

Invited Paper

STRUCTURAL EVOLUTION IN BIORENEWABLE SOY BASED POLYURETHANES

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Abstract Spectroscopic studies have revealed that the amount of polyureas formed and the kinetics of their formation in soy based polyurethane systems are considerably different from traditional systems employing ethylene oxide-propylene oxide (EO-PO) based polyols. The aggregation of polyureas was characterized by the hydrogen bonds formed utilizing FTIR spectroscopy. This study offered the opportunity to assign the previously undefined infrared features. The structural transformation is reflected in the segmental relaxation kinetics characterized by spin-spin diffusion most conveniently measured using low field NMR. The reaction kinetics and the products formed are directly related to the hydrophobic nature of the soy based polyols and its inability to disperse water.

Keywords: Spectroscopy; Miscibility; Polyurethanes.

INTRODUCTION

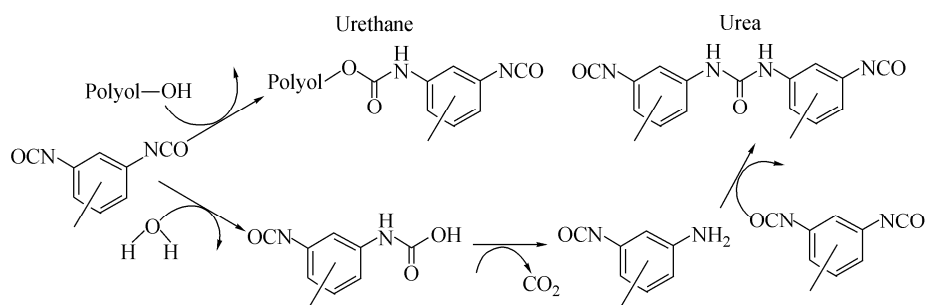
Polyurethane is one of the most studied subjects in polymer science. It is interesting because of the flexibility involved in the reaction chemistry to produce a range of physical properties for applications in coatings, structural foams, cushioning materials, and adhesives among others^[1]. One of the research areas undertaken in our laboratory is to control and extend the limits of the physical properties of polyurethane foams^[2–7]. Previous studies have demonstrated the complexity of this seemingly simple polyurethane reaction^[2–4]. The structure and physical properties of the product can be modified easily depending on a number of parameters such as the functionality of the polyol^[8–13], the type of isocyanate used^[2, 14, 15], surfactants or catalysts package^[11, 16, 17]. The overall physical properties are dependent on the morphology as well as the chemical structure^[12, 18–22].

The focus of the current study is to employ soy based polyols in polyurethane foam formulations. Utilization of this flexible bio-based polyol is attractive from both fundamental and environmental perspectives^[9, 14, 23–25], although the long term economic benefit has yet to be established. Soybean oil usually has widely varying chemical composition depending on the species and growing conditions. The *ca.* 85% of the unsaturated fatty acids derived from soybean oil are dominated by structures containing 1 to 3 double bonds per molecule^[26]. They can be converted into soy based polyols to be used for polyurethane synthesis^[27]. The first step in this modification involves the hydroformylation of the double bonds into aldehydes using metal catalysts. The next step transforms the aldehydes into primary hydroxyls through hydrogenation, and this product is further reacted under transesterification conditions to yield the final polyol^[23].

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Scheme 1 General polyurethane foaming reaction

In this study, infrared spectroscopy in conjunction with low field NMR spectroscopy is used to characterize the reaction kinetics and the products formed as shown in Scheme 1. A number of infrared studies have been carried to characterize polyurethane reactions^[2–4, 12, 13, 28–34]. Specific infrared features associated with urethane and urea units were assigned. Although the time resolved infrared spectroscopic measurements have proven to be useful to follow the structure formation in the phase separated polyurethane systems, a relatively new cost effective technique, low field NMR^[35], also has tremendous potential to characterize the structure and the segmental dynamics of the crosslinked polyurethane system. In this case, the time needed for spin-spin relaxation, can be correlated with the segmental motion. A number of studies have demonstrated the capability of this low field NMR technique to follow the crystallization dynamics^[36, 37], water permeation behavior/plasticization^[38], crosslinking density^[39] and dynamic order parameter^[35] in polymers. In this study, low field NMR has been used to characterize the foaming process, the structures produced and the segmental dynamics. This combination of infrared and NMR techniques provided a very clear description of the chemical reactions in soy based polyol. They clearly describe how the various components affect the polyurethane reaction and the phase separated structures formed. Our results are reported here.

EXPERIMENTAL

Materials

The diisocyanate employed for the study is a mixture of 2,6-toluene diisocyanate (20%) and 2,4-toluene diisocyanate (80%) (T-80). The soy based polyol (DWK 4200) is a Dow Chemical developmental polyol, with a hydroxyl number of 95.9 mg KOH/g and an equivalent weight of 584.9 g/mol. The initiator used for this polyol is a glycerine initiated ethylene oxide based polyether polyol. The catalyst package used in this study is a mixture of Dabco BLV and Dabco T-9 (Air Products and Chemicals Inc.). The poly (alkylene oxide methyl siloxane) surfactant used is Nias L-620 (OSI Specialties/ Witco Corp.). All of the catalysts and surfactant were used as received. Deuterium oxide, 99.8 atom % D, for ²H-NMR was obtained from Acros.

Foam Preparation

All foams were prepared using the Dow Chemical soy based polyol, unless otherwise specified. The isocyanate index used throughout the foaming reactions was 1.05. The general procedure is as follows: A total of ca. 10.00 g of polyol, 0.025 g catalysts with the appropriate amount of deionized water are mixed in a plastic beaker using a glass rod for 3 min. To this calculated amount of T-80 is added rapidly using a plastic syringe and stirred vigorously for 20 s, at which time foaming was observed.

Foaming Kinetics Using Time Resolved Infrared Spectroscopy

The experiment is similar to the procedure reported previously^[2]. Infrared spectra were obtained using a Bruker Optik Tensor 27 system with a narrow-band MCT detector. All spectra were collected at 4 cm^{−1} resolution. Eight scans were signal averaged in order to record time-resolved spectra of sufficient quality for analysis. The infrared spectra were then collected from the 30th second from the start of mixing the foam formulations. The temporal resolution was as follows, every 10 s for the first 10 min, then every 30 s from 10 min to 15 min, every

60 s from 15 min to 30 min and every 300 s from 30 min to 1 h. A nine-pass attenuated total reflectance (ATR) Harrick cell with a ZnSe crystal was used to measure the foaming kinetics. A drop of the foaming mixture was dripped onto the internal reflecting crystal. The crystal acted as a heat sink, and the reaction temperature at the foam/crystal interface was controlled by heating the sample cell to the desired temperature. All of the reaction kinetics was carried out at 40°C. The sample temperature was simultaneously monitored using two other thermocouples. They were placed in close proximity with the edge of the crystal to ensure thermal equilibrium.

Low Field NMR Measurements

Low field NMR experiments were performed using a Bruker Minispec NMR spectrometer with an operating frequency of 20 MHz. The magnet and sample chamber were maintained at 40°C, same as the infrared experiments. The foam samples were prepared as described in the infrared section and placed into a standard glass 180 mm × 10 mm low field NMR tube. Standard free induction decay was recorded with 8 scans and 2000 data points per spectrum following the initial 90° pulse. The transverse relaxation time (T_2) was determined using an exponential fitting of the signal decay by means of an exponential fitting method in the Bruker Minispec software. For all foaming experiments, the sample density continues to decrease as a function of time. Even in that case signal to noise ratio is still quite acceptable even for the kinetics data obtained at one hour.

RESULTS AND DISCUSSION

Time Resolved Infrared Spectroscopy Studies

Similar to previous studies, time resolved infrared spectroscopy was used to characterize the reaction kinetics for the soy based polyols^[2, 12, 13, 24]. The infrared spectra were obtained and shown in Fig. 1. It should be emphasized that the measurements are taken at a constant temperature (40°C), thus eliminating many of the temperature-induced effects^[13, 32]. Because of the exothermic nature of the isocyanate reaction, this temperature may be much lower than the temperature actually observed in commercial foam reactions^[5–7]. But by keeping all experiments at the same temperature, it is possible to illustrate the differences in the reaction kinetics under identical experimental conditions.

Infrared active features have been used to analyze structures in polyurethanes^[2, 13, 28–30, 33, 34]. These features are generally divided into two parts. One type in the 1700 cm^{-1} region can be associated with the urethane functional groups. The other group in the 1600 cm^{-1} region deals with the formation and organization of polyureas. Of course, the extremely intense band at 2264 cm^{-1} is assignable to the asymmetric NCO stretching vibration of the isocyanates. The decrease of this band as a function of time during reaction is directly correlated to the increase in the intensity of the carbonyl stretching vibrations (in the 1600 and 1700 cm^{-1} range) associated with the formation of various urea and urethane linkages during foaming reaction.

The vibrations at 1657 and 1640 cm^{-1} have been assigned unambiguously to hydrogen bonded monodentate and bidentate urea linkage, respectively. There are several other C=O stretching vibrations in the 1600–1700 region. These have been assigned to hydrogen bonded urethane units or free ureas^[2, 13, 28–30, 33, 34]. But some differences in these assignments exist. For example, the C=O stretching hydrogen bonded urethane may exist at 1723 cm^{-1} ^[29]. This band may also be found at other positions ranging from a low of 1700 to 1715 cm^{-1} depending on the chemical species or the strength of the hydrogen bonds formed^[2, 13, 30, 33].

We have assigned the 1717 cm^{-1} component observed to be the hydrogen bonded urethane units. This position is consistent, but not identical to previous studies. The intensity of this component directly affects our interpretation of the structure evolution and the physical properties achieved. Therefore, we carried out additional experiments to establish this assignment. Reactions were performed with polyols with diisocyanate without any water being added. The infrared spectra of the bands in the C=O stretching region are shown in Fig. 2. For this type of reactions, we expect the formation of only urethane units. These experiments show unambiguously that the urethane C=O stretching free from hydrogen bond is associated with the sharp singlet found at 1732 cm^{-1} . The hydrogen bonded component is found at the lower side at approximately 1715 cm^{-1} . It should also be noted that soy based polyol has a relatively weak ester stretching vibration appearing near the 1732 cm^{-1} urethane band.

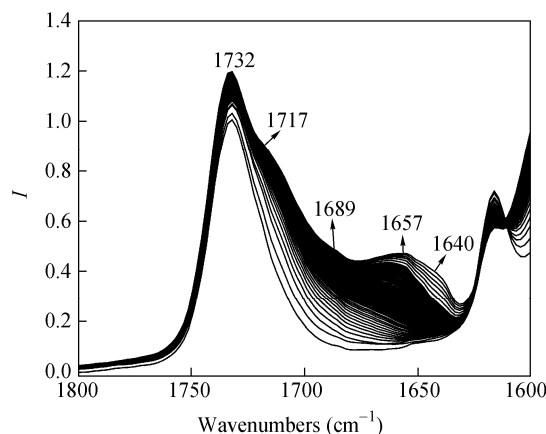


Fig. 1 Time resolved Infrared spectra in the carbonyl region for the soy based sample with diisocyanate and water at 40°C
1732: free urethane, 1717: H-bonded urethane, 1689: free urea, 1657: H-bonded monodentate urea, 1640: H-bonded bidentate urea; Y-axis corresponds to normalized intensity.

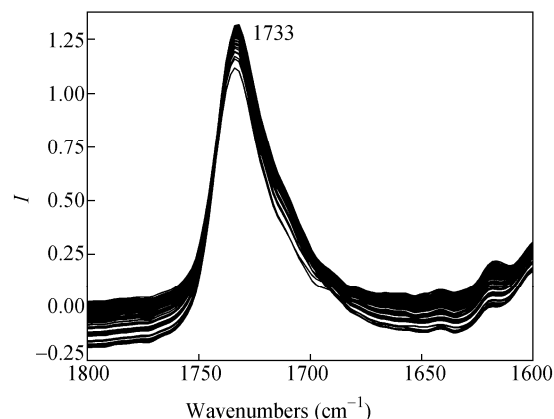


Fig. 2 Time resolved Infrared spectra in the carbonyl region for the soy based sample with diisocyanate in the absence of water at 40°C
1733: free urethane C=O; Y-axis corresponds to normalized intensity.

As the band assignments are established, it is then possible as in previous studies, to employ the intensity changes in these spectra to follow the reaction kinetics, the products formed and evolution of phase separated morphology. The formation of inter-urethane and inter-urea hydrogen bonding and hence the phase separated morphology can be ascertained based on the C=O stretching vibration^[31, 32, 40]. It is assumed that band height measurements can be used to represent the changing band intensity as a function of time without significant error^[34]. In order to account for sample differences, the integrated intensity of asymmetric and symmetric CH stretching vibrations in the region between 2800 and 3000 cm^{-1} was used for this purpose^[40].

The reaction products formed as a function of time are shown quantitatively in Fig. 3. The changes in the infrared spectra as a function of time are clear. As compared to traditional polyols, it is obvious that for the soy based polyols, there are fewer polyureas generated, at a slower speed which cannot form hydrogen bonds as easily. The amount of bidentate polyureas, a criterion for ordered hard segment domain formation, is shown in Fig. 4. These data are derived from the intensity of the 1640 cm^{-1} band in the infrared spectra obtained as a

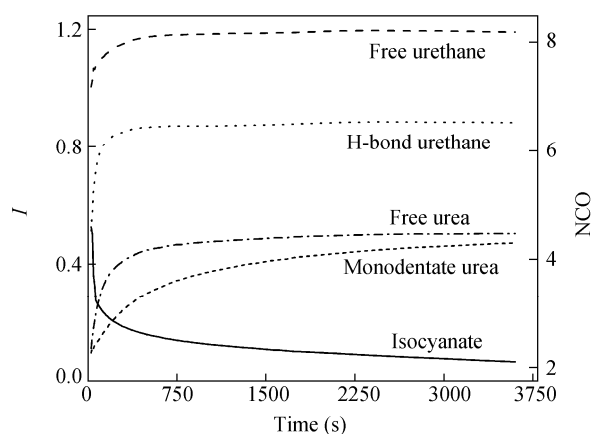


Fig. 3 Kinetic plot based on the time resolved Infrared spectra for soy based polyol with diisocyanate and water

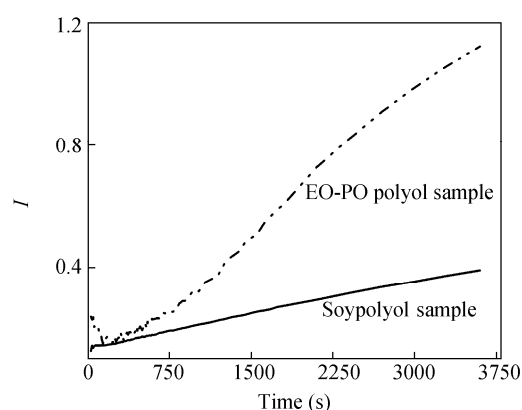


Fig. 4 Kinetic plot for bidentate urea formation at 1640 cm^{-1} for soy based polyol and EO-PO polyol with diisocyanate and water (see Ref. [2])
Y-axis corresponds to normalized intensity.

function of time. It should also be noted that the depletion of isocyanate also occurs at a much faster rate in soy based polyol as compared to the traditional EO-PO system^[2].

As mentioned above the phase separated morphology in polyurethanes is well established^[30, 32–34, 41–43]. The hard segment domains usually are extremely ordered with well defined bidentate polyureas held together by hydrogen bonds. As can be seen in Fig. 4 obviously, it is not the case for soy based polyols. Because of the large number of hydroxyls incorporated in the structure, there is little doubt that a substantial amount of urethanes are formed in the soy based system. Based on the broadening of the urethane band on the lower frequency side (Fig. 1), it can be concluded that these urethane units formed hydrogen bonds, not as inter-urethane hydrogen bonds, but as urethane-urea hydrogen bonds. This is supported by the experiments conducted when polyols were reacted with diisocyanate without any water (Fig. 2). It is clear that urethane linkages are being formed quickly in the soy based system with few inter-urea hydrogen bonds present.

The difference in the reaction kinetics and products produced can be attributed to the chemical nature of the polyol structure and the environment of the water. The changing miscibility behavior can be readily seen visually as represented in Fig. 5. The optical appearance of various polyols in water changes with the water concentration. For example, at lower concentrations of water (1 vol%), soy based polyol is completely miscible. For samples with 3 vol%–5 vol% water, the solution is turbid. This sample again turns into a clear solution with 10% water. For higher compositions of water, the turbidity increases again suggesting a phase separated system. There is little doubt that the miscibility of water in the inherently hydrophobic soy based system strongly influences the chemical reactions and the morphology developed. Previous studies have shown that minute changes in the polyol structure can significantly influence the “hard” polyurea formation^[44, 45].

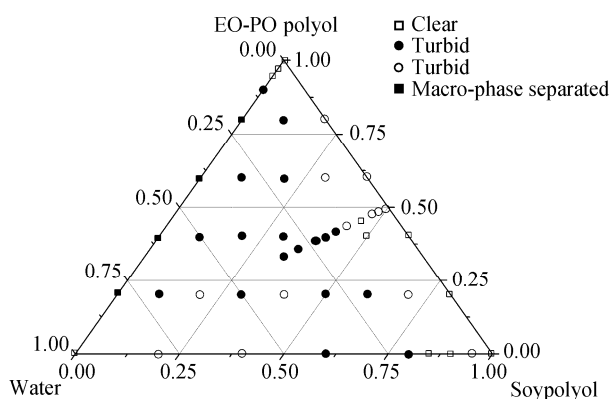


Fig. 5 Ternary phase diagram for the soy based polyol/EO-PO polyol/water system

Low Field NMR Studies

Even if the exact mechanism cannot be determined, it is fruitful to examine the effects of phase behavior on the polyurethane reaction and the products formed. In the present study, the polyols were mixed with either 5 wt% or 10 wt% D₂O. The miscibility behavior clearly is different in the two compositions used. How these differences translate into structural features is a matter of great interest. As mentioned previously, a substantial amount of polyureas are formed in the regular EO-PO polyols. A lesser amount of polyureas are formed in soy based system as presented here. In many applications, the viscoelastic behavior is a very important property to evaluate. As mentioned above, previous low field NMR studies have more than demonstrated the utility of this new technique to assess the chain dynamics of various polymer systems^[35, 37, 38]. In conjunction with the infrared data described above, it is possible to analyze the physical nature of the polyurethane reaction products as they evolve while reacting. This will elucidate the effect of polyurea formation and the associated phase separation process. In polyurethanes, the evolution of urethane bonds contributes to chain extension while polyurea formation creates hard segments, restricting chain motion and altering the dynamics of the system. The spin-spin transverse relaxation time constant, T_2 is a direct measure of the physical environment of the system. Following

a 90° pulse is the magnetic moment relaxation which in the x-y plane is governed by the following relationship^[46].

$$M_y(t) = M_y(0)e^{(-t/T_2)}$$

Where $M_y(0)$ is the initial magnetization along the y-direction, $M_y(t)$ is the magnetization at time 't' and T_2 is the relaxation time. The decay is fitted with an exponential fit in accordance with relaxation to Boltzmann equilibrium of the magnetic moment^[47], to yield a T_2 on the order of microseconds to milliseconds depending on the dynamics of the system. It is possible to follow the evolution of the reaction in terms of chain dynamics as it relates to the formation of various domains with structural differences within the polyurethane system. The relaxations observed for the products synthesized from the two compositions with different water content are shown in Fig. 6. This difference is directly related to the physical "crosslinking" in this system.

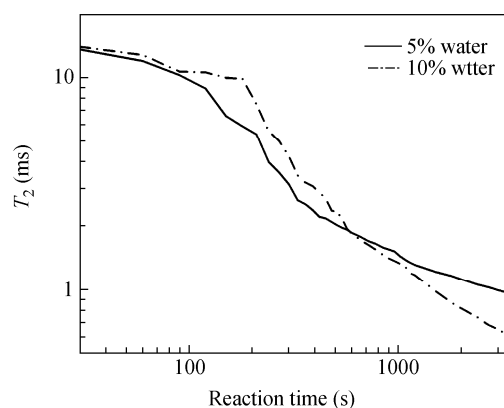


Fig. 6 A plot of relaxation time versus reaction time in the lg-lg scale for samples prepared from 5% water and 10% water

It is apparent that the formation of polyurea domains is delayed in the higher water content system. First, in the sample with 5% water, there is an initial decrease in T_2 . This directly correlates with the infrared data shown in Fig. 7, where free urea at 1689 cm^{-1} forms at the start of the reaction. This is followed by monodentate urea appearing at 1657 cm^{-1} approximately at 200 s of the reaction time and finally capped off by bidentate urea formation (appearing at 1640 cm^{-1}) at approximately 300 s of the reaction time. An overall gradual increase in free urea to ordered urea suggests the gradual transition to a more rigid system as indicated in the Fig. 6. The situation in the sample with 10% water is quite different with a higher T_2 during the initial stages of the reaction. For this sample the infrared data shown in Fig. 8 suggests that the bidentate urea formation was seen only after 450 s of the reaction which then increased in intensity to form more bidentate urea with time. The difference in reaction time and ordering is mostly likely attributed to the water being phase separated and taking a longer time to react with the isocyanate and form rigid polyurea segments, let alone align in doubly hydrogen bound moieties. The T_2 values of the two samples intersect at approximately 460 s of reaction time, followed by a continual decrease of T_2 in both foams, which is also evidenced in the infrared data. This trend is not surprising as the formulation has the potential to form more polyurea hard domains due to higher water content.

Overall, at the beginning of a polyurethane reaction, prior to the addition of the isocyanate component, the T_2 of the sample is of the order of a liquid (21 and 16 ms for samples with 5% and 10% water, respectively) indicating that the polyols and water are a relatively dynamic and mobile system. The T_2 of the final products will be similar to an ordered polymer solid depending on their water content. The values of T_2 for the samples with 5% and 10% water upon complete curing are two orders of magnitude lower (0.3 ms) than the polyol/water mixture, indicating an increasing restriction of chain motion accompanying the formation of ordered polyurea domains. The final T_2 values are indicative of not only the amount of polyurea segments formed, but the degree of association and alignment of the chains into their hydrogen bound orientation as well.

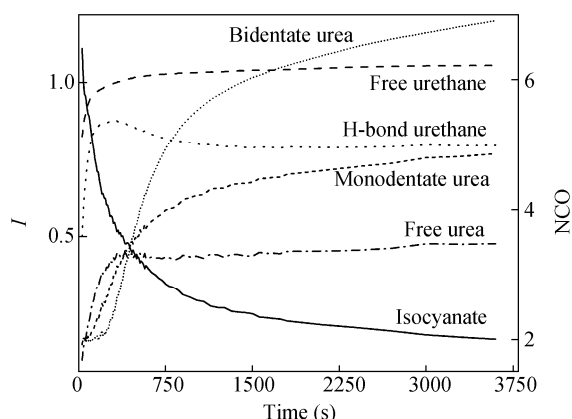


Fig. 7 Kinetic plot based on the time resolved infrared spectra for sample prepared from 5% water

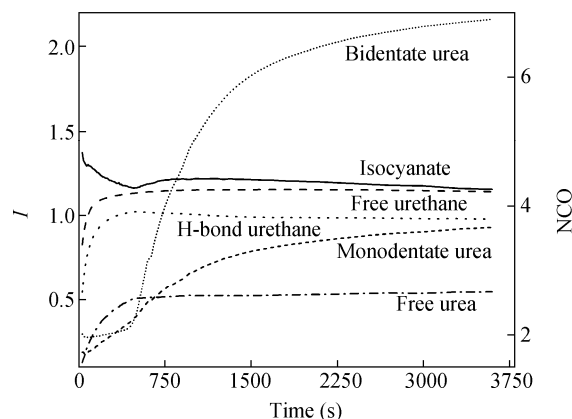


Fig. 8 Kinetic plot based on the time resolved infrared spectra for sample prepared from 10% water

CONCLUSIONS

The structural evolution during polyurethane foam formation is highly dependent on the polyols used in the study. The evolution of urea and urethane units and their aggregation forming physically crosslinked structures was followed using time resolved infrared and low field NMR spectroscopies. Soy based polyols produced a smaller amount of bidentate urea when compared to conventional EO-PO polyol. In addition, the urethanes free from hydrogen bonds appear first followed by the hydrogen bonded component in the soy based polyol. This is considerably different from the expected behavior in conventional polyols.

The difference in the reaction kinetics and products produced depended not only on the chemical nature of the polyol but also on the environment of the water in the two polyols. We deduce that during the reaction, the aromatic diisocyanate monomer segregates itself along the hydrophobic hydrocarbon regions of the soy based polyol, unable to react with the isolated bulk water clusters. This reduces the probability of urea formation. On the other hand, when sufficient urethane linkages are formed, they tend to associate through hydrogen bonding. Low field NMR data confirmed the above finding that the segmental relaxation in the soy based polyol system is slower due to the absence of polyurea hard segment domains. When different amounts of water are used in the reaction, FTIR as well as low field NMR studies showed that 5% water system formed bidentate urea domains much faster than 10% water system. This unexpected difference is caused by the presence of phase separated water in 10% system. But after the reaction was allowed to proceed further, more bidentate urea was found in the 10% water system consistent with a faster segmental relaxation. Hence a combination of infrared and NMR techniques allowed a very clear description of the chemical reactions taking place in different polyols. Unambiguously, miscibility of the various components affects the polyurethane reaction and the phase evolution.

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