

Rheological Behavior of Polymer Solutions during Fabric Coating

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ABSTRACT: The overall performance of coated products is determined by the intrinsic material properties in solution and processing conditions. To characterize the behavior of these materials, the viscosity of polymers in solution at various concentrations was measured and the experimental data were fitted with the Carreau model. The results

describe the rheological behavior of coating materials, and provide a basis for the modeling of polymer flow during the coating process. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2317–2321, 2008

Key words: polymer; solution; rheology; coating

INTRODUCTION

Coating materials used for technical textiles are mainly thermoplastic polymers, which are long-chain linear molecules, and can be formulated in solution as a viscous liquid,¹ to be spread on the surface of a textile substrate. This process is followed by a drying or curing process, which hardens the coating. The rheological properties of these polymeric materials directly influence the durability and performance of the end product.

Rheology is the science that studies the behavior under flow (deformation) of fluids that cannot be described by a linear relationship between stress and deformation rate.² During coating, the uniform spreading of the polymer paste on the fabrics is determined by the polymer paste rheological behavior under the particular process conditions. The study of the polymer rheology is therefore very important for the quality of the coating.³

Rheological behavior of polymer solutions is complex and influenced by numerous factors. Two persistent challenges in polymeric fluid mechanics are the development of accurate rheological models to describe the stress–strain relationship in the fluid and the development of efficient numerical techniques to solve the resulting governing system of equations.

Despite significant appreciation of the importance of the rheological behavior of polymer materials in

chemical processing,^{4–8} the complete formulation concerning the polymer solution for fabric coating needs serious investigation. The present work is concerned with the measurement of the viscosities of the polymer solutions under given coating conditions, to define this rheological behavior. This work is particularly significant in the area of technical textiles because functional and multifunctional textiles find increasing uses in diverse industries such as medical, aerospace, and automotive and the rheological behavior of their polymer solutions are significant in the engineering of their performance and functionality.

PROPERTIES OF COATING MATERIALS

Polymers possess certain unique problems in coating processing. Because of the chain nature of polymers, the molecular structure tends to align when subjected to a shear field. Such a change in structure usually results in non-Newtonian flow, in which the shear viscosity of these materials is a nonlinear function of the rate of shear.⁹

Viscosity is an intrinsic property of polymeric liquids.¹⁰ It is essential for quality coatings that the viscosity of polymer solutions be optimum for the base fabric being processed, and this viscosity must be stable during the coating process.¹¹

Viscosity can be measured quantitatively by viscometers or rheometers. Rotational rheometers are among the instruments used for experimental measurements of viscosity. Many attempts have been made to adapt traditional rotational rheometers to measure polymer liquids because these instruments are commonly used in the laboratory.¹² Rotational rheometers for coating materials apply shear stress

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to the polymer solution at different shear rates to measure the fundamental rheological parameters of yield stress and viscosity.

This work on coating solution viscosity measurement involved using rotational rheometers that feature parallel plate geometry, and coaxial cylinders geometry, both of which are depicted schematically in Figure 1.

In a parallel plate rheometer, the fluid is sheared between two plates. The upper plate is rotated at an angular velocity Ω rad/s, and couple C is likewise measured on the upper plate.¹³ The shear rate varies from zero at the centre to a maximum at the edge of the plates. The shear rate at the edge is given by

$$\dot{\gamma}_R = \frac{R\Omega}{h} \quad (1)$$

where R is the plate radius and h is the gap between the plates.

The viscosity (evaluated at this edge shear rate) is given by

$$\eta = \frac{3Ch}{2\pi R^4 \Omega (1 + \frac{n}{3})} \quad (2)$$

where $n = d \log C / d \log \Omega$.

When data are collected at various values of ω and h , a flow curve can be built up as corresponding values of viscosity and shear rate.

EXPERIMENTAL

Based on the preliminary work and after extensive discussions with industry, the polymer paste formulation chosen was a typical hydrophilic polyurethane

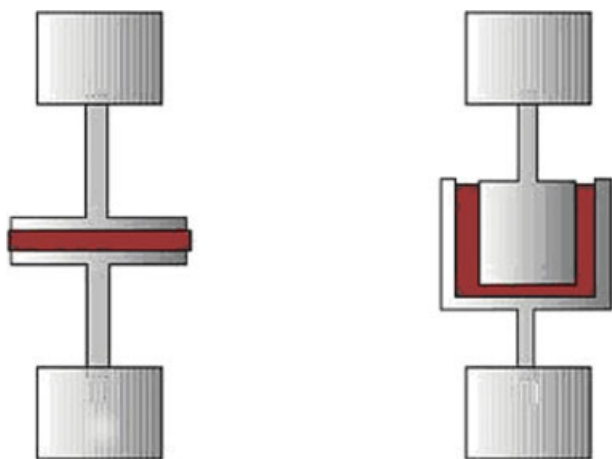


Figure 1 Testing geometries of dynamic rheometers: parallel plates (left), and concentric cylinder (right). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
Recipe Used in the Formulation

Materials	Solids (wt %)	Solvent
Polyurethane resin	45	MEK
M-F resin	~ 5	Isopropanol
PTSA	~ 3	Isopropanol

coatings mainly used for medical textile applications. Its formulation consists of a polyurethane film-forming polymer dissolved in an organic solvent mixture, together with a synergistic heat-activated cross-linking system (Table I). In terms of molecular structure, the polymer is relatively hydrophobic, providing a barrier to liquid water.

The Coatema Base Coater, a small-scale continuous pilot coating machine was used for this investigation, consisting of a doctor blade of length 250 mm, made of stainless steel over a chrome-plated roller for fabric coating. The shear rate of the polymer paste was in the range of $0.1\text{--}1\text{ s}^{-1}$, according to the coating speed of the machine. The process of polymer spreading on the surface of a substrate was at room temperature, until the coated fabric is dried and cured.

The thickness of the coating on a fabric is determined by regulating the height of the knife. In the roller coating process, the liquid flows into a narrow gap between the rotating cylinder and the knife. However, under certain conditions—at low speed, small knife gap, high viscosity, etc.—flow instability appears in which the coating becomes uneven or “ribbed.” Therefore, the viscosity of the polymer solution must be controlled to provide efficient flow of the polymer into the fiber preforms in an online continuous process. This variation in viscosity was achieved by adding additional solvent to the formulation. The solvent content in the polymer was 10, 20, 30, and 40 mL, respectively in 1000 g of the paste formulation.

Based on these conditions, the viscosity of the samples was measured at room temperature using a rotational parallel-plate rheometer, which has 2 cm plate geometry and a gap of $500\text{ }\mu\text{m}$.

RESULTS AND DISCUSSION

Figure 2 provides a schematic representation of the flow curves; the plot of shear stress versus shear rate at four concentrations. It is clear that the samples (coating paste formulation) correspond to a non-Newtonian system, because in the fluid the proportionality between shear stress and shear rate is not constant with increasing shear rate. The samples also show pseudoplastic behavior as the shear stress

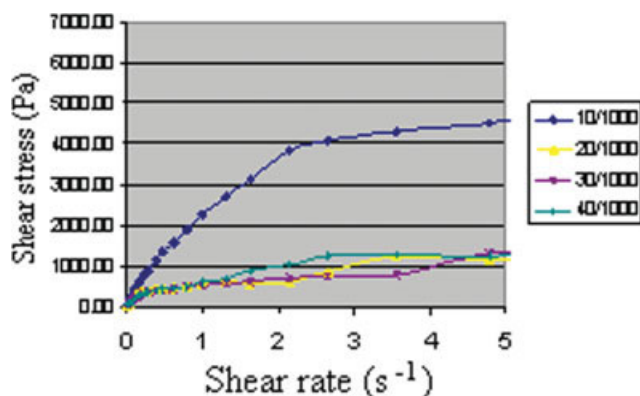


Figure 2 Shear stress (Pa) versus shear rate (s^{-1}) plots of the paste formulation at four concentrations. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

increases, and the increase rate decreases with increasing shear rate under the measured range. It was observed during the test that when shear rate is greater than $2 s^{-1}$, the samples were rolled; therefore, the data in that range was ignored.

It can also be found from Figure 2 that the rheological properties changed considerably with the addition of solvent, and the increase of shear rate. With regard to rheological behavior, it is recommended that an additional 20–30 mL of solvent must be introduced into the paste formulation, because any further dilution of the paste had little effect on the rheological response of the whole range.

Figure 3 is a schematic representation of viscosity versus shear rate, plotted logarithmically, which shows the shear-thinning behavior, typical of non-Newtonian fluids, as the viscosity decreases with increasing shear rate for all samples in the measured

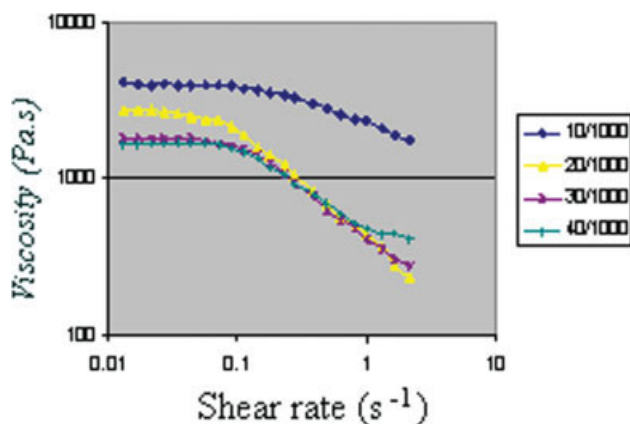


Figure 3 Viscosity (Pa s) versus shear rate (s^{-1}) of the paste formulation plotted logarithmically at four concentrations. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

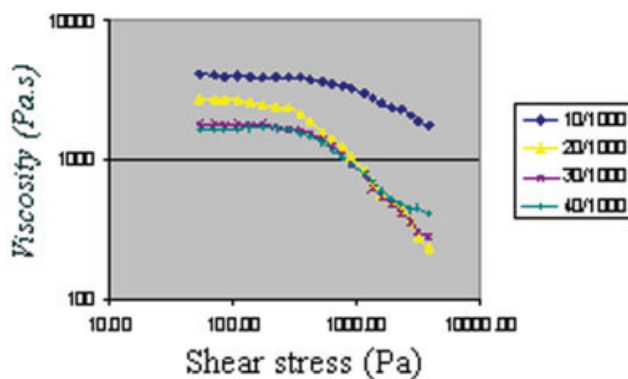


Figure 4 Viscosity (Pa s) versus shear stress (Pa) of the paste formulation plotted logarithmically at four concentrations. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

range. The shear-thinning behavior is further illustrated in Figure 4, showing flow curves of viscosity versus shear stress plotted logarithmically for samples at four concentrations.

The experimental sample data provided by the parallel-plate rheometer at a given condition consists of several points on the viscosity curve. Determination of the viscosity curve over a range of shear rate values is essential for solving the flow equations. This can be done by fitting the data points to one of the viscosity models, as discussed in the next section.

VISCOSITY MODEL

To characterize the flow behavior of the paste formulation, it was necessary to calculate the intrinsic viscosity for fitting an appropriate equation. For shear-thinning liquids, a series of models are available and each equation is applicable only in a certain range of $d\gamma/dt$, this must be specified with the equation parameters.

The shear-viscosity flow curves obtained in the viscosity measurements were analyzed using various rheological models (Bingham, Power, Herschel-Bulkley, and Carreau), and it was found that Carreau model fitted adequately at the condition during the coating (room temperature and the shear rate range). The Carreau model [eqs. (3) and (4)] is a four-parameter equation that describes the whole curve of a typical structured liquid. This has been used to describe the rheology of polymer solution.^{13,14}

$$\eta = \eta_{\infty} + (\eta_0 - \eta_{\infty}) \left[1 + (\lambda \dot{\gamma})^2 \right]^{\frac{(n-1)}{2}} \quad (3)$$

$$\dot{\gamma} = \sqrt{\frac{1}{2} \left[(2u_x)^2 + (u_y + v_x)^2 + (2v_y)^2 \right]} \quad (4)$$

where, η_0 represents the zero shear rate viscosity, η_∞ is the infinite shear rate viscosity, λ is a parameter with units of time, and n represents the shear rate sensitivity ($0 < n < 1$).

The Carreau model parameters obtained from the software are shown in Table II. Because of the limitation of the viscosity measurements device, it was not possible to obtain the values of η_0 . In this study, the zero shear viscosity η_0 was determined by direct extrapolation of low-shear data from the plot of the viscosity versus shear rate. The rheological parameters λ and n decreased with solvent fraction increase; however, no significant differences were observed in rheological data at solvent fraction range of 20–40/1000.

Figure 5 shows the plot of measured data for coating paste samples at two concentrations and fitted with the Carreau model. The dotted and dotted-dashed lines were plotted based on the experimental data for two typical samples, whereas solid and dashed lines were plotted according to the Carreau model. It can be seen from Figure 5 that the Carreau model fits well with the measured data describing viscosity dependence of the paste formulation on shear rate. Different solvent volume fractions lead to different parameters, indicating that the rheological behavior of coating materials can be controlled by introducing solvents. This is important because it contributes to the engineering of coating functional and performance properties of the coated fabrics.

CONCLUSION

This study on the rheological behavior of coating paste formulations has led to an understanding of the behavior of the coating materials and the properties of the coated products. These properties are in turn determined by intrinsic material parameters and processing conditions.

The rheological behavior of the paste formulations corresponds to a non-Newtonian, shear thinning fluid as the viscosity decreases with increasing shear rate. The same behavior is observed for all samples. The Carreau model was fitted with measured data describing viscosity dependence of the paste formu-

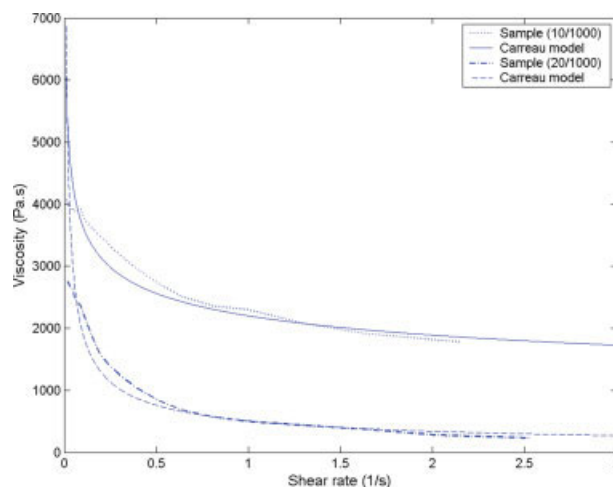


Figure 5 Viscosity versus shear rate plot of the paste formulation at two concentrations, fitted with the Carreau model. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

lations on shear rate, with coefficients varying with solvent volume fraction.

The coating quality can be controlled by improving penetration, adhesion, or uniformity. To that effect, the viscosity of paste formulations can be tuned by introducing solvent. It is recommended that 20–30 mL of solvent is a suitable concentration to be introduced into the polymer (1000 g) under the coating condition, as further dilution had no significant effect on the rheology of the system. The coating quality control by tuning the viscosity of coating paste is an efficient way for engineering the performance and functionality of technical textile fabrics.

From the measured data obtained, a better understanding of the rheology of the polymer paste formulations is established when polymer paste is spread on the surface of a substrate during coating. With the parameters of paste formulations, computer simulation of coating can be carried out to relate the coating quality with coating material properties and coating process parameters. This work forms the basis of future publications.

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TABLE II

Carreau Model Parameters for Coating Paste Samples

Solvent fraction	η_∞ (Pa s)	η_0 (Pa s)	λ	n
10/1000	0.10	11,000	1,500	0.78
20/1000	0.10	11,000	200	0.42
30/1000	0.10	11,000	180	0.41
40/1000	0.10	11,000	170	0.41

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