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Thermoviscoelastic Properties of Phenolic Resin/Polymeric Isocyanate Binder Systems[1]

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Thermoviscoelastic properties of phenolic resin/polymeric isocyanate binder systems (i.e., ISOCURE Parts I and II) are reported. The effects of blend composition and the reaction between the binders on these properties of the systems are also considered. The viscous properties of binders and their blends were measured using computer-controlled rotational viscometers (Brookfield HBDV-II+ viscometer and HAAKE Rotovisco 12 rheometer in the cone-and-plate mode). The elastic properties of the phenolic urethane polymer (the blend composition) were measured by means of a modified jet thrust technique based on measuring the thrust of a liquid jet. Although both binders are Newtonian liquids, their blends exhibit viscoelastic non-Newtonian fluid flow behavior. The viscosity of the blends increases both with time and with an increasing Part I content and may reach comparatively high values at high values of either parameter. This behavior is explained as a result of the rubbery nature of the phenolic urethane polymer, which was produced as a product of reaction between Part I and Part II. The use of the jet thrust method allowed determination of the relaxation time of various blends at different shear rates.

KEY WORDS: elasticity; phenolic resin/polymeric isocyanate binder system; relaxation time; thermoviscoelastic properties; viscosity.

1. INTRODUCTION

The coldbox process was introduced to the foundry industry in 1968. It allowed the production of cores with a good tensile strength, hot strength, and a high dimensional accuracy. The phenolic urethane amine coldbox

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process is the most prevalent one used in the metal casting industry. The relatively low cost and general availability of binders for this process, along with their many versatile properties, have created a broad market for these materials. Moreover, this process can be used with all types of sands available. The process uses a two-part binder system, including a Part I binder (a phenol formaldehyde polymer blended with solvents and additives) and a Part II binder (a polymeric methylenebisphenol diisocyanate). Sand is coated with the Part I and Part II components and blown into a pattern at room temperature. The tertiary amine catalyst vapor then purges through the pattern to harden the contained sand–binder mixture instantly. This cycle is followed by an air purge to introduce amine vapor throughout the sand mass and to remove residual amine from the hardened core [1].

A phenol formaldehyde polymer and a polymeric methylenebisphenol diisocyanate are blended with solvents to yield low-viscosity resin solutions to facilitate their blending and the coating of the sand. The hydroxyl groups of the phenolic resin react with the isocyanate groups of the polymeric isocyanate. In the presence of the amine catalyst, this reaction produces the solid urethane resin. This urethane resin bonds the sand grains together.

The development of binders has concentrated on improving several drawbacks of their properties. Most binders require the following property improvements.

- The speed of the reaction between Part I and Part II must be controllable.
- The phenolic urethane polymer structure must have enough hot strength for use in all types of metal castings.
- Resin-coated sand must have a high flowability until the desired strip time.

Investigations on the binders have been done because of their commercial importance. For example, the compressive strength of the system has been widely investigated in previous work [2]. However, there are few data on the rheological properties of Parts I and II and no data on their blends.

These binders and their blends in foundry processes frequently require rheological characterization for flow equipment design. To develop analytical or numerical models of sand–binder mixing and a sand core-making process requires information on the rheological and thermal properties of binders and their blends. The problem for the experimental rheologist is the engineering approach, that is, the development of quantitative design procedures based on the measured material properties.

In this article, the thermoviscoelastic properties of binders (Parts I and II) are reported. The effects of blend composition and the reaction between the binders on the rheological and thermal properties of the system are also considered.

2. TEST MATERIALS, EXPERIMENTAL APPARATUS, AND PROCEDURE

As a coldbox binder system we used the ISOCURE system produced by Ashland Chemical Company, Dublin, OH. This system consists of an ISOCURE Part I phenol–formaldehyde binder and an ISOCURE Part II binder containing a polymeric isocyanate with solvents and additives.

The ISOCURE Part I binder is a clear, amber liquid with a density of 1.12 $g \cdot cm^{-3}$. The ISOCURE Part II binder is a dark-brown liquid with a density of 1.13 $g \cdot cm^{-3}$. The reaction between Part I and Part II results in the formation of a phenolic urethane polymer.

According to the existing procedure of the sand core-making process in the foundry industry and following the manufacturer's instructions, in most experiments we used the blend composition at a 55/45 ratio of ISOCURE Part I binder/ISOCURE Part II binder. The blend was prepared using a magnetic hot-plate stirrer (3 min at 20 rpm). To calibrate the experimental apparatus we used glycerol/water mixtures as the Newtonian liquid and polyacrylamide solutions as the non-Newtonian viscoelastic liquid.

The viscous properties of the binders and their blends were measured using computer-controlled rotational viscometers.

(i) Brookfield HBDV-II+ viscometer: Disk and cylindrical spindles were used as sensors. Angular velocities of spindles were from 0 to 100 rpm.

(ii) HAAKE Rotovisco 12 rheometer in the cone-and-plate mode: The cone geometry has a 0.00872-radian angle and a 2.5-cm radius. The rotation speed of the cone was from 0 to 512 rpm. The thermal analyses were performed over the temperature range from 20 to 60°C.

Both the Brookfield HBDV-II+ and the HAAKE Rotovisco 12 rheometers were calibrated using Newtonian and non-Newtonian calibration liquids. The calibration data for the viscosity as a function of the temperature and shear rate were in good agreement with data from the literature [3].

The elastic properties of the phenolic urethane polymer (the blend composition) were measured by means of a jet thrust technique. This method is based on measuring the thrust of a jet of liquid. The average axial stress in the liquid at the nozzle exit is the difference between the momentum flux and the measured thrust (corrected for surface tension effects) divided by the cross-sectional area of the jet [4]. For developed velocity profiles in tubes, the momentum flux is determined as [5]

$$\Phi_{\mathrm{dvp}} = 1.33\Phi_{\mathrm{ft}} \tag{1}$$

where Φ_{ft} is the momentum flux for a jet with a flat-topped velocity profile and the same density and viscosity as the liquid under test. The thrust of a Newtonian jet of liquid at the same Reynolds number as the test liquid gives an adequate approximation of the momentum flux.

The average axial stress in the liquid at the tube exit is [6]

$$\tau_{11} = 4(\Phi_{\mathrm{N}} - \Phi_{\mathrm{m}})/(\pi D^2) \tag{2}$$

where Φ_{m} is the measured thrust, Φ_{N} is the thrust of a jet of a Newtonian liquid of similar density and viscosity, and D is the diameter of the tube.

The measured thrust should be corrected for surface tension effects [7]:

$$\Phi = \Phi_{\mathrm{m}} + \pi D\sigma \tag{3}$$

where σ is the surface tension.

Oliver and Ashton [5] suggested plotting the data dimensionlessly as $((\Phi/\Phi_{\mathrm{ft}}) - 1)\,\rho/\rho_{\mathrm{w}}$ versus the Reynolds number, where ρ and ρ_{w} are the densities of the test liquid and water, respectively. The data for Newtonian (inelastic) and elastic liquids should be plotted in this way. The dimensionless separation of the two lines multiplied by $\rho_{\mathrm{w}}\langle v\rangle^2$ gives the average axial stress τ_{11}, where $\langle v\rangle$ is the average exit velocity of the test liquid. The axial stress in the liquid at the tube exit τ_{11} may be plotted against the flow shear rate in the tube.

Figure 1 illustrates modified equipment used for the axial stress measurements. Under compressed air the test liquid was delivered from the stainless-steel cylinder (1) into the stainless-steel capillary tube (3). This tube had a length of 220 mm and an internal diameter of 1.5875 mm. A horizontal jet of test liquid struck the light aluminum disk (9) connected to the load cell (5) and then drained into a beaker (6). During the experiments the distance between the exit of the capillary tube and the aluminum disk was adjusted so that the liquid jet would strike the center of the disk.

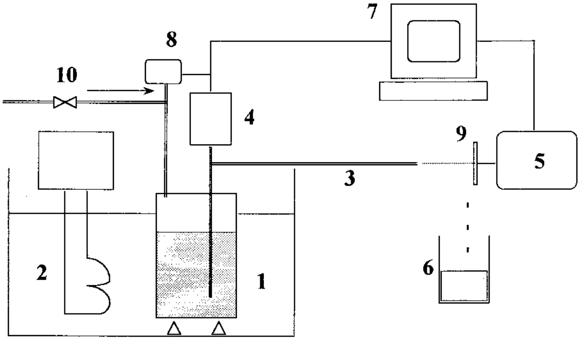

Fig. 1. Modified jet thrust apparatus: (1) stainless-steel cylinder filled with test liquid; (2) water bath; (3) capillary tube; (4) pressure gauge; (5) load cell; (6) beaker; (7) computer; (8) manometer; (9) light aluminum disk; (10) valve to control air pressure.

The pressure at the entrance to the capillary tube was measured by a pressure gauge (4). The temperature of the test liquid was controlled using a water bath (2). The outputs of the load cell (5) and the pressure gauge (4) were fed to a computer (7). The load cell was calibrated in a vertical position, with the aluminum disk upward, by placing weights at its center. The compressed air pressure delivered into the cylinder (1) was controlled by a valve (10).

3. RESULTS AND DISCUSSION

Figure 2 shows the viscosity of the ISOCURE Parts I and II binders as a function of the angular velocity of the spindle at $T = 23°C$. It is obvious that the viscosity of Parts I and II is not affected by the shear rate (or the angular velocities of the spindle). Therefore, both liquids may be adequately described by a Newtonian fluid model. In our experiments we determined that the viscosity (or shear stress) of ISOCURE Part II shows almost no temperature dependence from 20 to 60°C. In contrast, the viscosity (or shear stress) of ISOCURE Part I decreases with increasing temperature (Fig. 3). At relatively low shear rates the shear stress decreases with increasing temperature, and at ~75°C it approaches that of constant viscosity. The uncertainty of all experimental data was determined as a cumulative of the uncertainties of the primary measured values.

Figure 4 shows the viscosity of the Part I/Part II blend as a function of the ISOCURE Part I composition for different time intervals at a fixed spindle angular velocity ($\omega = 50$ rpm) and temperature ($T = 23°C$). As shown in this figure, the viscosity increases with the ISOCURE Part I

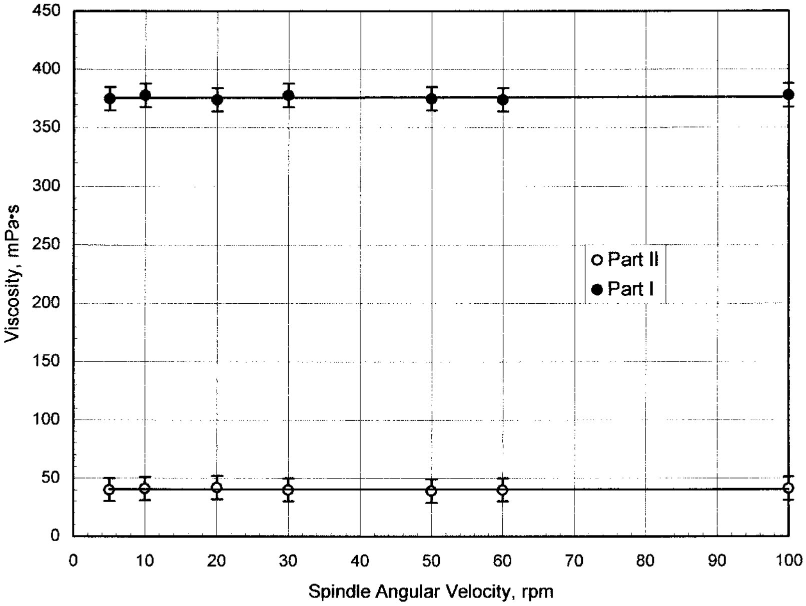

Fig. 2. Viscosity measurements for ISOCURE Parts I and II at $T = 23°C$.

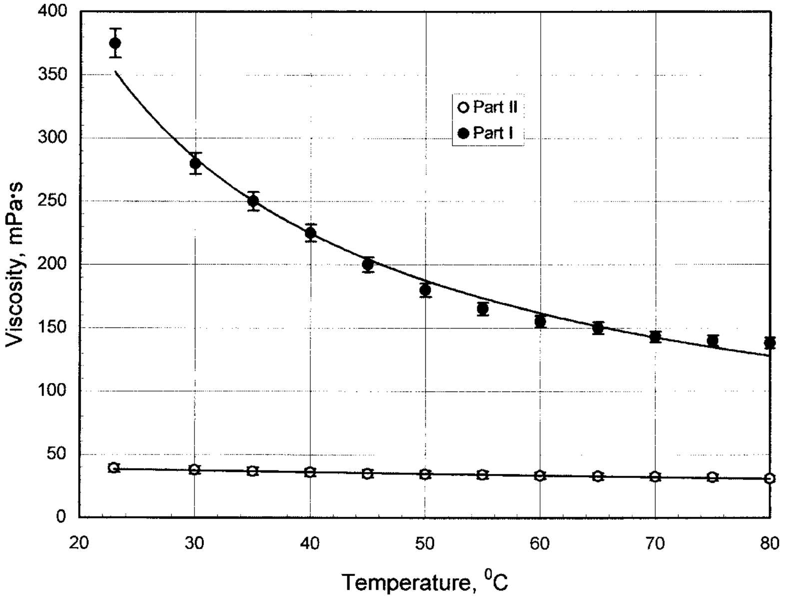

Fig. 3. Variation of the viscosity of Parts I and II with temperature ($\omega = 50$ rpm).

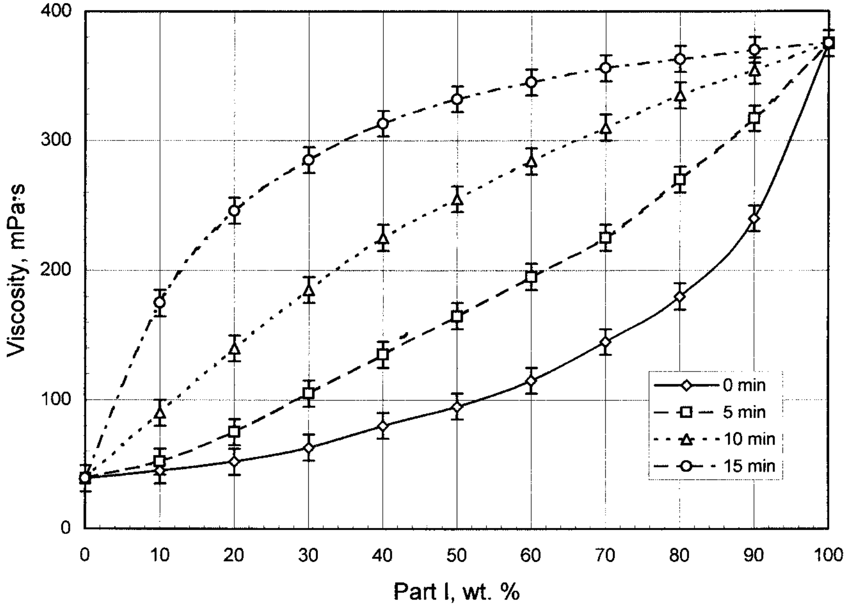

Fig. 4. Variation of the viscosity of Part I/II blends as a function of the Part I composition at different time intervals ($\omega = 50$ rpm, $T = 23°C$).

content. The increase in the viscosity of blends should be expected as the result of the rubbery nature of the phenolic urethane polymer produced in the reaction between Part I and Part II. Therefore, the viscosity of the blend also increases with time. For example, for a Part I/II blend at a ratio of 55/45 (the concentration recommended by the manufacturer based on the sand core qualities), the viscosity after 15 min increases by a factor of almost three.

The viscosity of a Part I/II mixture at a ratio of 55/45 at different spindle angular velocities and temperatures is represented in Fig. 5. It is obvious that the mixture exhibits a shear thinning non-Newtonian fluid flow behavior. However, the viscosity of the mixture is restored with a decrease in the spindle angular velocity. Therefore, one would suggest that as the spindle angular velocity is increased, the polymer chains of the urethane resin structure are oriented in the direction of flow and are disentangled from one another; hence, their dynamic viscosity decreases [8]. At high angular velocities of the spindle (>80 rpm), the behavior of the liquid differs slightly from Newtonian.

To characterize non-Newtonian flow, we introduced the "thixotropic index," which is the ratio of the fluid viscosity as measured at two speeds.

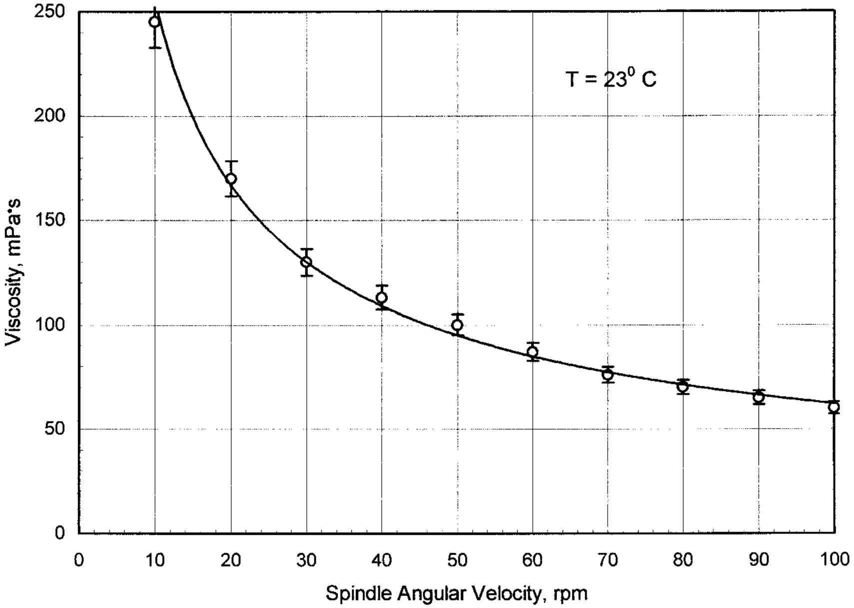

Fig. 5. Variation of the viscosity of a Part I/II blend (55/45) with the spindle angular velocity ($T = 23°C$).

The viscosity value at the "lower" speed (η_ℓ) should be placed in the numerator; the value at the "higher" speed (η_h), in the denominator. The thixotropic index is defined by the following expression:

$$\Gamma = \log\left(\frac{\eta_\ell}{\eta_h}\right) \tag{4}$$

Figure 6 represents the variation of the "thixotropic index" with a "lower" spindle angular velocity for a Part I/II blend at a ratio of 55/45. The data were obtained at a 10-rpm difference between the "higher" and the "lower" values of the spindle speed. As shown in Fig. 6, as the degree of pseudoplastic behavior increases, the "thixotropic index" exceeds 0.1.

During the viscometric measurements, we observed a temperature rise in the mixture of binders. In Fig. 7 we present the temperature change of the ISOCURE Part I/II mixture (in a ratio of 55/45) with time as measured by a computer-controlled thermocouple. During the first 40 s the temperature increases dramatically, from 23 to 30.7°C. Furthermore, the temperature of the mixture decreases until the initial temperature is reached. One is drawn to the inescapable conclusion that the mixing of

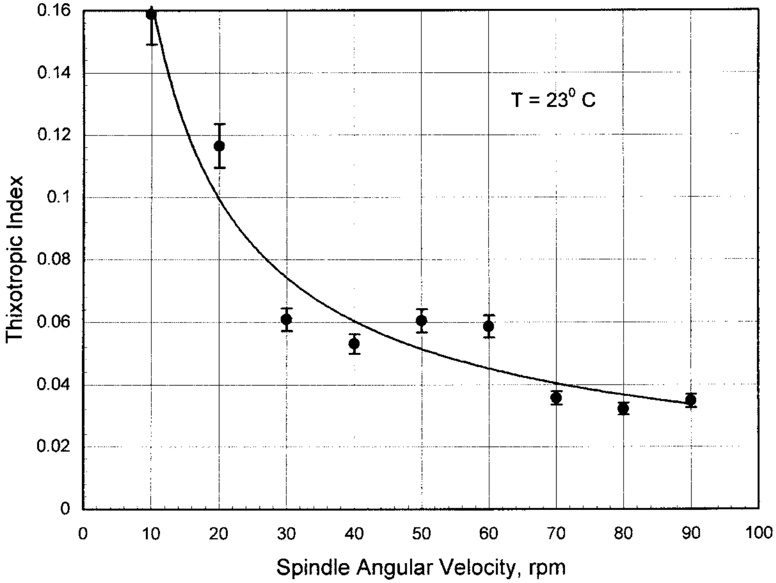

Fig. 6. Variation of the thixotropic index with the spindle angular velocity for a Part I/II blend at a 55/45 ratio at $T = 23°C$.

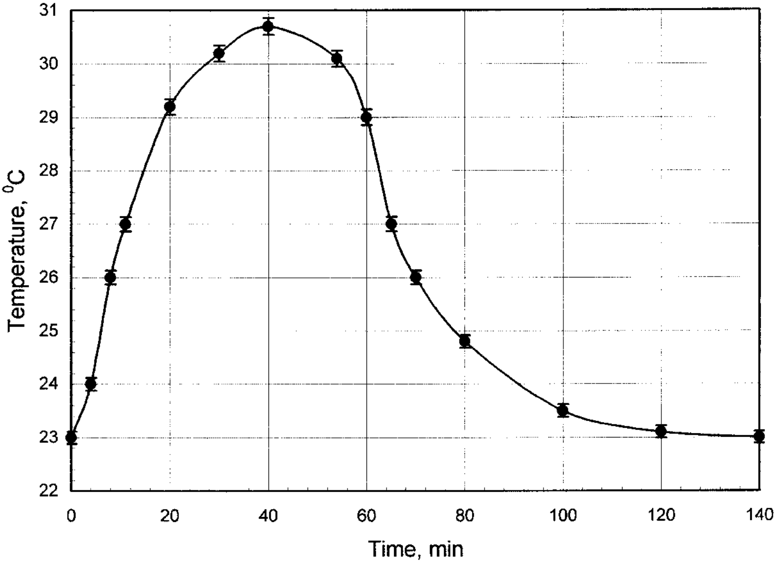

Fig. 7. Variation of the temperature yielded at the thermoreaction between Part I and Part II at a ratio of 55/45 with time.

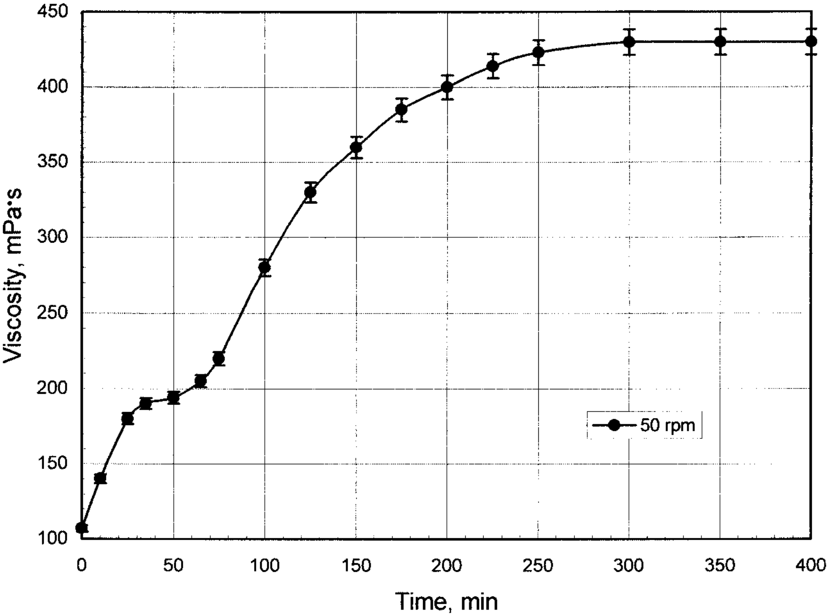

Fig. 8. Variation of the viscosity of a Part I/II blend at a ratio of 55/45 with time at $\omega = 50$ rpm.

ISOCURE Part I and ISOCURE Part II binders yields a thermoreaction. It is of practical interest to observe the variation of the viscosity of the Part I/II blend with time. At constant spindle angular velocities, the dynamic viscosity of the ISOCURE Part I/II mixture increases rapidly due to structural changes (Fig. 8). Due to the combined effects of the thermoreaction and structural phenomena, after ~50 min the viscosity does not change noticeably for 10 to 15 min. Then the viscosity continues to increase, and after 250 min the viscosity reaches a limit and becomes essentially time independent. Here one would conclude that at this point the cross-linking process is complete and the material reaches its shear-independent viscosity.

The first normal stress difference

$$N = \tau_{11} - \tau_{22} \tag{5}$$

for the ISOCURE Part I/II mixture at a ratio of 55/45 is measured by the jet thrust method described above, and the relaxation time λ is computed from

$$\lambda = \frac{(\tau_{11} - \tau_{22})}{2\dot{\gamma}\tau} = \frac{N}{2\dot{\gamma}\tau} \tag{6}$$

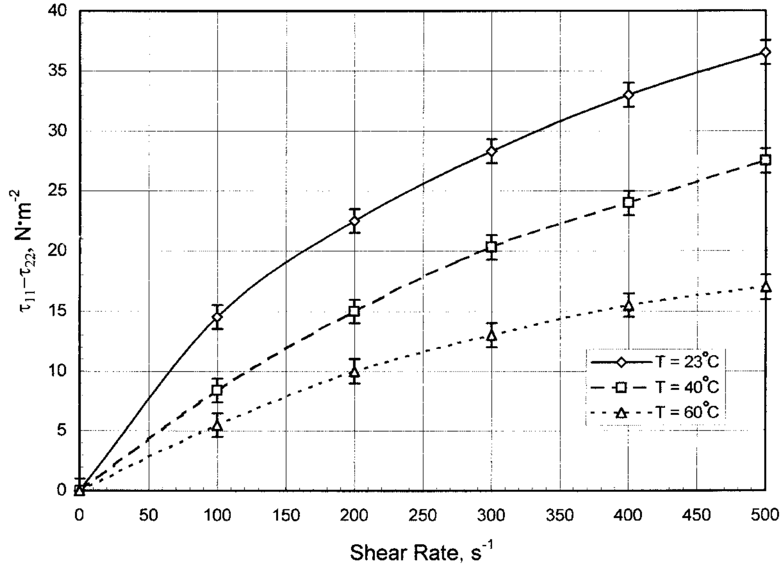

Fig. 9. Variation of the first normal stress difference of a Part I/II blend at a ratio of 55/45 with the shear rate.

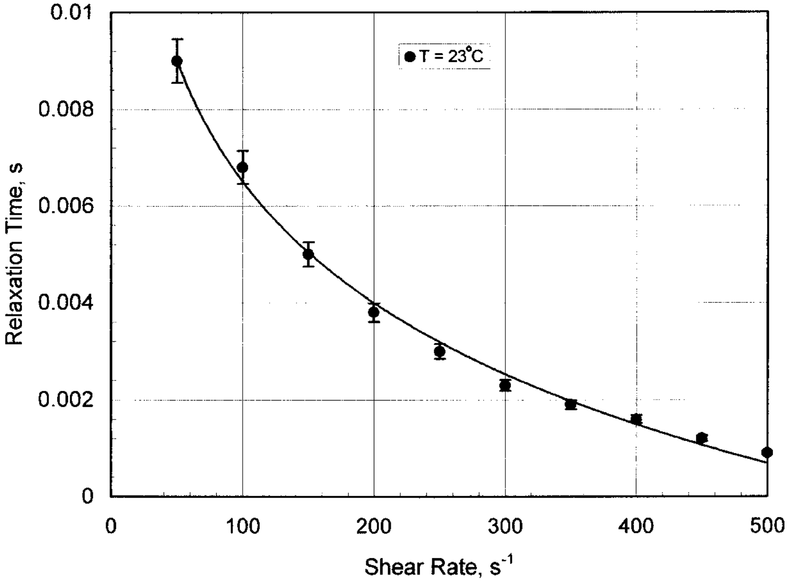

Fig. 10. Variation of the relaxation time of a Part I/II blend at a ratio of 55/45 with the shear rate.

and the results are plotted in Figs. 9 and 10. The measured thrust was corrected for the surface tension effects using Eq. (3). A conventional pendant drop technique was used to measure the surface tension of the test material [3]. The results of the measurements revealed that the surface tension force is about 3% of the thrust of the jet.

From the same data plotted as the fluidity coefficient (reciprocal of the dynamic viscosity) versus the total stress $\tau+(\tau_{11}-\tau_{22})$, it may be concluded that the mixture of binders can be described by the "generalized linear fluidity model" introduced in Ref. 9 (Fig. 11):

$$\varphi=\varphi_0+\theta_{\mathrm{T}}\Psi \tag{7}$$

where $\Psi=\tau+(\tau_{11}-\tau_{22})$; φ_0 is the fluidity in the limit of $\Psi\to 0$, and θ_{T} is the structural fluidity coefficient. Experimental data show that a Part I/II blend at a ratio of 55/45 is characterized by the following values of these coefficients: $\varphi_0=0.0032\ \mathrm{mPa}^{-1}\cdot\mathrm{s}^{-1}$ and $\theta_{\mathrm{T}}=0.0001\ \mathrm{Pa}^{-2}\cdot\mathrm{s}^{-1}$.

4. CONCLUSIONS

The rheological and thermal properties of a phenolic resin (ISOCURE Part I) and a polymeric isocyanate (ISOCURE Part II), and their blends,

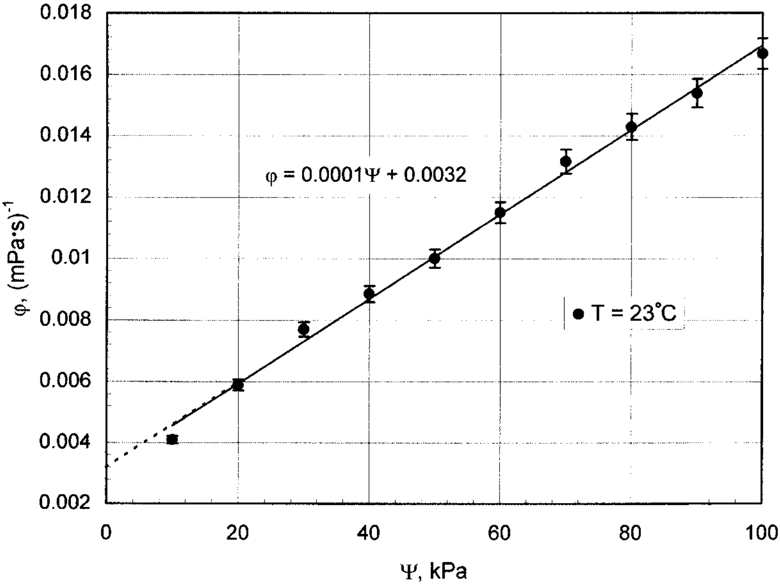

Fig. 11. Variation of the fluidity coefficient of a Part I/II blend at a ratio of 55/45 with the total stress.

were investigated experimentally. We determined that although both binders are Newtonian liquids, their blends exhibit non-Newtonian shear-thinning fluid flow behavior and elasticity. The viscosity of the blends increases both with time and with increasing ISOCURE Part I content and may reach comparatively high values at high values of either parameter. The increase in viscosity of the blends is explained as the result of the rubbery nature of the phenolic urethane polymer produced as a product of the reaction between Part I and Part II. Due to the polymer chains being oriented in the direction of flow and disentangling from one another at high shear rates, the viscosity of the blend decreases. At fixed shear rates we observed a temperature rise during the mixing of binders. Using a jet thrust method, the normal stresses and the relaxation times of the blends were determined at different values of shear rate and temperature. The experimental data revealed that the "generalized linear fluidity model" could adequately describe the mixture of binders.

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