[1,*] Y. TANAKA,[2] K. KUME,[1] K. SATOH,[1] N. TERAMAE,[3] and Y. GOHSHI[4]

[1]Polymer Research Laboratory, Idemitsu Petrochemical Co., Ltd., 1-1 Anegasaki-Kaigan, Ichihara-shi, Chiba 299-01, Japan; [2]Polymer Applications Development Laboratory, Idemitsu Petrochemical Co., Ltd., 1-1 Anegasaki-Kaigan, Ichihara-shi, Chiba 299-01, Japan; [3]Research Center for Advanced Energy Conversion, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan; [4]Department of Industrial Chemistry, Faculty of Engineering, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

## SYNOPSIS

FTIR spectroscopy and X-ray photoelectron spectroscopy (XPS) were applied to examine the slip-reducing mechanism of polypropylene-laminated films. The relationship between the slip and the amount of lubricants was established on the basis of quantitative analysis of lubricants on the cast and laminated polypropylene film surfaces. The results suggested that erucic amide used as a lubricant for the cast film migrated from the film surface into the adhesive layer, probably due to intermolecular interactions (hydrogen bonds) with an isocyanurate–ether–polyol used as an adhesive for laminating the films. This enabled us to understand the slip-reducing mechanism in the laminated films. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

A variety of chemical products are added to commercially available polymer films to give diversity of qualities, and analysis of such additives are important for understanding the qualities of the polymers. It is necessary to know the distribution of the additives in the polymer films in order to clarify the physical properties of the film surfaces. Investigating the mechanism of the slip of polymer films is one of the important research themes.

It has been known that the slip of laminated films is influenced considerably by lubricants on their surfaces.[1] It has been also found in the process of our research that the slip substantially depends on the type and amounts of lubricants in the films. The favorable slip was obtained for polypropylene cast film when erucic amide, an unsaturated fatty acid amide, was used as a lubricant. We have found, however, that the slip of laminated films is extremely reduced when isocyanurate–ether–polyol is used as

an adhesive. It was found, on the other hand, that when behenic amide, a saturated fatty acid amide, was used as a lubricant for the cast films the slip of laminated films became favorable. The fact that the different kinds of lubricants and film processing conditions give different slips is considered to result from whether or not lubricant molecules migrate to the film surfaces. Hence, understanding of the migrating mechanisms of the lubricants in the film interior is important for the development of high-quality films. The present paper reports the slip-reducing mechanisms observed for laminating cast films containing erucic amide as additives.

Among the procedures currently employed for analyzing the surface conditions and chemical species distribution in the polymer substance, there exist infrared spectroscopies (including infrared microspectroscopy,[2-6] ATR,[7-11] and PAS[12]). Raman spectroscopy,[13] XPS,[14-18] SIMS,[19-21] and Rutherford back-scattering spectroscopy.[22] Investigations applying FTIR spectroscopy to analyze the interaction among different polymers were reported by Coleman et al.[23-27] They examined the intermolecular interaction between polar groups, such as the hydrogen bond, by observing spectral shifts of a specific IR absorption band.

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* To whom correspondence should be addressed.

To analyze an amount of lubricants on film surfaces quantitatively, we employed both FTIR ATR and XPS, which have often been used for studying the surfaces of polymer substances. To investigate the interaction between lubricants and adhesives, FTIR spectroscopy was employed.

## EXPERIMENTAL

### Sample Preparation

Polypropylene cast films were prepared by adding lubricants (1000 wt ppm) together with the least amount of an antioxidant, 3.6 wt %, to a random polypropylene powder ethylene content, followed by compounding and pelletizing the mixture and cast-forming procedures. The cast films were 30 $\mu$m in thickness. The lubricants added were erucic amide [$CH_3(CH_2)_7CH = CH(CH_2)_{11}CONH_2$] and behenic amide [$CH_3(CH_{20}CONH_2$]. Laminated films were made of both cast and drawn polypropylene films (to which no lubricants had been added and whose thickness was 20 $\mu$m) using isocyanurate–ether–polyol as an adhesive. The thickness of the adhesive layer was about 5 $\mu$m. Prior to the measurement of lubricant contents on the film surface by FTIR ATR and XPS, aging procedures were carried out at 40°C for 24 h for the cast film and at 40°C for 48 h for the laminated film, respectively. The aging was done in air.

### Measurement of the Lubricants on the Film Surface by FTIR ATR

FTIR ATR spectra were measured using Bio-Rad Laboratories Digilab Division, Model FTS-80, FTIR spectrometer with a Harrick variable-angle ATR attachment at an incident angle of 60°. A KRS-5 parallelogram 5 × 50 × 2 mm prism was used. The detector used was a wide-band MCT. The analyzed surfaces of the cast and laminated films were anti-corona-treated. The FTIR measurement was carried out with 4 cm$^{-1}$ resolution and 500 scans.

### Measurement of the Lubricants on the Film Surface by XPS

The XPS unit of Shimadzu, ESCA-1000, was operated at the X-ray voltage of 10 kV and current of 30 mA. All film surfaces were analyzed at a takeoff angle of 90°. The takeoff angle is defined as the angle between the surface normal and the axis of the analyzer lens. For insulating samples, charging was

encountered. Binding energy is 288.5 eV for the $C_{1s}$ peak. This peak is usually assigned a binding energy of 284.7 eV for an uncharged sample. No attempt has been made to correct for the shift and therefore all features in the spectra presented here occur at $\sim$ 3 eV higher binding energy than for an uncharged sample. No evidence was obtained for radiation damage to the sample from long-term exposure to the X-ray beam.

### Measurement of the Interactions between the Lubricants and the Adhesive by FTIR

Two grams of isocyanurate–ether–polyol adhesive of Toyo Molton (two-liquid type) was dissolved at room temperature by adding 50 g of a mixed solvent of ethyl acetate and chloroform (1:1). After adding 2 g of erucic amide to this solution, the mixture was air-dried at room temperature. Erucic amide was dissolved with the adhesive in a mixed solvent of ethyl acetate and chloroform (1:1), while behenic amide was not dissolved with the adhesive in a same solvent. Then, a film was formed by heating the mixture for more than 48 h at 40°C. Another film was also formed in the same manner by adding behenic amide instead of erucic amide. Both films were analyzed using a Bio-Rad Laboratories Digilab Di-
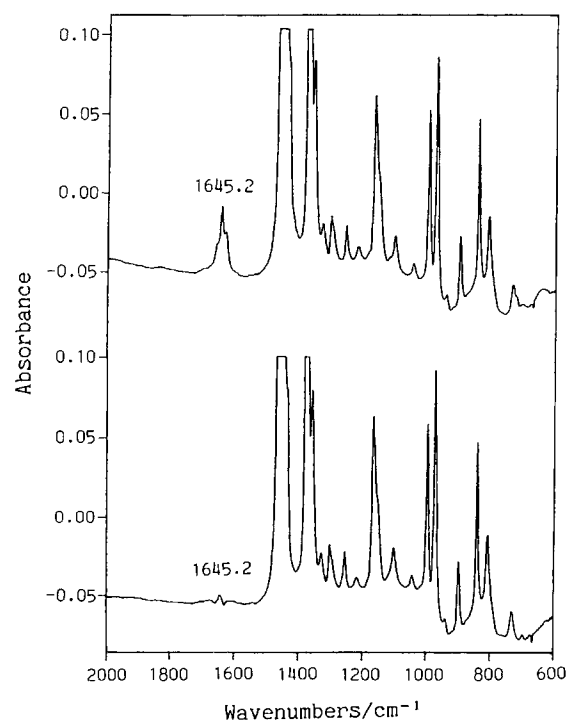


**Figure 1**  FTIR ATR spectra of cast film (upper) and laminated film (bottom) containing erucic amide.
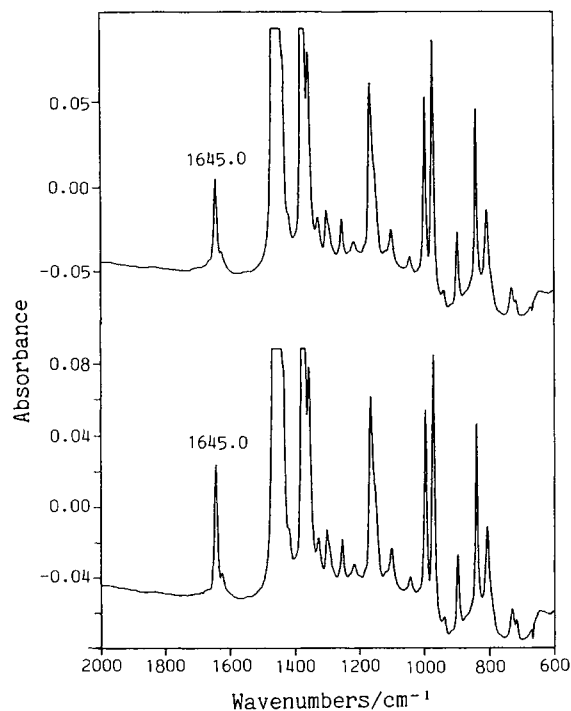
**Figure 2**  FTIR ATR spectra of cast film (upper) and laminated film (bottom) containing behenic amide.

vision, Model FTS-80, FTIR spectrometer by the transmittance method. The detector used was a wide-band MCT. The measurement conditions were 4 cm$^{-1}$ resolution and 100 scans.

## Measurement of Kinetic Friction Force on the Film Surface

The kinetic friction force was measured according to JIS K 7125: "Procedures to test coefficients of friction of plastic films and sheets."

## RESULTS AND DISCUSSION

Figure 1 shows the FTIR ATR spectra of cast polypropylene film (upper) and laminated film (bottom) containing erucic amide as a lubricant. The absorption of erucic amide by the C $=$ O stretching vibrational mode was observed at 1645.2 cm$^{-1}$. Comparing the two spectra in Figure 1, it is immediately seen that the absorbance by the C $=$ O stretching vibrational mode of the cast films was greater than that of the laminated films, though the spectral patterns look similar in the range from 1500 to 600 cm$^{-1}$. Next, behenic amide was added as the lubricant. FTIR ATR spectra of polypropylene cast films and laminated films are shown together in Figure 2. The

absorption of behenic amide by the C $=$ O stretching vibrational mode was observed at 1645.0 cm$^{-1}$. As in the case of Figure 1, the two spectra were of almost the same pattern in the range lower than 1500 cm$^{-1}$. It is found, however, that the absorbance by the C $=$ O stretching vibrational mode of the laminated films was increased more pronouncedly than that of the cast films, contrary to the case in Figure 1. The results obtained in Figures 1 and 2 indicate that a greater amount of lubricant molecules existed on the surface of the cast films than on the laminated films in the case of the erucic amide, whereas in the case of behenic amide, there existed more lubricant molecules on the laminated film surface.
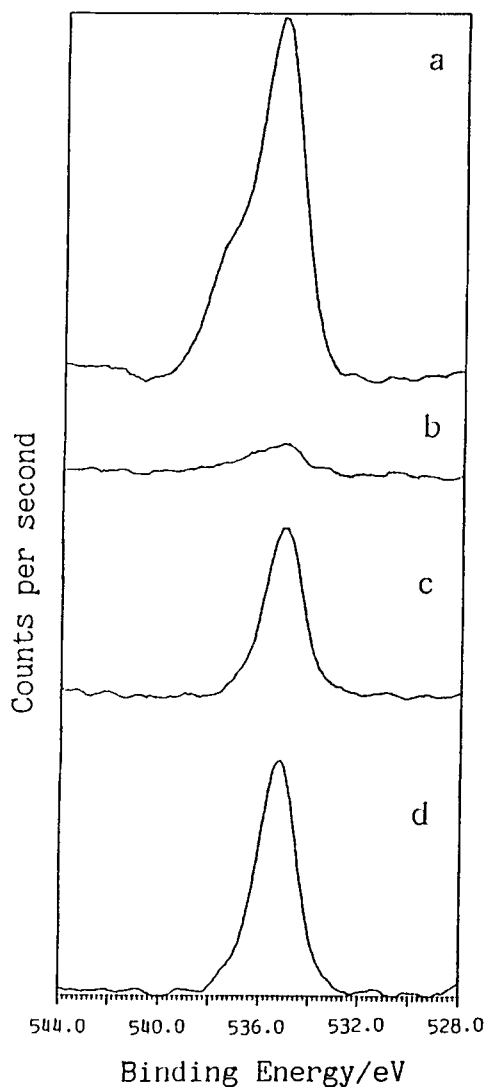


**Figure 3**  O$_{1s}$ spectra for cast films and laminated films: (a) cast film containing erucic amide; (b) laminated film containing erucic amide; (c) cast film containing behenic amide; (d) laminated film containing behenic amide.
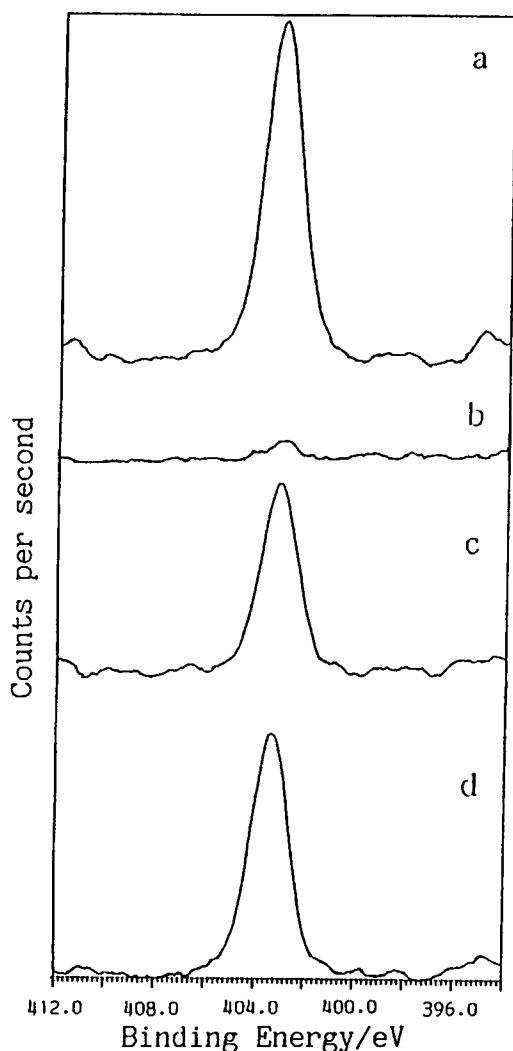
XPS was applied for further analysis of the surface conditions. Figures 3 and 4 show the XPS spectra of the surface of cast polypropylene films and laminated films containing erucic amide and behenic amide. In the case of the films to which erucic amide was added, peaks of $O_{1s}$ and $N_{1s}$, which indicates the existence of the erucic amide, were observed in both spectra. Binding energy is 535.2 eV for the $O_{1s}$ peak and 403.2 eV for the $N_{1s}$ peak, respectively. The same binding energies were observed for the $O_{1s}$ and $N_{1s}$ peaks of behenic amide. It was found that the absorbances of the laminated films were extremely reduced in both peaks. In the case of the films containing behenic amide, it was found, on the contrary, that the absorbances of the laminated films were increased in both $O_{1s}$ and $N_{1s}$ peaks compared with those of the cast films.

In Table I, we summarize the following three parameters obtained experimentally: (i) the kinetic friction forces of the surfaces of the cast and laminated films; (ii) the FTIR ATR absorbance ratios of the $C=O$ stretching vibrational mode originating from lubricants to that of the CH deformation vibration/$CH_2$ twisting vibration modes from polypropylene (1255 cm$^{-1}$); and (iii) the element composition of carbon, oxygen, and nitrogen obtained by XPS. It was found that when erucic amide was added the kinetic friction force at the cast film surface was as small as 43 g and that the slip of such a film was good. On the other hand, the kinetic friction force of the laminated films was 205 g and the slip of the film was bad. The ratio of absorbance of the $C=O$ stretching vibrational mode to that of the CH deformation vibrational/$CH_2$ twisting vibration mode (1255 cm$^{-1}$) was 1.83 for the cast films and 0.26 for the laminated films. The concentration of erucic amide on the laminated film surface was found



**Figure 4** $N_{1s}$ spectra for cast films and laminated films: (a) cast film containing erucic amide; (b) laminated film containing erucic amide; (c) cast film containing behenic amide; (d) laminated film containing behenic amide.

**Table I   Relation between the Slip of Film and Concentration of Lubricants Obtained from FTIR ATR and XPS**

| | Kinetic Friction Force (g) | FTIR ATR Absorbance Ratio ($C=O/CH_2,CH$) | XPS Elemental Composition | | |
| --- | --- | --- | --- | --- | --- |
| | | | C (%) | O (%) | N (%) |
| Erucic amide cast film | 43 | 1.83 | 92.7 | 4.4 | 2.9 |
| Erucic amide laminated film | 205 | 0.26 | 99.2 | 0.6 | 0.2 |
| Behenic amide cast film | 208 | 0.87 | 96.3 | 1.8 | 1.9 |
| Behenic amide laminated film | 80 | 2.16 | 94.8 | 2.7 | 2.5 |

to be extremely reduced, corresponding to the result of the kinetic friction force. The concentrations of oxygen and nitrogen of erucic amide on the laminated film measured by XPS were found 0.6 and 0.2%, respectively, which were extremely reduced compared with those of the cast films. This suggests that a correlation exists between these elemental concentrations and the kinetic friction forces.

These findings suggest that erucic amide on the cast film surface was migrated into the adhesive layer when the laminated films were produced by using an isocyanurate–ether–polyol adhesive. When behenic amide was added, the kinetic friction force at the cast film surface was increased to 208 g and the slip was poor. While the force at the laminated film surface was 80 g, the slip was good. The ratio of absorbance of the $C = O$ stretching vibrational mode as measured by FTIR ATR to that of the CH deformation vibration/$CH_2$ twisting vibration mode ($1255 \text{ cm}^{-1}$) was 0.87 for the cast films and 2.16 for the laminated films. This indicates that the concentration of behenic amide at the laminated film surface is higher than that at the cast film. This also corresponds to the results the kinetic friction force. The concentrations of oxygen and nitrogen of behenic amide in the laminated film analyzed by XPS were 1.5 and 1.3 times larger, respectively, than those of the cast films. These findings have led us to a presumption that behenic amide at the cast film surface migrates to the laminated film surface during a process of producing the laminated film, without being subjected to any interactions with the isocyanurate–ether–polyol adhesive.

To clarify the migration mechanism of erucic amide in the laminated film, the interaction between erucic amide and the isocyanurate–ether–polyol adhesive was investigated. We examined the mixture of erucic amide and the adhesive at the composition ratio of 1:1 and the intermolecular interaction was studied by the FTIR method. As a result, erucic amide and the adhesive were found to be compatible with each other. Figure 5 shows the FTIR transmittance spectra of adhesive, erucic amide, and behenic amide. Figure 6 shows the FTIR transmittance spectra of the adhesive, erucic amide, and the mixture of the adhesive and erucic amide in the N—H stretching vibration region. In the spectrum of the adhesive, an absorption peak of a free N—H band was found at $3440 \text{ cm}^{-1}$ and a peak of the hydrogen-bonded N—H band was found at $3199.2 \text{ cm}^{-1}$. In the spectrum of erucic amide, the absorption peaks of the hydrogen-bonded N—H band were found at $3364.2$ and $3189.3 \text{ cm}^{-1}$ and a peak of the free N—H band was found at $3395.0 \text{ cm}^{-1}$. In the spectrum of

the mixture of the adhesive and erucic amide, absorption peaks of the hydrogen-bonded N—H band were found at $3357.9$ and $3193.4 \text{ cm}^{-1}$. Although the free N—H band, observed in the spectrum of the adhesive near $3440 \text{ cm}^{-1}$, was hardly observed in that of the mixture, the hydrogen-bonded N—H band at $3357.9 \text{ cm}^{-1}$ shifted by $6.3 \text{ cm}^{-1}$ to a lower wavenumber, and the absorbance of the band increased more than that of erucic amide. Figure 7 shows the FTIR transmittance spectra of the adhesive, erucic amide, and the mixture of the adhesive and erucic amide in the region of $1800–1550 \text{ cm}^{-1}$. In the spectrum of the adhesive, an absorption peak by a free $C = O$ band was found at $1730.1 \text{ cm}^{-1}$. In the spectrum of the adhesive, an absorption peak by the $C = O$ stretching vibrational mode was found at $1646.6 \text{ cm}^{-1}$ and an absorption peak by the N—H deformation vibration mode was also found at $1633.5 \text{ cm}^{-1}$. In the spectrum of the mixture of the adhesive and erucic amide, absorption peaks by the hydrogen-bonded $C = O$ stretching vibrational mode were
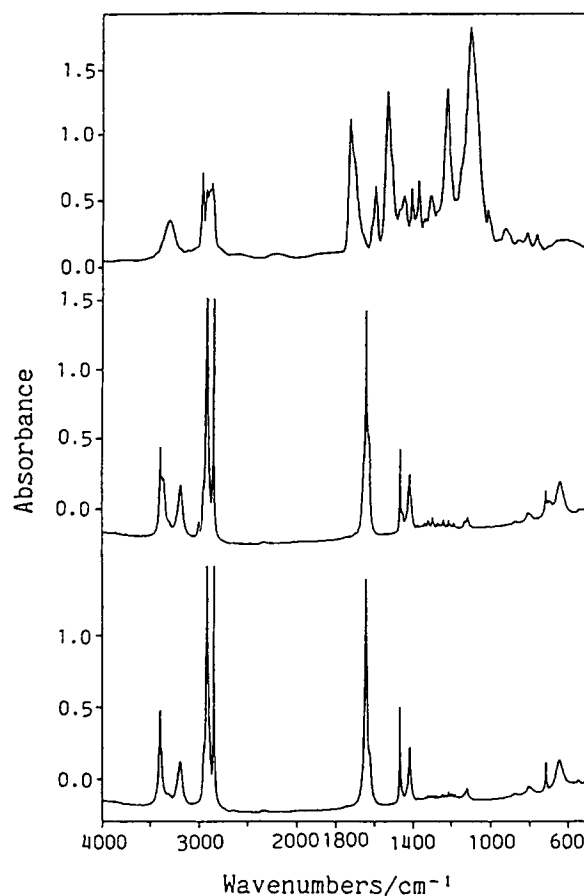


**Figure 5**   FTIR transmittance spectra of adhesive (top), erucic amide (middle), and behenic amide (bottom).
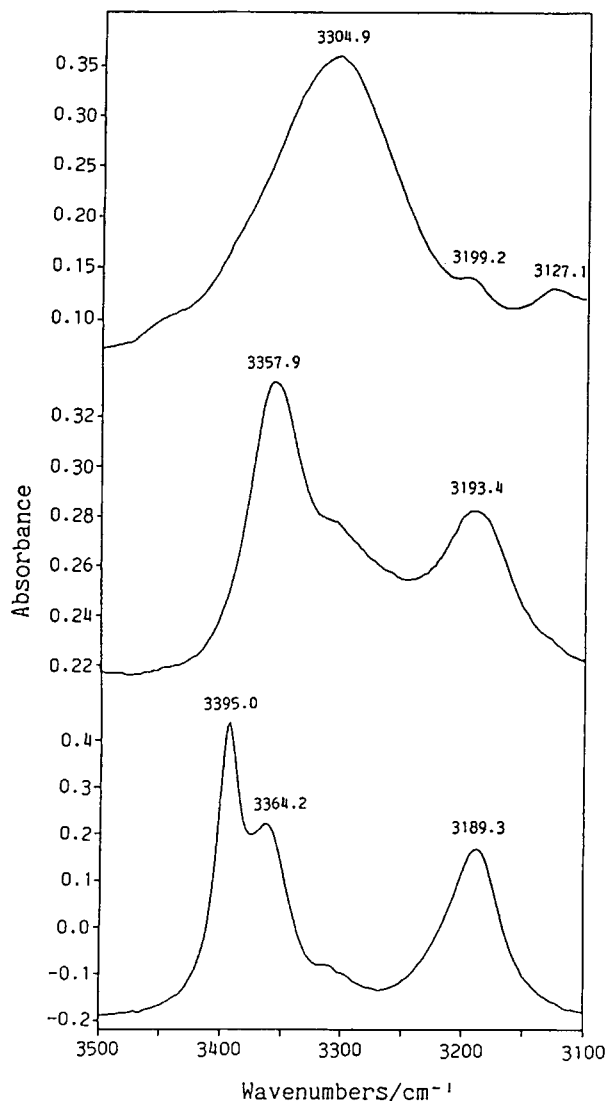
**Figure 6** FTIR transmittance spectra of the N—H stretching region, adhesive (top), adhesive-erucic amide blends (middle), and erucic amide (bottom).

found at 1705.7 and 1659.6 cm$^{-1}$. Compared with the spectrum of the adhesive, the absorbance at 1705.7 cm$^{-1}$ was increased. The peak by the hydrogen-bonded C=O stretching vibrational mode was newly found at 1659.6 cm$^{-1}$.

Based on the above-mentioned results, it was concluded that the intermolecular interaction (hydrogen bonds) had occurred in the mixture of erucic amide and the adhesive. We think that these hydrogen bonds were produced within the laminated film and erucic amide was migrated into the adhesive layer by intermolecular interaction. On the other hand, the mixture of behenic amide and the adhesive was incompatible and resulted in the phase sepa-

ration. Therefore, no absorption peak by intermolecular interaction was observed in the FTIR spectra of this mixture.

## CONCLUSION

We have clarified the relationship between the slip and the amount of lubricants on the surfaces of polypropylene cast films and laminated films by using FTIR and XPS. When erucic amide, an unsaturated fatty acid amide, was used as a lubricant for polypropylene cast films, the slip was found to be
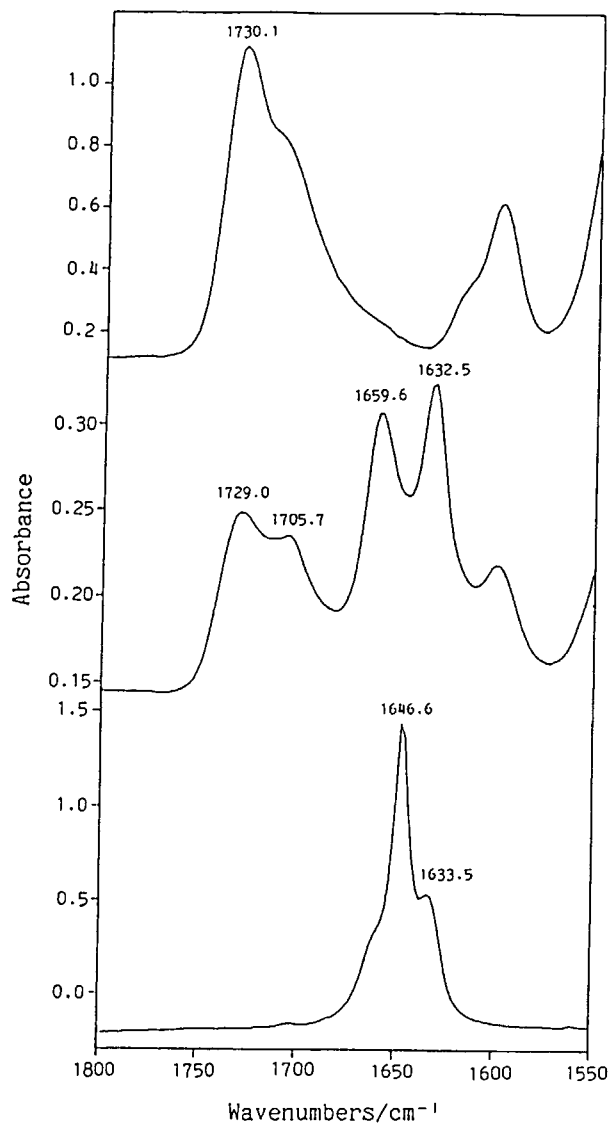


**Figure 7** FTIR transmittance spectra of 1800–1550 cm$^{-1}$ region, adhesive (top), adhesive–erucic amide blends (middle), and erucic amide (bottom).

extremely reduced in laminated films for which an isocyanurate–ether–polyol adhesive was used. To clarify this slip-reducing mechanism, the lubricants and the adhesive were directly mixed, and the intermolecular interaction between the lubricants and the adhesive was investigated using FTIR spectroscopy. It has been observed that erucic amide is compatible with the adhesive and the intermolecular interactions (hydrogen bonds) have been generated. We conclude that erucic amide is migrated into the adhesive layer because of the presence of the hydrogen bonds within the laminated film.

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