Rheological Properties of Composite Polymer Liner Based on Hydroxyl-Terminated Polybutadiene

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ABSTRACT: An experimental study to determine the dependence of the viscosity and shear stress of hydroxyl-terminated polybutadiene (HTPB) and dimeryl diisocyanate (DII) liner on curing time is presented. Viscosity and shear-stress were measured by HAAKE RheoStress 600 rheometer with parallel disks configuration at a constant temperature of 65 °C. The viscosity and shear-stress change were monitored for 8 h. Analysis of data showed that the liner viscosity and shear-stress dependency on time matched to pseudoplastic fluid model. For low shear-rates, the viscosity build-up is highest, with the logarithm of the viscosity being practically linear with time and the viscosity increases by more than two orders of magnitude for these cases. When the shear rates increase, the viscosity build-up slows down considerably with time and the viscosity is increased only by one order of magnitude.

KEYWORDS: Solid rocket motor; Shear-thinning; Curing.

INTRODUCTION

Liner for solid propellants is an elastomeric adhesive, improving mechanical properties between the insulation and the propellant (Quagliano *et al.* 2015). The common hydroxyl-terminated polybutadiene (HTPB) based liner is a composite matrix that consists mainly of filler powder, HTPB and various additives that determine the rheological and mechanical properties. This is a common technique that is used in many composite materials (Keller *et al.* 2017; Keller *et al.* 2018).

During the liner preparation, an isocyanate type curing agent is added to the slurry, which reacts with hydroxyl groups on the HTPB binder forming polyurethane bonds. In the hydroxyl-terminated polybutadiene dimeryl-diisocyanate (HTPB-DDI) binder, the NCO/OH ratio of 0.9–1.3 is used. Liner viscosity is increased until fully cured. The rate of viscosity buildup and the time needed for a fully cured liner may not be correctly predicted and depends on the curing agent properties and characteristics (Randall and Lee 2003).

Hydroxyl-terminated polybutadiene is cured with various isocyanates (Cunliffe *et al.* 1985; Coutinho *et al.* 1986) which differ mainly in their rate of reaction. Aliphatic isocyanates, such as hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI), have a slower rate of cure, compared to toluene diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI), both of which are primary aromatic isocyanates (Sutton and Biblarz 2001).

Temperature has a significant role in liner viscosity buildup, which affects cure rate (Quagliano *et al.* 2015). Increased temperatures decrease viscosity but increase cure rate which is reflected in higher viscosities; thus, a complex dependence is usually observed. In HTPB-TDI systems the viscosity slowly decreases for 90 min up to curing temperature of 45 °C. If the temperature increased beyond this value, the viscosity will increase sharply (Bandgar *et al.* 2003).

The non-Newtonian nature of the composite polymer fluid is characterized by pseudoplastic or shear thinning behavior. The common rheological models for HTBP-based polymer fluids are based on the thermochemical models derived from the reaction kinetics for isothermal curing process (Kenny *et al.* 1989; Kiuna *et al.* 2002; Liang and Chandrashekhara 2006; Chai *et al.* 2016; Stanko and Stommel 2018).

Similar models are used to characterize rheological behavior of epoxy composited curing (Geissberger *et al.* 2017; Russo *et al.* 2019); Different models can be used to characterize rheological behavior of HTPB-based polymer. The presented approach uses generalized Newtonian fluid (GNF) constitutive equation described by Chhabra (2010) and Natan and Rahimi (2002):

$$\mathbf{T} = \eta\left(\mathbf{\Gamma}\right) \cdot \mathbf{\Gamma} \tag{1}$$

The shear stress tensor T and the non-Newtonian viscosity η are dependent on the shear rate tensor Γ. The GNF equation is generally reduced from its full tensor form to one-dimensional model involving only shear stress. The GNF constitutive equation models steady-shear flows well but does not account for thixotropic behavior. The advantages and limitations of the GNF model are discussed by Bird *et al.* (1987). The GNF model is most commonly used with the Ostwald–de Waele model, or commonly known as power-law (PL) model:

$$\tau = K \cdot \gamma^{n} \tag{2}$$

where: K is flow consistency constant and θ is the flow behavior constant. As can be noticed from the results, the PL model can be adopted for fluids with time dependency parameters, and the compatible form which takes those into account:

$$\tau\left(\dot{\gamma}, t\right) = K\left(t\right) \cdot \dot{\gamma}^{n(t)} \tag{3}$$

Another widely used model for non-Newtonian fluids is the Herschel–Bulkley (HB) model:

$$\eta\left(\dot{\gamma}\right) = K \cdot \dot{\gamma}^{n-1} + \frac{\tau_y}{\dot{\gamma}} \tag{4}$$

The HB model includes a term for the yield stress of the fluid τy. Shear stresses applied to the fluid below their yield shear stress produce no fluid flow and merely result in an elastic deformation of the fluid. The pseudoplastic fluids do not have a yield stress, nevertheless they behave nonlinearly. They flow instantaneously upon application of stress but also display shear thinning behavior. Since having a zero-yield stress, the HB model backslides to GNF model combined with the PL model, both modified for time dependency:

$$\eta\left(\dot{\gamma}, t\right) = K\left(t\right) \cdot \dot{\gamma}^{n(t)-1} \tag{5}$$

This study highlights the preparation of the liner and viscosity measurement. It investigated the rheological behavior of the liner during the curing phase. The measurements were performed at various time intervals using rheometer. The purpose was to construct a mathematical correlation between viscosity rising and curing time and take into account the dependencies of viscosity and shear-stress at different shear-rates.

MATERIALS AND METHODS

The preparation of the liner was according to standard procedure. The ingredients used to prepare the liner were HTPB, filler powder and additives. At the final stage, curing agent DDI was added to the slurry liquid. The filler was silica powder. The powder consisted of spherical particles, with d50 = 7 μm. The solids loading by volume was 0.18%. Viscosity was measured using Thermo Scientific HAAKE *RheoStress 600* rheometer, with parallel disk configuration and 20 mm disk diameter. The parallel disk is one of few configurations suitable for measuring the shear rate dependent viscosity of non-Newtonian fluids (Cross and Kaye 1987; Macosko 1996). It was chosen due to relative ease of sample loading.

The liner specimen was encapsulated between the two disks and held at a constant temperature of 65 °C during the experiment. Dimeryl diisocyanate has a slow cure rate compared to HTPB-TDI. Therefore, viscosity was measured at hourly intervals with the first measurement was taken an hour after the addition of curing agent. Measurement of shear stress and viscosity conducted at shear rates of 1-100 s^{-1}, which covers the shear rates of the expected application.

RESULTS AND DISCUSSION

The measured shear stress and viscosity data are shown in Fig. 1 and 2 correspondingly. As can be expected from the curing processes, the viscosity increases with time for all shear rates. For low shear stresses, the viscosity increases by three orders of magnitude, and for high shear stresses, the viscosity increases by just one order of magnitude. The chemical reaction between the liner ingredients as the curing agent added to the slurry result in non-Newtonian behavior is manifested only after 3 h. The flow behavior constant given in Table 1 supports that conclusion. Non-Newtonian behavior does not appear for all shear rates, but rather starts at some critical shear rate. With time, the critical shear rate moves to lower values, and towards the end of the experiment the non-Newtonian behavior is exhibited for all the range of the shear rates.
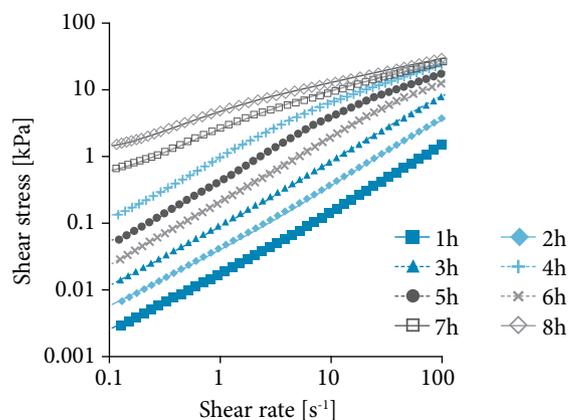
Figure 1. Variation in shear-stress of the liner with shear-rate.

The liner becomes more shear thinning with time. The power-law parameters for each time point are shown in Table 1. It can be seen that the flow behavior constant starts almost Newtonian (n ≈ 1), but reaches n = 0.392 as the liner becomes fully cured. As result, the flow consistency constant is increased by more than two orders of magnitude.

Figure 3 shows a variation of the flow behavior constant n. It can be seen that the time dependence can be divided to three parts. In the first part, for 1 h ≤ t ≤ 3 h, the change is mild, and curves are practically flat. The rate of change of n with time at this interval is n = −0.0272 h^{-1}. The second part is between t = 3 h and t = 4 h, where *a* sharp decrease in n, for n_{3h} = 0.94 to n_{4h} = 0.76 occurs. The third part is for t > 4h, where there is a linear decrease at the rate n = −0.09 h^{-1}. This is a much sharper decrease rate than in the first interval.
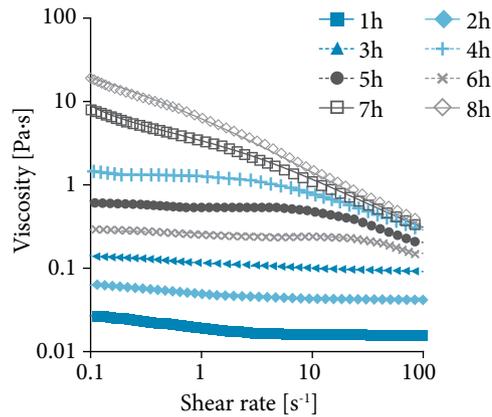
Figure 2. Variation in viscosity of the liner with shear rate.

Table 1. Values of flow consistency and flow behavior constants.

Time [h]	K [Pa·s]	n	R²
1	17	1.00	1.000
2	47	0.98	1.000
3	128	0.94	1.000
4	469	0.76	0.992
5	1094	0.65	0.992
6	1860	0.60	0.997
7	3525	0.48	0.998
8	6010	0.39	0.997
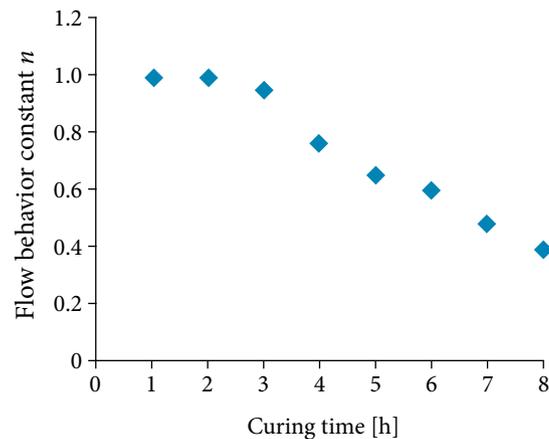
Figure 3. Variation in flow behavior constant of the liner with curing time.

Figure 4 shows the change of the flow consistency constant with time. It can be seen that it rises systematically. Here, no different regions are seen. A mathematical relation can be derived for the time dependency of flow consistency constants and it can be seen in Eq. 6. The fit is excellent ($R^2 = 0.997$):

$$K(t) = 0.05356 e^{0.5916t} \tag{6}$$
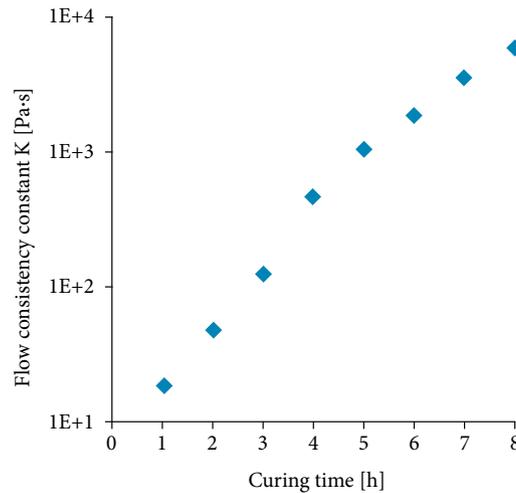
Figure 4. Variation in flow consistency constant of the liner with curing time.

Figure 5 shows the time dependence of the viscosity for various shear rates. It can be seen that the viscosity is very sensitive to shear rates after 3 h. A look at the values indicates that for low shear rates a linear relation between log η and curing time can be easily found. For shear rates higher than single digit s^{-1} this relation becomes more complicated. For shear rates above 50 s^{-1} three staged viscosity rate change is observed. Here we saw condensation of isocyanate groups with OH functionalities decrease after a certain time. This may be explained by the reactivity of the curing agent, the rate of period and it observed as a decline in viscosity build-up rate.
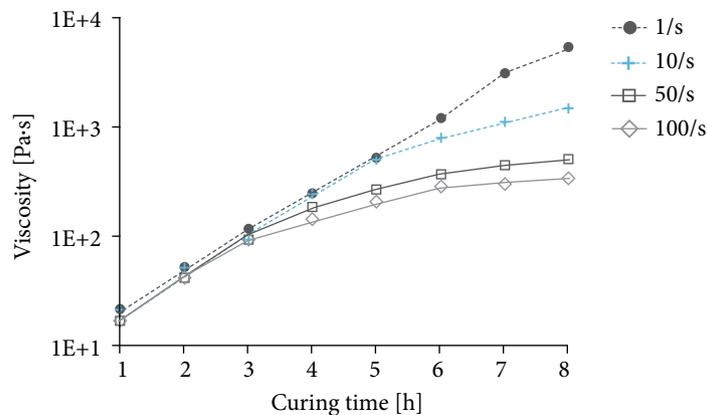
Figure 5. Variation in viscosity of the liner with time.

Elimination of multistage viscosity buildup can be done by increasing the curing temperature, as observed by Sekkar *et al.* (2002). Single-stage viscosity build-up occurred when the reaction conducted at 70 °C. Under this condition, it was expected that the reactivity difference narrows down to some insignificant level, resulting in the coalescence of stages. Moreover, no multistage process was observed by Sekkar *et al.* (2002) using hydrogenated diphenylmethane diisocyanate (HMDI) as the curing agent combined with a catalyst. Both DDI and HMDI are aliphatic isocyanates and share some similarities; therefore, the authors of this work, predict that, if the reaction is conducted without any catalyst, viscosity multistage buildup could not be noticed.

CONCLUSIONS

The core of this study was to characterize the rheological behavior of an HTPB based composite liner. A combination of GNF and power-law model provides a good description of the liner rheological behavior.

The time-dependent behavior of the liner is a complex one. At first, it behaves as almost a Newtonian fluid. Only after 3 h, the onset of non-Newtonian behavior is visible. It is also not always a gradual process, the shear-thinning changes rapidly in the beginning, and slower towards the end. The shear rate at which non-Newtonian behavior start to be seen also changes (becomes lower) with time.

Examining time development of the viscosity shows that the process is not uniform. For low shear rates, it can be seen that the viscosity changes gradually with time; however, for higher shear rates, there are two or even three different stages of viscosity buildup. It is clear that viscosity related-predictions of the liner behavior (such as flow rates and shear stresses) must take into account the expected shear rate.

Examining Fig. 2, the initial chosen range of shear rate, 1-100 s^{-1} for shear stress and viscosity measurements found to satisfy the chosen relations. Increasing the shear rate interval can be incorporated in future work.

Future work will include viscosity measuring in different time intervals, comparison to different measuring technique — cone and plate. Verifying temperature effect on the cure process and comparing between viscosity buildup rate that would be derived.

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AUTHOR'S CONTRIBUTION

Conceptualization: Sapozhnikov I.; Data curation: Sapozhnikov I. Formal analysis: Sapozhnikov I. and Chernov V.; Investigation: Sapozhnikov I.; Methodology: Sapozhnikov I. and Chernov V.; Project administration: Chernov V.; Resources: Sapozhnikov I.; Supervision: Chernov V.; Validation: Sapozhnikov I. and Chernov V.; Visualization: Chernov V.; Writing — original draft: Sapozhnikov I.; Writing — review & editing: Chernov V.

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