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Determination of Physical Properties of Reaction-Injection-Molded Polyurethanes by NIR-FT-Raman Spectroscopy

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Near-infrared-FT-Raman spectroscopy can be used to nondestructively analyze reaction-injection-molded (RIM) polyurethane elastomers. Unlike conventional 514.5-nm excitation, the 1064.1-nm excitation of NIR-FT-Raman spectroscopy does not produce significant sample fluorescence. In this work, the ability of NIR-FT-Raman spectroscopy to determine flex moduli of polyurethane elastomers is evaluated. Comparisons are made between NIR-FT-Raman, dispersive Raman with 514.5-nm and 752-nm excitation, and NIR diffuse reflectance spectroscopy for polyurethane analysis.

Index Headings: Analysis for polymers; Near-IR Raman spectroscopy; Raman spectroscopy.

INTRODUCTION

Polyurethane block copolymers made by Reaction Injection Molding (RIM)¹ are used predominantly for automotive applications.² These polymers are comprised of hard blocks with urethane and urea functionalities and soft blocks with aliphatic functionalities. As the production of these materials increases, there is increased demand for rapid quality evaluation.

Several methods can directly determine the quality of a RIM product, such as rheometry,^{3,4} differential scanning calorimetry,^{3,5,6} and FT-IR spectroscopy.^{3,7-9} However, these methods require either long analysis times or substantial sample preparation. As a result, they might not be adequate for routine quality evaluations. In contrast, NIR-FT-Raman spectroscopy has been used to provide rapid analyses without substantial sample preparation.¹⁰⁻¹² For the analysis of polymeric materials, NIR-FT-Raman (with 1064.1-nm excitation) usually avoids the fluorescence difficulties that are commonly experienced with conventional Raman spectroscopy (typically 488-nm or 514.5-nm excitation). Excellent frequency precision is another feature of NIR-FT-Raman that ought to be important for quantitative studies. In this work, the method of NIR-FT-Raman is applied to the determination of flex moduli of RIM polyurethanes.

EXPERIMENTAL

Materials. Reaction-injection-molded (RIM) polyurethanes were obtained from ICI Polyurethanes Group (Sterling Heights, MI). The polymers were prepared from 4,4'-diphenylmethane diisocyanate (MDI), diethyl toluene diamine (DETDA), and an ethylene oxide-capped

poly(propylene oxide) triol with a molecular weight of approximately 6000. The chemical structure of the polymers is shown in Fig. 1. The hard block of the polymers contains urea, urethane, and aromatic functionalities, and the soft block contains propylene oxide (and some ethylene oxide) repeat units.

A total of 18 RIM polyurethane plaques (4 ft × 5 ft) were prepared, which covered a 12.5% range of hard-block percentage (where the hard-block percentage corresponds to the mass percentage of MDI and DETDA units in the final polymer, see Fig. 1). A 1-in. × 3-in. sample was cut from three different positions of each plaque: the gate (corresponding to the part of the plaque closest to the injection point), the middle (corresponding to the middle of the plaque), and the end (corresponding to the part of the plaque furthest from the injection point). As a result, 54 samples, which vary in hard-block percentage and density, were used for this analysis. A more specific design of the samples used in this analysis is provided in Ref. 13.

Physical Tests. Nondestructive flex modulus measurements at 23°C (ASTM method D-790-86)¹⁴ were performed on a Universal Testing Machine (Instron). A single flex modulus measurement was performed for each sample before Raman sampling.

NIR-FT-Raman Spectroscopy. The spectrometer used for Raman sampling was a Perkin-Elmer Model 1800 FT-IR that was modified as described in an earlier report.¹⁵ The spectra were obtained with 6 cm⁻¹ nominal resolution, and data were collected every 2 cm⁻¹ over the spectral range from 9500 to 6500 cm⁻¹. This spectral range corresponds to Raman shifts of -102.4 to 3297.6 cm⁻¹. The 180° sampling geometry was similar to that described previously,¹² except that the spot diameter at the sample was 2.5 mm. About 750 mW of 1064.1-nm light was incident on the samples. Each spectrum is a result of 6 min (100 cycles) of signal averaging. The Rayleigh scattering peak (0 cm⁻¹) was used to monitor the overall scattering intensities of the samples. A single Raman spectrum was obtained from each sample.

Dispersive Raman Spectroscopy. One of the samples used for NIR-FT-Raman analysis was analyzed by dispersive Raman spectroscopy with 514.5-nm and 752-nm excitation. Both the 514.5-nm laser (Spectra-Physics) and the 752-nm laser (Lexel Ramon Ion) were set to 400 mW for sample excitation. The 752-nm excitation beam was passed through a prism, then through a 752-nm plasma line filter and a pinhole before reaching the sample. The excitation slit width for both lasers was 200 μm. A grating monochromator instrument (Princeton Instru-

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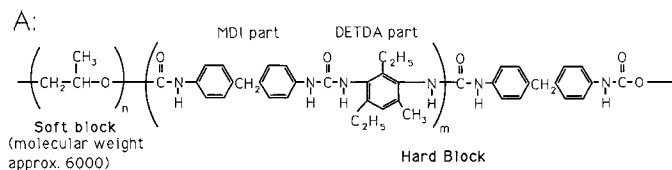


FIG. 1. Chemical structure of the polyurethanes used in this work.

ments, OMA IRY-700G) was used for detection in both cases. The Raman shift range of 1450 to 1750 cm^{-1} was used for these studies.

Data Analysis. For each NIR-FT-Raman spectrum, every intensity point was normalized with respect to the intensity of the Rayleigh scattering peak. The intensity of the Rayleigh scattering peak, scaled so that its variance over all samples is equal to the average variance of intensities in the Raman spectra, was used as an additional variable (called the scattering variable) for this analysis. Every three consecutive intensity points were averaged, and spectral regions with no appreciable Raman intensity were removed. These manipulations resulted in spectra covering Raman shifts of 301.6 to 1897.6 cm^{-1} , and 2503.6 to 2997.6 cm^{-1} in 6-cm^{-1} increments, for use in the quantitative studies.

Three separate calibrations for flex modulus at 23°C were prepared, with the use of three different sets of spectral variables: (1) normalized Raman spectra only, (2) normalized Raman spectra with the scattering variable, and (3) the scattering variable only. The method of Partial Least Squares (PLS) was used for the multivariate analyses (analyses 1 and 2), and a univariate least-squares calibration was used for analysis 3. All spectral data were mean-centered before PLS analyses. For each analysis, the samples were split into a calibration and a prediction set. Samples in the calibration set were used to construct a calibration model, and samples in the prediction set were used to determine the prediction error of the model. The method of cross-validation was used to determine the optimal number of spectral factors for the PLS calibrations. Calibration error is indicated by the Standard Error of Estimate (SEE):

$$\text{SEE} = \sqrt{\frac{\sum_{i=1}^{NC} (\hat{c}_{i,c} - c_i)^2}{(NC - 1)}} \quad (1)$$

where $\hat{c}_{i,c}$ is the flex modulus of calibration sample i that is estimated from the calibration model, and NC is the number of calibration samples. Prediction error is indicated by the Standard Error of Prediction (SEP):

$$\text{SEP} = \sqrt{\frac{\sum_{i=1}^{NP} (\hat{c}_{i,p} - c_{i,p})^2}{(NP)}} \quad (2)$$

where $\hat{c}_{i,p}$ is the flex modulus of prediction sample i predicted from the calibration model, $c_{i,p}$ is the known flex modulus of prediction sample i , and NP is the number of prediction samples. Relative errors were calculated as the standard error divided by the range of flex moduli of the samples used in the analysis.

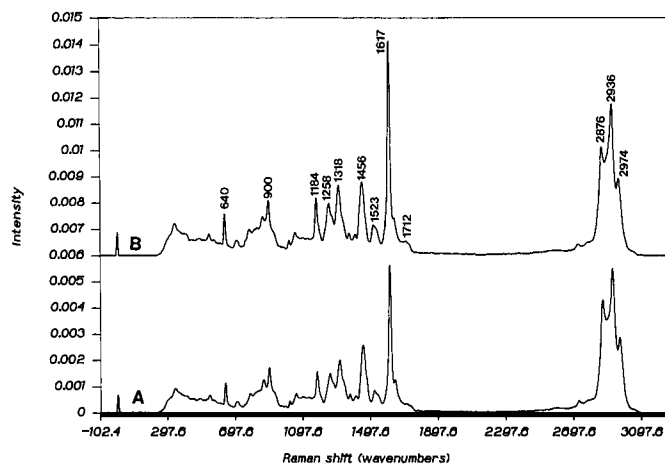


FIG. 2. NIR-FT-Raman spectra of two different RIM polyurethanes, collected with 1064.1-nm excitation (100 cycles).

RESULTS

The complete NIR-FT-Raman spectra of two RIM polyurethanes with different hard-block percentages are shown in Fig. 2. Tentative assignments of the bands are made from reference to earlier Raman analyses of n -hexane,¹⁶ para-substituted benzenes,¹⁷ and urea-formaldehyde resins.¹⁸ Bands at 2974 cm^{-1} (CH_3 stretch), 2936 and 2876 cm^{-1} (CH_2 stretch), and 1456 cm^{-1} (CH_2 bend) originate from the poly(ethylene oxide) and poly(propylene oxide) units in the soft block of the polymers. The other bands are from vibrations of aromatic and urea groups in the hard block of the polymers. Bands at 640 , 900 , 1184 , and 1617 cm^{-1} are from benzene ring modes, the band at 1712 cm^{-1} is a carbonyl stretching band, and the band at 1523 cm^{-1} is an amide I band. The 1318-cm^{-1} band might be an N-C-N stretching band, and the 1258-cm^{-1} band might arise from the penta-substituted benzene ring in the DETDA chain extender in the hard block of the polymer.

In Fig. 3, the NIR-FT-Raman spectrum of one of the polyurethane samples is compared to the dispersive Raman spectra obtained from 514.5-nm and 752-nm excitation. The NIR-FT-Raman spectrum (A) has significant vibrational structure and no observable fluorescence effects. In contrast, the spectrum obtained from 514.5-nm excitation (B) has a sloping background and very high absolute intensities. These results are indicative of sample fluorescence. The only observable vibrational band in this spectrum is the strong aromatic ring band at approximately 1610 cm^{-1} . The spectrum obtained from 752-nm excitation (C) has significant vibrational structure, and does not show fluorescence effects. The signal-to-noise ratio of the aromatic band is lower in this spectrum than in the NIR-FT-Raman spectrum (A). However, signal-to-noise improvement by multiple scanning of the 752-nm -excited spectrum is certainly possible. Although both the NIR-FT-Raman and the 752-nm dispersive Raman methods avoid fluorescence difficulties with the polyurethane samples, the frequency precision of the FT method makes it more suitable for this initial investigation.

The differences in relative band amplitudes in the NIR-FT-Raman spectra (for example, the relative amplitude

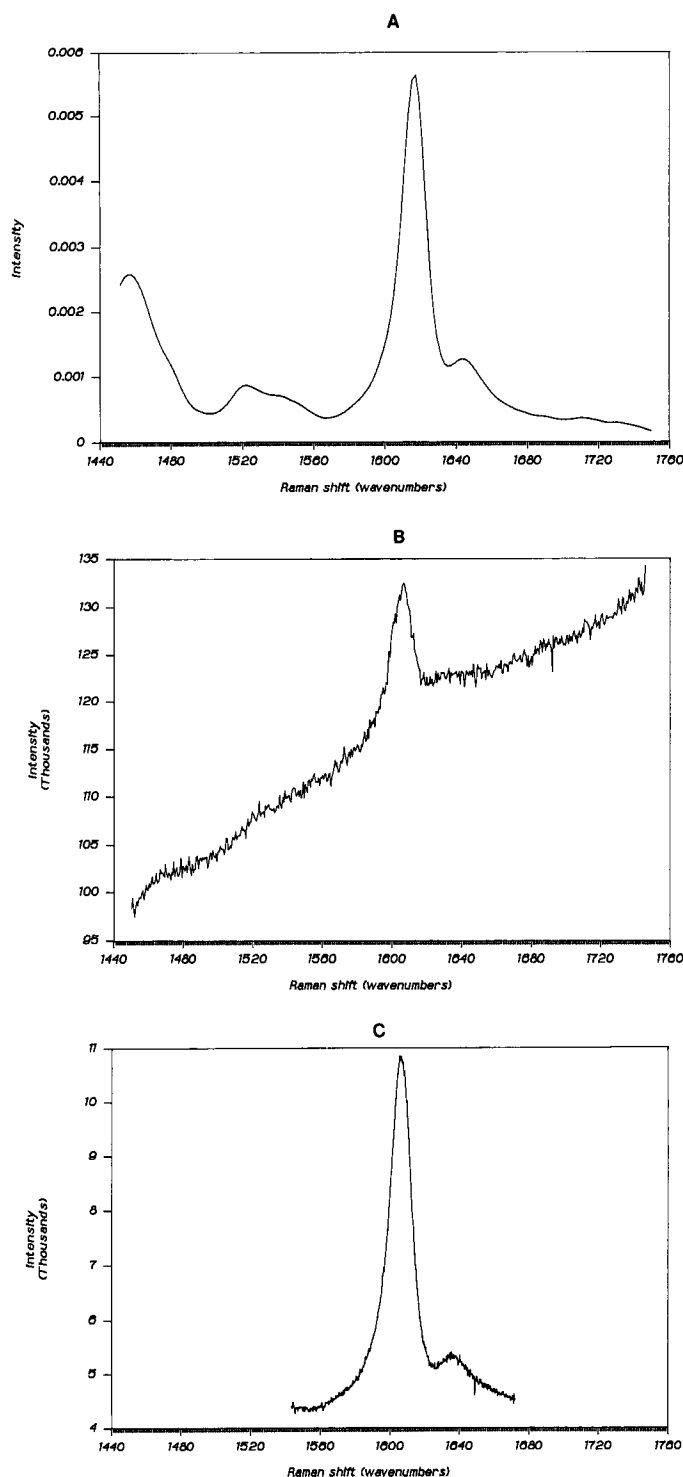


FIG. 3. Raman spectra of a RIM polyurethane sample used in this work, collected from 1064.1-nm excitation (A), 514.5-nm excitation (B), and 752-nm excitation (C), in the region 1450 to 1750 cm^{-1} .

of the 1617- cm^{-1} and 2936- cm^{-1} bands in Fig. 2) are a result of differences in the composition of the polymers. It is also observed that the overall intensity, indicated by the scattering reference band at 0 cm^{-1} , is slightly greater for spectrum B than for spectrum A. Visual observation of the RIM samples revealed that the overall scattering intensity is proportional to the concentration of nitrogen voids in the sample, and is therefore inversely

TABLE I. PLS calibration and prediction results, NIR-FT-Raman determination of flex modulus at 23°C.

Data used	Num-ber of PLS fac-tors	Calibration		Prediction	
		SEE ^a	Rela-tive error (%)	SEP ^a	Rela-tive error (%)
1. Normalized NIR-Raman spectra	2	3.4	10.9	2.5	8.4
2. Normalized NIR-Raman spectra, with scattering variable	3	2.1	6.6	1.7	5.8
3. Scattering variable only	...	10.8	34.5	11.0	37.4

^a SEE and SEP values are in units of 10^{-7} N/m².

proportional to the density of the sample.¹³ Because the density of a RIM material greatly affects its modulus, the overall scattering intensity observed in the Raman spectrum (indicated by the scattering variable) is expected to be important for the determination of flex modulus.

The PLS cross-validation results are shown in the second column of Table I. They indicate that two factors are necessary for the PLS calibration that uses the Raman spectra alone, and three factors are necessary for the calibration that uses Raman spectra with the scattering variable. Two important results are obtained from this observation: (1) the scattering variable adds information not present in the Raman spectra, and (2) a third factor (in addition to density and composition) is influencing the Raman spectra. As mentioned earlier, the information supplied by the scattering variable is probably the sample density. The additional factor influencing the Raman spectra might be phase separation, which involves the self-association (or hydrogen-bonding) of hard blocks in the polymer.^{9,19} It is possible that differences in phase separation in the polymers can be detected by shifts in the amide, carbonyl, and aromatic ring bands in the spectra. However, more detailed studies are necessary to identify the Raman spectral features that indicate phase separation.

The PLS calibration and prediction results are also shown in Table I. Results are improved if the scattering variable is added to the Raman data. However, prediction from the scattering variable alone gives poor results. These results suggest that both the scattering variable, which primarily indicates sample density, and the Raman spectrum, which contains information about composition and phase separation, are necessary to accurately predict the flex modulus of a sample.

DISCUSSION

Results of this work indicate that NIR-FT-Raman spectroscopy can be used to perform nondestructive quantitative analyses of RIM polyurethanes. An earlier analysis¹³ indicated that near-infrared diffuse reflectance spectroscopy is also a suitable method for nondestructive analyses of polyurethanes. Direct comparison of the smallest prediction errors (for flex modulus at 23°C) for the NIR-FT-Raman method (5.8%, Table I) and for the NIR diffuse reflectance method (4.0%) suggests that the diffuse reflectance method more accurately predicts flex modulus. However, several improvements on the Raman

method can be made. Unlike the Raman spectrometer system used in this work, a specifically designed "black-box" Raman system for analysis of polyurethanes can be constructed. Such a system could be optimized for several analysis parameters, such as sample placement reproducibility, sampling geometry, and nominal resolution, and could be properly shielded to eliminate safety hazards associated with laser instrumentation. In addition, compensation for laser power fluctuations could be employed, which would also improve the prediction ability of the method.

Although NIR diffuse reflectance spectroscopy has many advantages in terms of instrumentation, there are several appealing instrumental features of NIR-FT-Raman spectroscopy. For research purposes, the same spectrometer can be used for both NIR-FT-Raman and NIR diffuse reflectance spectroscopy. The frequency precision advantage of the FT instrument is also obtained. In addition, because the wavelengths of light detected in NIR-FT-Raman spectroscopy are not appreciably absorbed by optical fibers, high-quality Raman spectra can be obtained over long distances of relatively cheap optical fibers.¹¹ In contrast, only expensive, low-hydroxyl fibers can be used for NIR diffuse reflectance spectroscopy; and the range of the spectra obtained is significantly limited by absorption of the optical fiber.²⁰ In terms of cost, an interferometer (for use in NIR-FT-Raman spectroscopy) is much more expensive than a dispersive instrument (for use in NIR diffuse reflectance spectroscopy). However, a relatively inexpensive dispersive Raman system with 752-nm excitation can also provide high-quality Raman spectra devoid of fluorescence interferences (see Fig. 3, C).

The chemical information obtained from NIR-FT-Raman spectroscopy is complementary to, and sometimes better than, the information obtained from NIR diffuse reflectance spectroscopy. The Raman spectrum has fundamental bands, which are sharper, less overlapped, and more accurately assigned than the overtone and combination bands in the NIR diffuse reflectance spectrum. As a result, multivariate analysis methods are not as necessary for NIR-FT-Raman spectroscopy as for NIR diffuse reflectance spectroscopy. In addition, single- or dual-wavelength calibrations in NIR-FT-Raman spectroscopy can be largely based on carefully derived band assignments, rather than on statistical wavelength-searching algorithms (which are commonly used with NIR diffuse reflectance spectroscopy).

In general, the Raman spectrum provides information about nonpolar groups (such as aromatic rings and polymer backbone groups),²¹ whereas NIR diffuse reflectance spectroscopy provides information about CH, NH, OH, and carbonyl groups. As a result, the appropriate spectroscopic method for polyurethane analysis strongly depends on the property of interest. In fact, both NIR-FT-Raman and NIR diffuse reflectance methods can provide sufficient, and complementary, information about the property of interest. For example, it is known that phase separation in polyurethanes causes a change in the second-overtone carbonyl bands in the NIR diffuse reflectance spectrum.²² However, because phase separation involves a change in the structure of the polymer chains, it is also possible that phase separation affects the poly-

mer backbone bands in the Raman spectrum. Because the information in NIR-FT-Raman spectroscopy and NIR diffuse reflectance spectroscopy are complementary, it might be advantageous to combine the two methods to provide even more accurate characterizations.

CONCLUSION

The lack of fluorescence effects in the NIR-FT-Raman spectra of polyurethane elastomers enables accurate non-destructive determinations of physical properties. Although prediction errors (for flex modulus) for the NIR-FT-Raman method in this work are slightly greater than for the NIR diffuse reflectance method described in an earlier work, significant improvements in the Raman method are possible. NIR-FT-Raman spectroscopy and NIR diffuse reflectance spectroscopy are both nondestructive, but each method has distinct advantages over the other. Because the two methods reveal different information, the most appropriate analytical method depends on the specific property of interest.

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