

Vibrational Spectra of Some Diisocyanates in the Liquid State or on EPDM-40 Rubber Surface

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SYNOPSIS

IR transmission and Raman spectra of toluylene diisocyanate and hexamethylene diisocyanate and IR spectra of diphenylmethane diisocyanate, partially polymerized diphenylmethane diisocyanate, and polyisocyanurate were obtained. Toluylene diisocyanate and partially polymerized diphenylmethane diisocyanate form associates in the liquid state, which leads to anomalous intensity changes and a frequency shift of the $\nu_{as}(\text{NCO})$ band in the spectrum of the treated rubber surface with time. The associate formation influences positively the properties of diisocyanates as rubber-surface modifiers for adhesion. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The use of diisocyanates as cross-linking agents in polymer materials is well known.¹ But their use as rubber-surface modifiers for increasing the reactivity of the surface layer and improving the adhesion is less recognized. When applying the liquid diisocyanates to a rubber surface, a number of their chemical reactions with reactive groups of the rubber surface layer and the adsorbed water occur to form urea, urethane, and biurea groups.² The properties of the modified rubber surface are determined by the concentration of reactive isocyanate groups remaining on the surface layer and chemically bonded to the polymer network of the rubber.³ At the same time, the kinetics of physical-chemical conversions of diisocyanates on the rubber surface is related to the properties of diisocyanates in the liquid state, in which they are applied on the surface. Therefore, the study of the behavior of diisocyanates in the liquid state and on the surface of a modified rubber is of interest.

Isocyanates have often been studied using the techniques of vibrational spectroscopy. The assignment of characteristic bands of the isocyanate group

is known: $\nu_{as}(\text{NCO})$, $\nu_{simm}(\text{NCO})$, $\delta_{||}(\text{NCO})$, and $\delta_{\perp}(\text{NCO})$. The $\nu_{as}(\text{NCO})$ band is observed for different isocyanates in the 2250–2300 cm^{-1} region.⁴ In the IR spectra, it has a high intensity and is often used for quantitative and qualitative analysis. The $\nu_{simm}(\text{NCO})$ band has a low intensity in the IR spectra and a middle intensity in the Raman spectra. Its position is still rather uncertain. The range from 1340 to 1450 cm^{-1} has been usually indicated for this band.^{5–7} The deformation vibrations of the isocyanate group are noted in the 600–650 cm^{-1} region.⁴

The calculations of the isocyanate vibrational spectra are known,⁸ which take into account the Fermi resonance and the anharmonism of $\nu(\text{NCO})$ vibrations using atom-atom potential techniques and the Morse function. The matrix of the potential energy was found by approximating four constants, and the force constants of C=N and C=O bonds were within 6.6–7.6 and 5.5–6.3 $\text{mdin}/\text{\AA}$, respectively.

The isocyanate group has a resonance electron structure that creates a partial separation of the charges on carbon and oxygen atoms,¹ which leads to the formation of a significant dipole moment of the isocyanate group and the whole molecule. This dipole moment contributes to the strong intermolecular interaction, which is able to form an ordered structure of molecules even in a liquid state (“liquid lattice”). This is defined by the appearance of intermolecular vibration bands in IR spectra.⁶ Appar-

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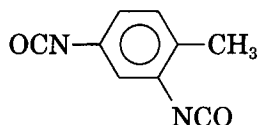
ently, such a structure permutation of diisocyanates in the liquid state is able to influence their properties, including those of rubber-surface modifiers.

In present work, the structure of diisocyanates in the liquid state and their behavior on the rubber surface was studied. The modifying ability of diisocyanates was estimated by their influence on the adhesive properties of a rubber in the joints with epoxy adhesives.

EXPERIMENTAL

The following diisocyanates were studied—

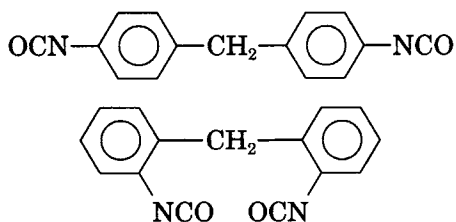
2,4-Tolylene diisocyanate (TDI):



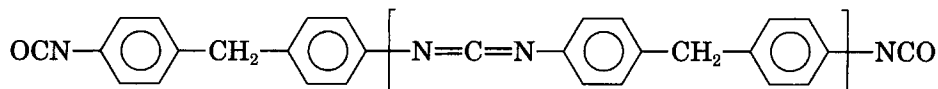
1,6-Hexamethylene diisocyanate (HMDI):



A mixture of isomeric 4,4'- and 2,2'-diphenylmethane diisocyanate (DMDI):

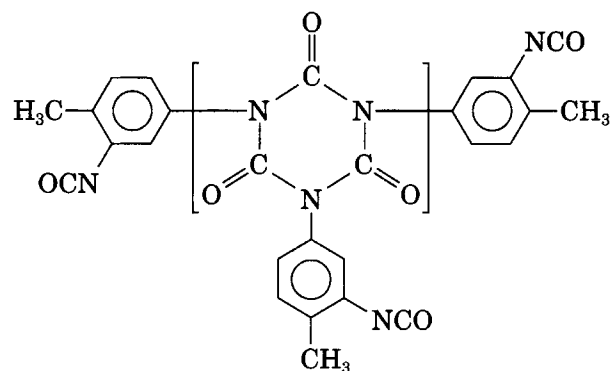


Partially polymerized 4,4'-DMDI (PDMDI):



IR spectra were recorded on UR-20 and Specord M-80 spectrometers with a resolution of 4 and 1 cm^{-1} , respectively. KBr and NaCl glasses were used. IR ATR spectra were recorded using an ATR accessory with a KRS-5 element (trapezoid), angle of 45° , and a reflectance number of 19. Raman spectra were obtained on a DFS-24 spectrometer (double monochromator) with He—Cd lasers LG-62 and LG-70. The exciting line was 441.6 nm. The spectral

Polyisocyanurate (PIU):



Before the spectra recording, the diisocyanates were dried in a box with CaCl_2 , the impurities, water, and urea were controlled by the IR spectra. Diisocyanates were applied to a rubber surface in a pure state or from 10% solution in Freon. On applying the solution, the rubber surface was dried for 10–15 min. The presence of Freon in the IR ATR spectrum was not observed. The amount of diisocyanates being applied was about 10 g/m^2 .

The surface of the ethylene-propylene-dicyclopentadiene (EPDM-40) rubber surface was studied. ^{60}Co -radiation-vulcanized pure rubber was used. For study of the strength, the vulcanized EPDM-40 rubber containing sulfur, tetramethylene thiuramdisulfide, 2-mercaptobenzothiazol, black carbon, and dioctylsebacinate was used. The detailed formulation of the vulcanized rubber is given in Ref. 9. Before applying the diisocyanates, the samples of rubber were dried under vacuum at a temperature of 353 K for 6 h. The polyisoprene-epoxy rubber (PDI) was used as an adhesive. It was cured by polydivinyl-nitrile-carboxyl rubber (SKD) at a temperature of 353 K.

width of the slit was varied from 1 to 5 cm^{-1} , using a 90° geometry for illumination.

The strength of the joint was determined by a fracture technique.⁹ The vulcanized rubber plates of 25 mm diameter and 2 mm thickness were bonded to the face of a steel cylinder using "Leykonat" adhesive. The adhesive-rubber was poured between plates and the joint in the Teflon form was placed

in a heat box for curving. The thickness of adhesive was 1 mm. The joint strength was determined using a tensile machine RM-500; speed of loading was 100 mm/min at 293 K.

RESULTS AND DISCUSSION

Figure 1 shows the IR spectra of TDI and HMDI. The $\nu_{as}(\text{NCO})$ band is well interpreted by the high-absorption intensity in the region of about 2270 cm^{-1} . The analysis of the decomposition of the band indicated that the band contains only one strong absorption component. Other components caused by Fermi resonance have a weak intensity. A gap in the region of about 2320 cm^{-1} is formed by the uncompensated CO_2 absorption in the channels of the spectrometer. The $\nu_{as}(\text{NCO})$ frequency in the spectrum of TDI appears at 2268 cm^{-1} , and in the spectrum of HMDI, at 2280 cm^{-1} . To symmetric vibrations of the isocyanate group, a weak band at 1440 cm^{-1} was attributed in the spectrum of TDI, and at 1433 cm^{-1} , in the spectrum of HMDI.

In the Raman spectra (Figs. 2 and 3), the $\nu_{as}(\text{NCO})$ band appears only for TDI and has a weak intensity. To $\nu_{\text{symm}}(\text{NCO})$ in the Raman spectra of TDI, one of the bands at 1436 or 1445 cm^{-1} may be assigned, and in the spectrum of HMDI, one of the bands at 1423 or 1432 cm^{-1} . The more accurate assignment of bands is difficult, but the symmetry of

these molecules allows the doublet of these vibrations. The ratio of band intensities of symmetrical and asymmetrical vibrations in IR and Raman spectra shows a good execution with group analysis of vibration for HMDI and a small derivation for TDI when concerning analysis of the vibration of the NCO group as a three-atom molecule. Apparently, the substituents exert little influence on the form of the NCO group vibrations, so that the isocyanate group vibrations may be considered as an approximation of an isolated fragment. The bands at 2275 , 2285 , and 2280 cm^{-1} are assigned to $\nu_{as}(\text{NCO})$ vibrations in the IR spectra of DMDI, PDMDI, and PIU, respectively (Fig. 4).

As the isocyanate group has a resonance electron structure,¹ which stimulates a partial separation of charges at the carbon and oxygen atoms, the NCO group and the whole diisocyanate molecule each have a significant dipole moment. This enables the formation of intermolecular associates even in a liquid state ("liquid lattice").

The formation of associations was observed for TDI. In the low-frequency region of the Raman spectrum, the weak band at 157 cm^{-1} is recorded (Fig. 5), which is assigned to the intermolecular vibration of the "liquid lattice." An analogous band attributed to intermolecular vibrations was observed earlier in the region at about 100 cm^{-1} for phenylisocyanate.⁶ In the Raman spectrum of HMDI, the band of intermolecular vibrations was not observed.

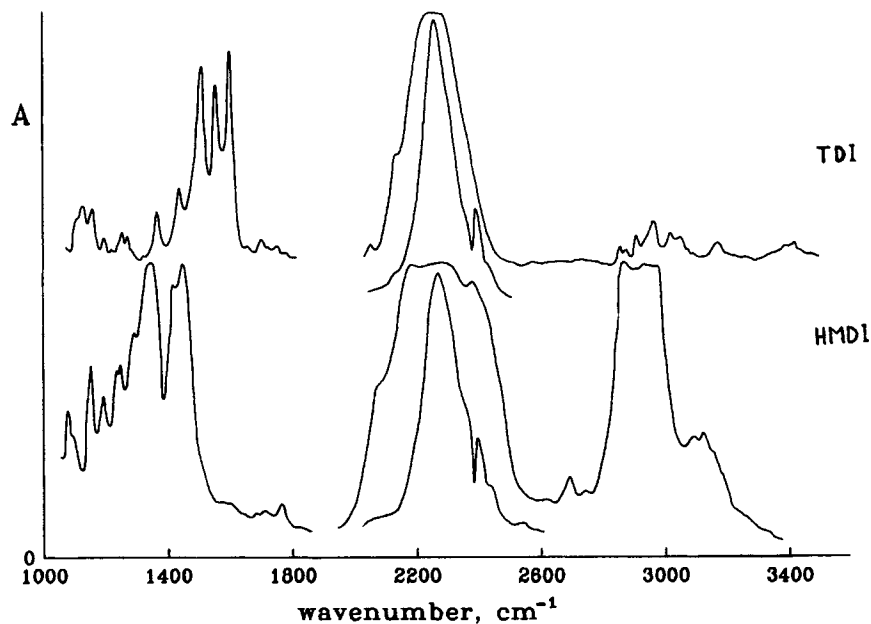


Figure 1 IR transmission spectra of TDI and HMDI.

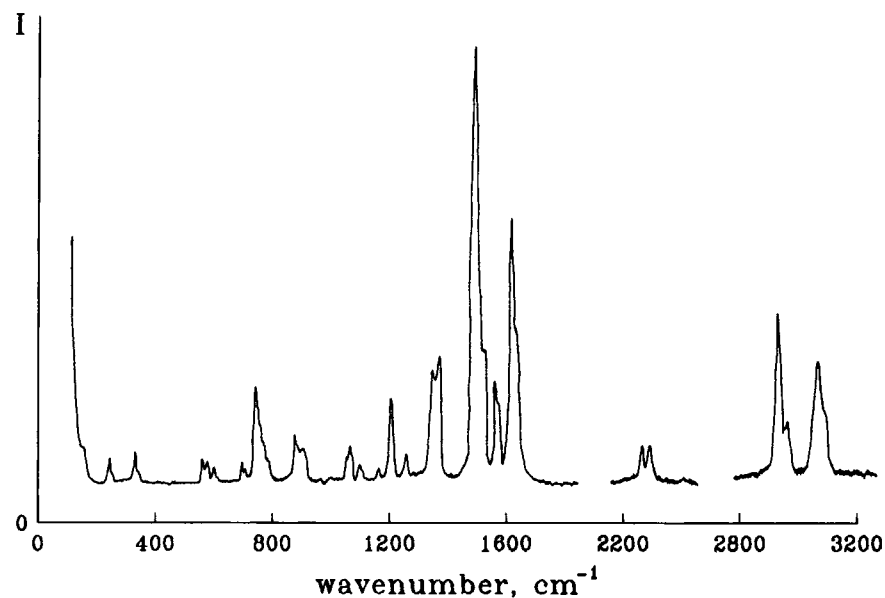


Figure 2 Raman spectra of TDI.

The nature of a rather strong intermolecular interaction is not quite clear. Two possible mechanisms may be assumed: dipole-dipole interaction of two differently directed isocyanate groups or coordinative interaction of an isocyanate group with π electrons of the aromatic ring. The second mechanism explains the absence of a strong intermolecular interaction for HMDI, where there are no aromatic structures. However, this conclusion needs additional verification.

When being applied to the EPDM-40 surface, the diisocyanates react with reactive groups of the rubber and adsorbed water. Only oxygen-containing groups (aldehyde, carboxyl, hydroxyl) may be present as reactive groups of the rubber, which were formed by the oxidation of the rubber surface under the action of the environment.⁹ Simultaneously with these reactions, there occurs the diffusion of diisocyanates into deeper layers of the rubber and the evaporation of diisocyanates. Their processes are

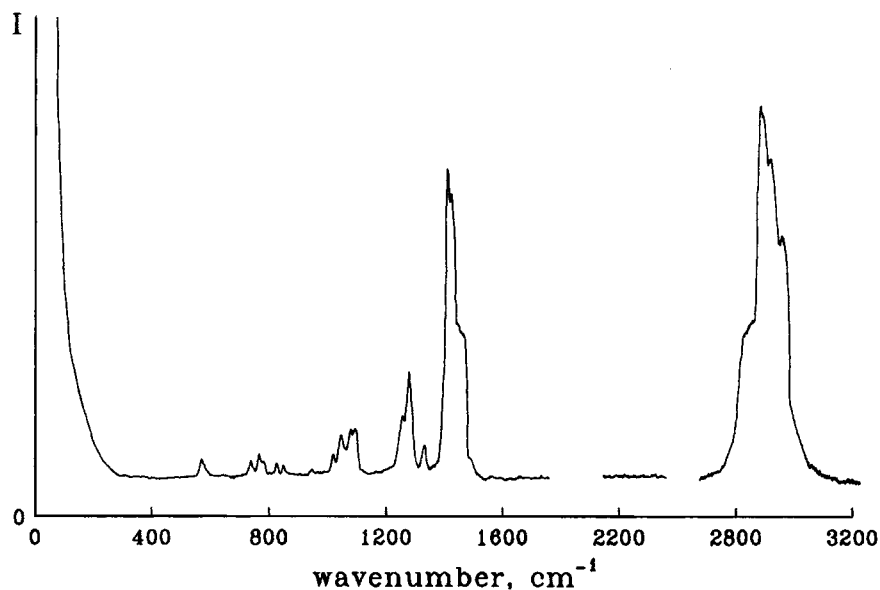


Figure 3 Raman spectra of HMDI.

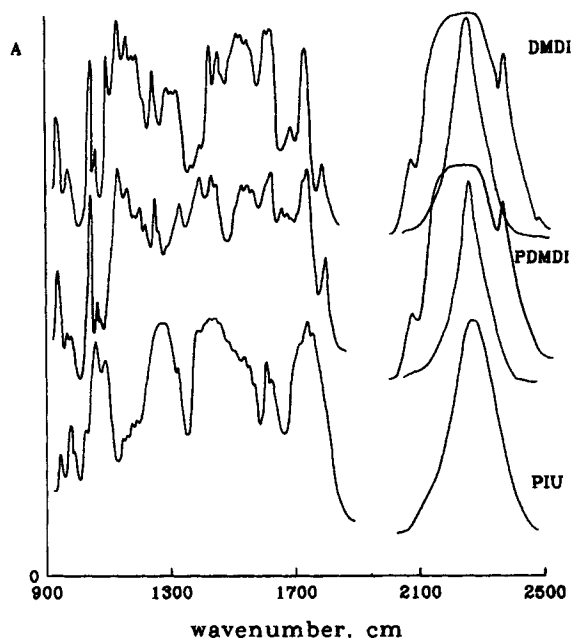


Figure 4 IR transmission spectra of DMDI, PDMDI, and PIV.

reflected in the IR ATR spectrum of the treated rubber surface.

Immediately after applying TDI, the spectrum (Fig. 6) of the surface shows the bands of the carbonyl group at 1765 and 1725 cm^{-1} of middle intensity and at 1670 cm^{-1} of weak intensity. The first of the two bands are assigned to the free carbonyl group and the band at 1670 cm^{-1} may be assigned to the

carbonyl group involved in the hydrogen bond. The appearance of bands of NH group vibrations is observed: a free NH group at 3420 cm^{-1} and a hydrogen-bonded NH group as a wide peak centered at 3365 cm^{-1} . Such a width of hydrogen-bonded NH group bands is caused by different types of hydrogen bonds. The lower-frequency shoulder from 3310 cm^{-1} corresponds to hydrogen bonds with the carbonyl groups, and the higher-frequency shoulder up to 3400 cm^{-1} , to hydrogen bonds with the aromatic ring.¹⁰ Deformation $\delta(\text{NH})$ vibrations are manifested in the region at 1550 and 1520 cm^{-1} . In addition, the bands of the TDI benzene ring and reactive isocyanate group are observed in the spectrum. The assignment of bands in the low-frequency part of the spectrum is rather ambiguous and was not used.

During the storage of the modified rubber in air in the laboratory under normal conditions, some changes of the IR ATR spectrum were observed. The intensity of the bands of a free carbonyl group at 1765 and 1725 cm^{-1} is decreased, and the intensity of the band of a hydrogen-bonded carbonyl group at 1670 cm^{-1} is increased. Two bands at 1660 and 1690 cm^{-1} appeared, which formed irregular shoulders about the 1670 cm^{-1} band. The overall intensity of carbonyl group bands increases with time, which corresponds to the reactions of isocyanate groups with reactive groups of the rubber surface (Fig. 7). In the $\nu(\text{NH})$ region, the intensity of the hydrogen-bonded NH group has been redistributed toward the lower-frequency shoulder, thus corresponding to the

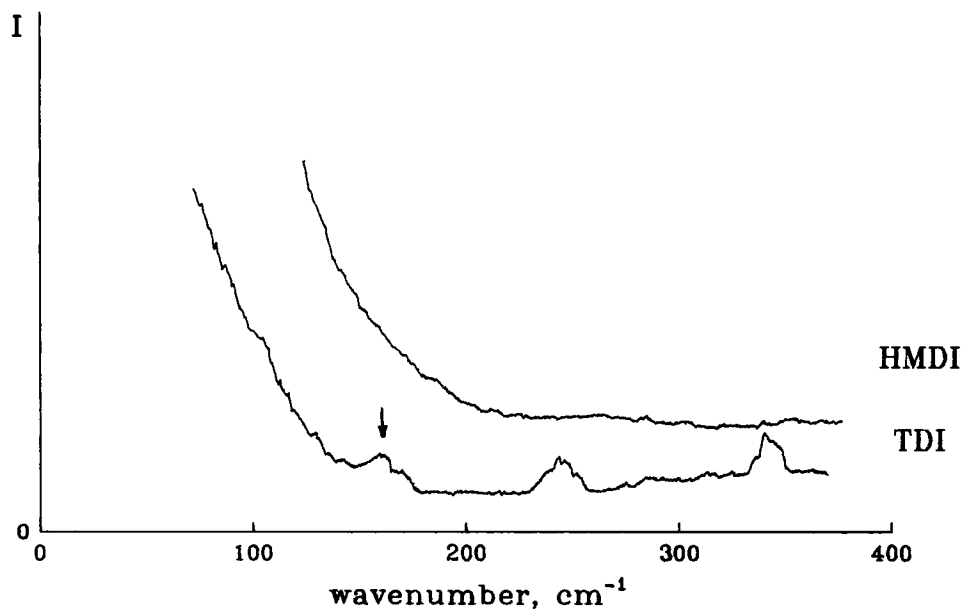


Figure 5 Low-frequency region of Raman spectra of TDI and HMDI.

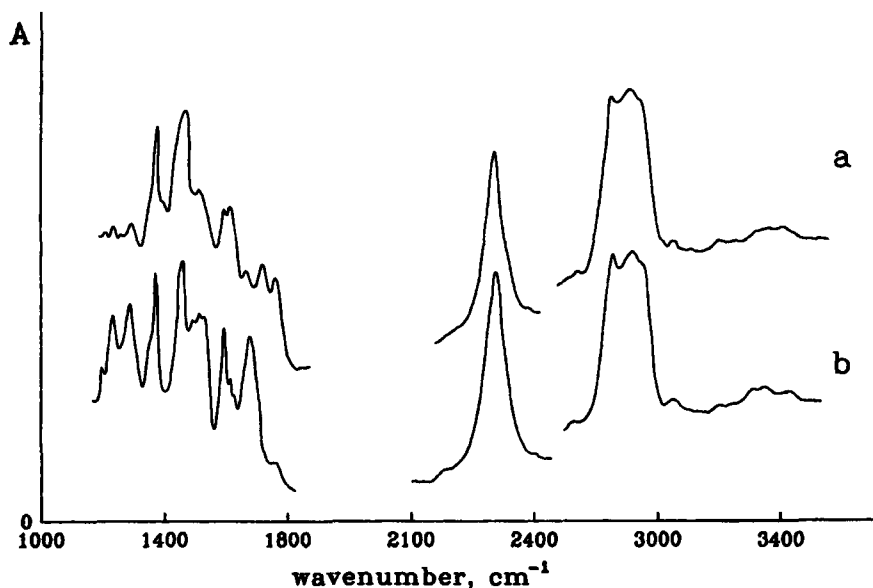


Figure 6 IR ATR spectra of the EPDM-40 surface modified by TDI: (a) immediately after applying TDI; (b) after 2 days.

increase in the number of NH groups involved in the hydrogen bond with the carbonyl group rather than with the aromatic ring.

When applying HMDI on the rubber surface, the same appearance of carbonyl group bands is ob-

served: weak at 1770 and 1735 cm^{-1} , middle at 1690 cm^{-1} , and weak at 1640 cm^{-1} (Fig. 8). The appearance of an intense band at 1690 cm^{-1} assigned to the hydrogen-bonded carbonyl group in the spectrum of the surface immediately after applying

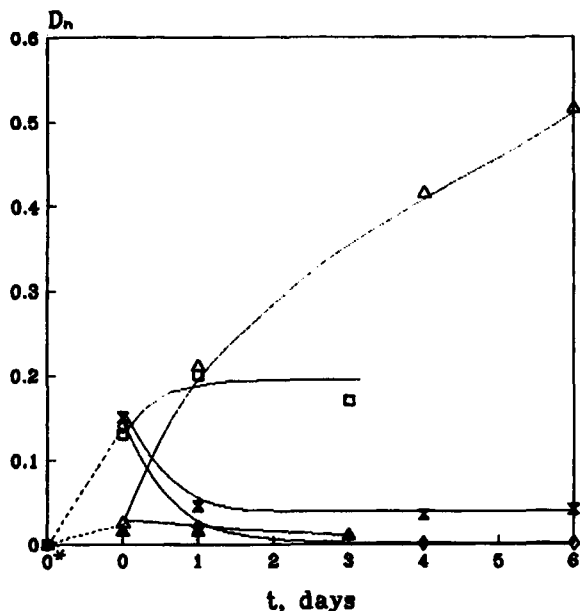


Figure 7 Optical density of ν (C=O) in the IR ATR spectra of the rubber surface modified by TDI and HMDI; (Δ) 1680 cm^{-1} (TDI); (\square) 1690 cm^{-1} (HMDI); (\blacktriangle) 1770 cm^{-1} (HMDI); (\blacktriangledown) 1765 cm^{-1} (TDI); (\diamond) 1720 cm^{-1} (TDI); "O*" refers to data of the nonmodified surface rubber.

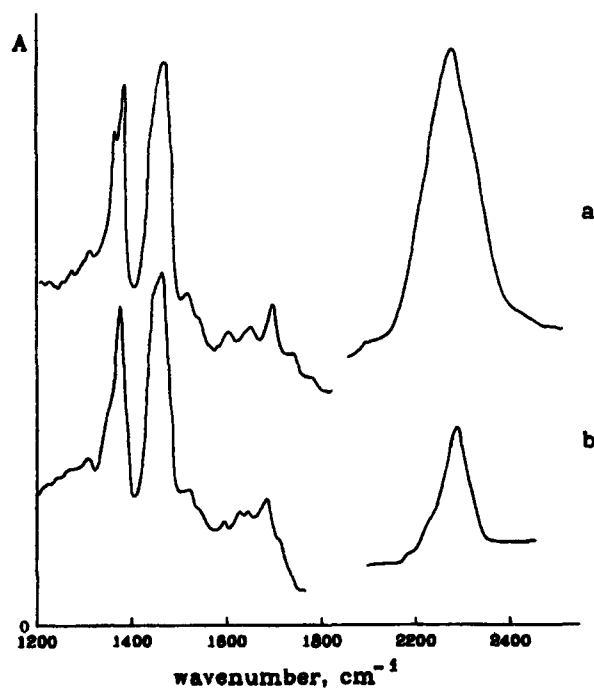


Figure 8 IR ATR spectra of EPDM-40 surface modified by HMDI: (a) immediately after applying HMDI; (b) after 2 days.

HMDI implies that the formation of hydrogen bonds when using HMDI occurs just after the reaction of isocyanate groups. The intensity of the band of the hydrogen-bonded carbonyl group is somewhat increased with time, but much less than after applying TDI (Fig. 7). One may say the same about the overall intensity of the carbonyl group bands. Therefore, the main stage of the reaction of isocyanate groups with reactive groups of the rubber and the formation of a stable system of hydrogen bonds when applying HMDI occurs rather fast as compared with TDI.

When TDI is applied to the surface of vulcanized rubber, similar changes in the IR ATR spectrum take place (Fig. 9), but the quantitative measurements of the intensity of $\nu(\text{C}=\text{O})$ and $\nu(\text{N}-\text{H})$ bands are difficult to perform, because in the analyzed region of the spectrum, the bands of other components of rubber are observed.

Both for pure EPDM-40 rubber and vulcanized rubber, the spectrum of the treated surface shows a strong $\nu_{\text{as}}(\text{NCO})$ band. The decreasing intensity of this band with time when applying HMDI corresponds to the course of physical-chemical processes discussed above (Fig. 10). However, in the case of TDI, the intensity of the $\nu_{\text{as}}(\text{NCO})$ band increased for 2 days, and only then, it begins to decrease, reflecting the trend to consuming isocyanate groups. A similar increase in the intensity of this band is

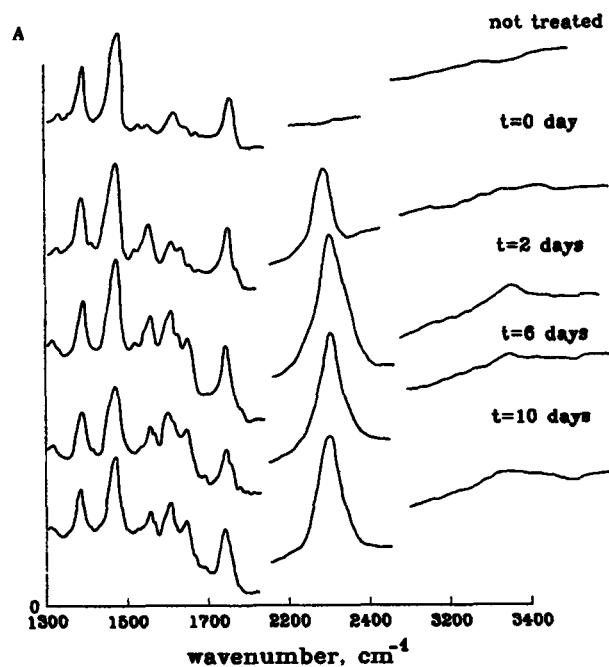


Figure 9 IR ATR spectra of vulcanized rubber modified by TDI with time.

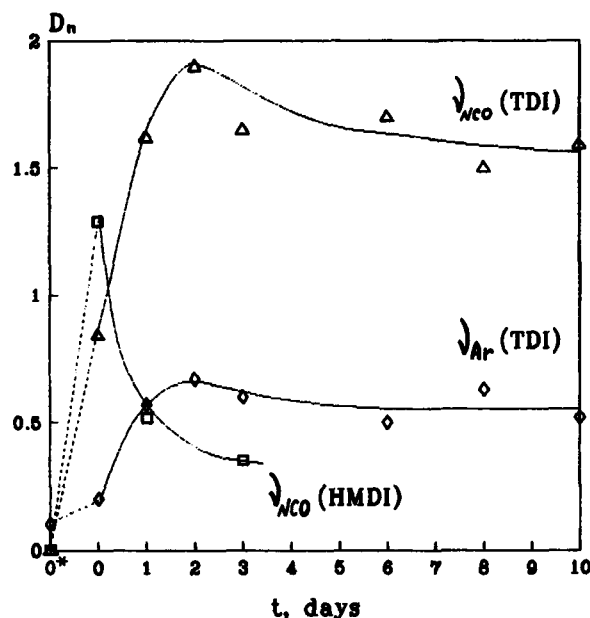


Figure 10 Optical density of $\nu(\text{NCO})$ and $\nu(\text{Ar})$ in the IR ATR spectra of the rubber surface modified by TDI and HMDI with time.

also observed in the IR transmission spectrum of EPDM-40 film whose surface was treated with TDI. Such a change in the intensity of the $\nu_{\text{as}}(\text{NCO})$ band may be explained only by the increase of the extinction coefficient ϵ in the Lambert-Beer law. Simultaneously with the change of intensity, the position of this band is varied from 2268 to 2295 cm^{-1} . A similar intensity change is observed for the band of the TDI aromatic ring at 1610 cm^{-1} . For HMDI, the variation in the position of the $\nu_{\text{as}}(\text{NCO})$ band with time is practically absent (frequency fluctuating from 2275 to 2280 cm^{-1}).

The observed changes in the surface spectrum for TDI may be accounted for by the influence of the decomposition of associations of TDI molecules being on the rubber surface. After applying the TDI layer on the rubber surface, the diffusion processes and chemical reactions occur only after the associations of TDI molecules are decomposed. In the course of the associate decomposition, there is observed a shift of the band of asymmetric vibrations of the isocyanate group to the higher-frequency region and an increase in the extinction coefficient of this band.

The chemical reactions of isocyanates resulting in $\text{C}=\text{O}$ and $\text{N}-\text{H}$ group formation occur rather fast after decomposition of associates, so that, at first, a rather stable structure of hydrogen bonds of the $\text{N}-\text{H} \cdots \text{Ar}$ type and free carbonyl groups are

formed, as is noticed in the IR spectrum (Fig. 6). This indirectly confirms the nature of associates formed through bonding the isocyanate group with the aromatic ring. Then, the rearrangement of hydrogen bond structures takes place to form $N-H \cdots O=C$ bonds as more stable ones.

In the case of HMDI, there is no associate formation and no analogous change in the intensity and position of the $\nu_{as}(NCO)$ band is noticed. Accordingly, the system of $N-H \cdots O=C$ hydrogen bonds is formed immediately after the chemical reactions of the isocyanate groups.

The possibility of associate formation in other diisocyanates was analyzed by the change in the intensity and position of the $\nu_{as}(NCO)$ band in the IR ATR spectra of the vulcanized rubber surface (Figs. 11 and 12). The spectral changes corresponding to the process of associate formation were observed for PDMDI and weakly for PIU. The anomalous changes in the spectra of DMDI was not noticed, which corresponds to the absence or small concentration of associates.

As the vulcanized rubber surface is modified, the strength of the joint is varied depending on the type of the diisocyanate (Table I). Increasing joint strength with respect to the strength of nonmodified rubber is noticed for all diisocyanates. The largest increase in the joint strength appears for TDI and PDMDI, and the smallest effect on the strength is exerted by HMDI and DMDI. Since the isocyanate

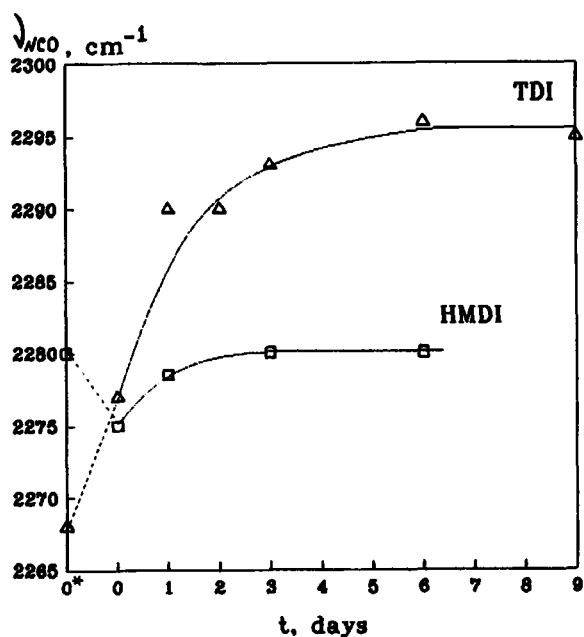


Figure 11 Frequency of $\nu(NCO)$ of TDI and HMDI in the IR ATR spectra of the modified rubber surface.

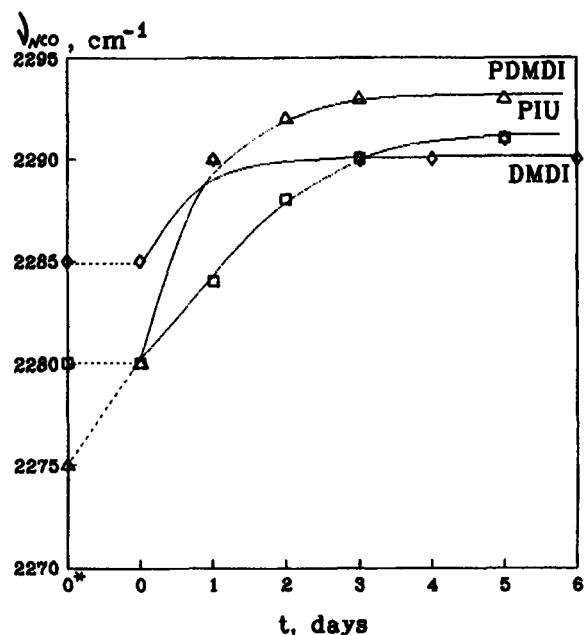


Figure 12 Frequency of $\nu(NCO)$ of DMDI, PDMDI, and PIU in the IR ATR the spectra of modified rubber surface.

groups of these diisocyanates are all sufficiently reactive toward the epoxy groups of the adhesive, the ability of diisocyanates to increase the joint strength correlates with the possibility of associate formation. The presence of associates of TDI and PDMDI molecules hampers the diffusion of diisocyanates into the bulk layer of the rubber, which promotes a fuller activation of the rubber surface and a deeper reaction with reactive groups of the polymer network of the rubber surface layer. This leads to a larger increase in the strength of an adhesive joint.

CONCLUSIONS

In this work, the IR and Raman spectra of TDI and HMDI and IR spectra of PDMDI, DMDI, and PIU

Table I Strength of Adhesive Joints of the Vulcanized EPDM-40 Rubber with an Epoxy Adhesive with Modification of the Rubber Surface by Various Diisocyanates

Diisocyanate	Joint Strength (MPa)
Without treatment	1.23
PDMDI	1.86
TDI	1.50
PIU	1.39
DMDI	1.27
HMDI	1.25

were studied in the liquid state and when applying diisocyanates on the surface of EPDM-40 rubber. The analysis of the spectra obtained shows that the diisocyanates TDI, PDMDI, and, partially, PIU are able to form associates presumably by means of a coordinative interaction of the isocyanate group with the aromatic ring. The diisocyanates HMDI and DMDI do not form associates in the liquid state. The ability to form associates in the liquid state is reflected in the behavior of diisocyanates on the rubber surface. Accordingly, the diisocyanates TDI and PDMDI were found to be more effective surface modifiers of the rubber for adhesion to epoxy adhesive.

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Received February 18, 1993

Accepted April 27, 1994