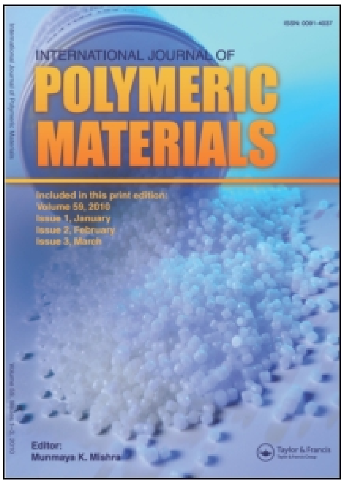

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A Novel Ultrasonic Method of Preparation of Polyurethane Materials

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A Novel Ultrasonic Method of Preparation of Polyurethane Materials

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The possibility of using ultrasonic waves in the reaction between methylene diphenyl diisocyanate (MDI) and polypropylene glycol (PPG) to create polyurethanes is described in this article. This normally slow reaction without chemical catalysts was found to occur to completion within minutes in the presence of ultrasonic waves. A commercially available ultrasonic apparatus was used and characterized for the ultrasonic power. The effect of varying the isocyanate/alcohol groups (NCO/OH) ratio in the presence of ultrasonic waves was also studied. These ratios were found to have a strong effect on the reaction time and mechanical properties of the materials. They also influence the thermal stabilities of the products. Higher NCO/OH ratios lead to faster curing times and harder but brittle materials.

Keywords: NCO/OH ratio, polyurethane, thermal properties, ultrasonic polymerization

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INTRODUCTION

High-intensity ultrasonic waves have been known to enhance polymerization reactions [1,2]. Most published works [3,4] refer to the radical polymerization of vinyl monomers where sonication can obviate the need for thermal initiators and allow some control over the molecular weight, tacticity and polydispersity. Considering the large number of industrially important polymers and plastics prepared via step-growth reactions (including condensation reactions), there have been relatively few publications dealing with the use of ultrasound in this area. Polyurethanes (PU) are the most widely used commercial polymeric materials produced by an exothermic reaction between polyisocyanates with polyols containing multiple hydroxyl groups. They are used as insulation materials, cushioning, automotive parts, and energy absorption materials [5–7]. It is the aim of this work to study the ultrasonic polymerization of PU in different NCO/OH ratios.

EXPERIMENTAL

Materials

Kumho Mitsui Chemicals, Inc. (KMCI) supplied Cosmonate MC-70, which is a modified methylene diphenyl diisocyanate (MDI) with NCO% of 36.5 and polypropylene glycol (PPG), which is a difunctional oligomer with molecular weight of 1000.

Characterization

Fourier transform infra-red spectroscopy was done using a Perkin-Elmer 2000 spectrophotometer in the attenuated total reflectance mode (FTIR ATR) using a zinc selenide crystal in the range of 650-4000 cm^{-1}. Tensile testing was done on dumbbell samples using the UTM (Lloyd Instruments, LR10K, UK) in accordance with ASTM D412 at a crosshead speed of 50 mm/min at room temperature. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out in a DuPont TA2100. DSC was run in the temperature range of -100 to 200°C at 10°C/min scanning rate in a nitrogen atmosphere. TGA was done in the temperature range of 30–700°C at 20°C/min heating rate in a nitrogen atmosphere.

Sonication Method

The main source of ultrasound used was a VCX-750 ultrasonic processor from Sonics & Materials Inc., USA, operating at 20 KHz

FIGURE 1 Ultrasonic apparatus.

(Figure 1). The transducer produces mechanical vibrations, which are coupled into the reaction mixture via a 13 mm diameter titanium alloy horn. A water bath was used with circulating cold water at 10–15°C, thereby achieving a constant low temperature since the reactions are highly exothermic. Sonication intensities were determined calorimetrically. The onset of polymerization is clearly observed by the sudden increase in the viscosity, while the completion is indicated by a clearly audible change in the pitch of the horn corresponding to the solidification of the reaction mixture.

Power Rating

The amount of ultrasonic energy involved in the reaction depends on the ultrasonic power of the horn. This power which is dissipated into the liquid was calculated by the following Equation (1)

$$Power\,(W) = C_P\,(dT/dt)\,M \tag{1}$$

where C_P is the heat capacity of water (4.2 J g^{-1}) and M is the mass of water used (50 g). dT/dt is the rise in temperature per second which was found to be 0.13863 experimentally. Ultrasonic power is independent of the initial temperature (0–40°C range) and is consistent with the fact that the variation of cavitation threshold in water with temperature is small below 50°C [2]. In this work, the initial temperature was measured at room temperature by using a thermocouple, which was immersed in the solution and was held at the half height of the solution. Power was determined to be 29.28 W.

RESULTS AND DISCUSSION

Ultrasonic energy produces an alternating adiabatic compression and rarefaction of the liquid medium being irradiated. In the rarefaction part of the ultrasonic wave when the liquid is unduly stretched or "torn apart," microbubbles form because of reduced pressure. These microbubbles contain vaporized liquid or gas that was previously dissolved in the liquid. The microbubbles can be either stable about their average size for many cycles or transient when they grow to certain size and violently collapse or implode during the compression part of the wave. The energy put into the liquid to create the microvoids is released in this part of the wave, creating high local pressures up to 1000 atmospheres and high transitory temperatures up to 5000 K [1]. This energy–releasing phenomenon of the bubble formation and collapse is simply called cavitation or acoustic cavitation ("cold boiling") [2]. These short-time extreme conditions are ideally suited for a fast chemical reaction like polymerization. The harsh conditions generated on bubble collapse lead to the production of excited states, to bond breakage and the formation of free radicals and very rapid and efficient mixing in multiphase systems. Ultrasonic-assisted polymerization of PU proceeded to completion and no after-cure treatment was necessary. The process involved a rapid exotherm, change in density and sudden stiffening of the polymer. It was also noted that in the case of silent reactions (without using ultrasonic waves), after the system gelled, the temperature rose to around 40°C in the stirred reactions, while in the sonochemical polymerizations $>$100°C was noted, thereby indicating that a greater extent of reaction has occurred in the latter case. It takes nearly 30 min for the completion of the reaction and there is only a marginal decrease in the reaction time with increase in the NCO/OH content. But, with increase in the amplitude of the ultrasonic waves, the reaction time is drastically reduced, sometimes as low as 10 min. Contrary to normal chemical reactions, lowering of reaction medium temperature increases the rate of reaction. This is attributed to the lowering of the solvent vapor pressure, which increases the intensity of cavitation. At low vapor pressure, less vapor has an opportunity to diffuse into the bubble and thus cushion the cavitational collapse, therefore making the implosion more violent. Also, as the temperature decreases, the amount of gas dissolved increases and the vapor pressure of the liquid decreases.

Functional Properties

To determine the functional structure of the polyurethane prepared by using ultrasonic waves, FTIR-ATR was performed. The results were consistent with the IR spectrum of polyurethanes, indicating the absorptions at 3295, 1735, 1536 and 1226 cm^{-1}, corresponding to the urethane linkages (-NH stretching), C=O stretching (bonded) in urethane, N-H bending in urethane and –C–O linkage respectively. In addition, the 1599 and 2963 cm^{-1} peaks for the phenyl group and CH_2 stretching were also observed.

Mechanical Properties

In this study, we observed that the mechanical properties increase with an increase in the NCO/OH ratio, as shown in Figure 2. It was also observed that soft materials were obtained for NCO/OH ratio of 0.6 and were found to be unsuitable for tensile testing. Tensile strength increases from 0.3 MPa to 28.33 MPa with a concurrent increase in the hardness and modulus. But, the elongation at break decreases drastically when the NCO/OH ratio goes beyond 1 and at very high ratios the material is extremely brittle with only 7.2% elongation. Mechanical properties did not change appreciably with additional post-curing time. This is because the possibility of further chemical reactions is very remote by physical diffusion process as the ultrasonic initiated reaction proceeds to completion even after

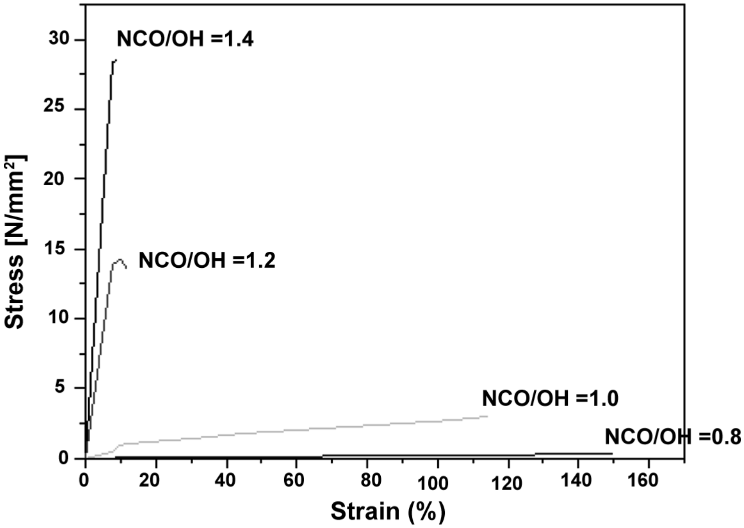

FIGURE 2 Mechanical properties of polyurethanes.

removal of ultrasonic sources. Crosslinking influences the mechanical properties of polyurethanes. Moreover, with an excess of diisocyanate (NCO/OH $>$ 1), allophanate or biuret bond also forms from excess diisocyanurate-urethane or excess diisocyanate urea that may cause chain branching and chemical crosslinking [5].

Thermal Properties

Figure 3 shows the TGA scans for the polyurethane resins with increasing NCO/OH ratios. At NCO/OH ratio of 0.6, we get a single stage of decomposition clearly at 362°C and it increases to two stages at 336°C and 366°C for 0.8 ratio. At ratio 1, the resin decomposes via three distinct stages of degradation, with peak temperatures at 331.8°C, 351°C and 360°C, obtained from the TG-DTA curve (Figure 4). The three stages of degradation shown in the figure indicate that this material possesses three different "thermo-labile" moieties in its polymer chains. However, with an increase in the NCO/OH ratio, the distinct differences in the thermal behavior of the above moieties merged to "two" in the case of an NCO/OH ratio of 1.2 and became "single" for the ratio 1.4. At 1.2 ratio, we get two distinct stages, with peak temperatures at 243° and 363°C. At 1.4 ratio, we get only a single-stage degradation with a characteristic peak temperature at 354°C. Increase in the NCO/OH ratios also increases

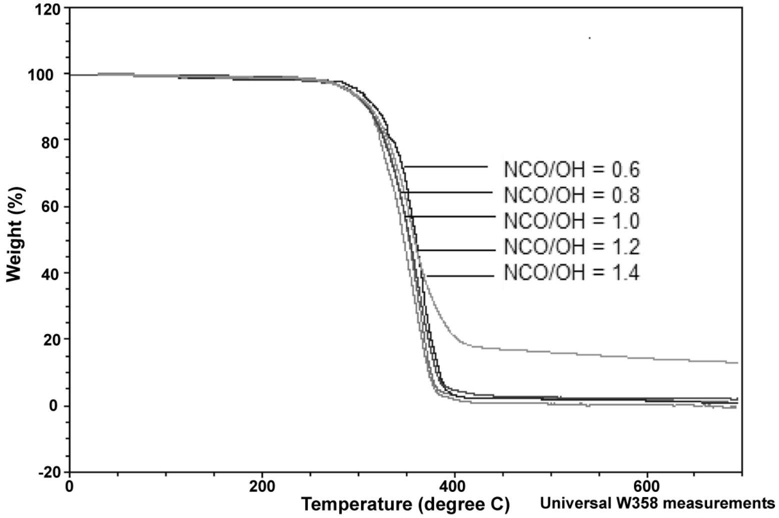

FIGURE 3 TGA curves.

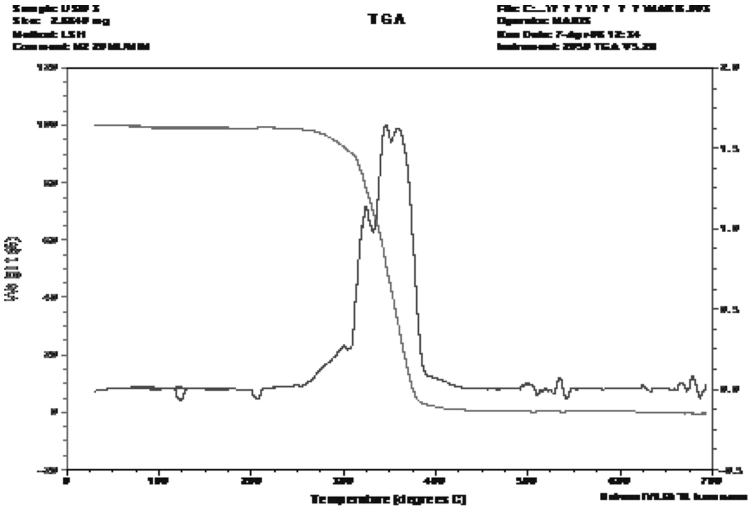

FIGURE 4 TGA and DTG of polyurethanes of ratio NCO/OH = 1.

the crosslinking density, which brings the polymer backbones closer together, making the material "harder," and reduces the molecular mobility and thus increases the thermostability. This also increases the softening point and glass transition temperature. However, in the DSC curves no T_g or softening points were observed for higher

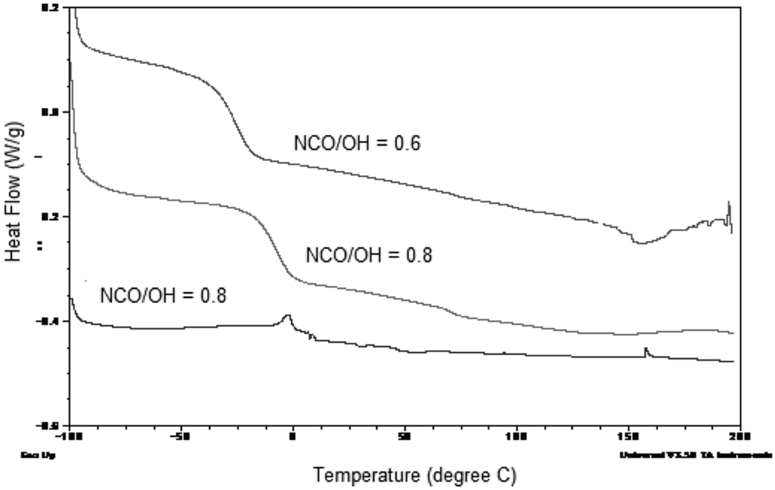

FIGURE 5 DSC thermograms of polyurethanes.

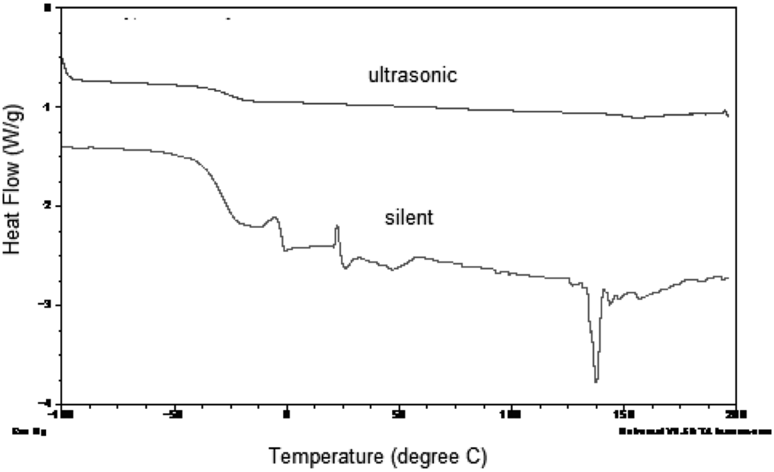

FIGURE 6 DSC thermographs of silent and ultrasonic-prepared PU.

isocyanate ratio, viz. higher than 1, while at ratios 0.6 and 0.8 a T_g at 25°C is clearly observed (Figure 5). Figure 6 clearly indicates the difference between silent and ultrasonic prepared PU of isocyanate ratio 1.2.

CONCLUSIONS

From this study, it can be concluded that ultrasonic waves can be successfully used to synthesize polyurethane materials of varying NCO/OH ratios. These ratios have a strong effect on the reaction time and mechanical properties of the materials. They also influence the thermal stabilities of the products. Higher NCO/OH ratios lead to faster curing times and harder but brittle materials.

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