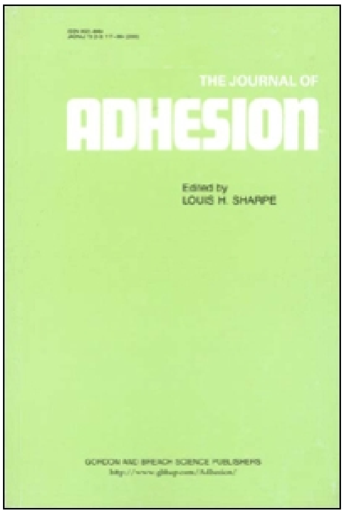

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Li, C. , Mazich, K. A. and Dickie, R. A.(1990) 'A Survey of Rheological Properties of One-Component Epoxy Adhesives', The Journal of Adhesion, 32: 2, 127 — 140
To link to this Article: DOI: 10.1080/00218469008030186
URL: http://dx.doi.org/10.1080/00218469008030186

J. Adhesion, 1990, Vol. 32, pp. 127–140
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Printed in the United Kingdom

A Survey of Rheological Properties of One-Component Epoxy Adhesives

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(Received January 30, 1990; in final form April 11, 1990)

Flow characteristics of seven commercially available one-component epoxy adhesive pastes were measured using a controlled shear stress rheometer and a controlled shear rate rheometer over a temperature range from 5°C to 60°C. Combining data obtained from both controlled rate and controlled stress experiments over a wide range of shear rates, we observed Newtonian flow (shear stress proportional to shear rate) at very low shear rates, a plateau "shear thinning" region at intermediate shear rates, and a second region of linear dependence of shear stress on shear rate at high shear rates. The adhesive pastes exhibited a very broad range of rheological behavior. Two flow parameters important to adhesive application technology, the plastic viscosity and the apparent yield stress, were measured for each adhesive. The plastic viscosity ranged from 11.6 to 329.5 Pa · s; the apparent yield stress ranged from 56.2 to 413 Pa. The temperature dependence of the rheological parameters of the epoxy adhesive pastes was also determined. The results are reported as the activation energies, E_η and E_σ, of plastic viscosity and apparent yield stress, respectively. The apparent yield stress of each adhesive paste was much less sensitive to changes in temperature than was the plastic viscosity. This suggests that the processing characteristics are likely to show qualitative as well as quantitative changes with temperature.

KEY WORDS Rheology; non-Newtonian fluid; adhesive flow properties; yield stress; plastic viscosity; temperature dependence.

INTRODUCTION

One-component adhesives based on filled epoxy formulations have been used or proposed for use in automotive manufacturing processes for various structural and semi-structural applications. These adhesives usually contain liquid epoxy resins mixed with reinforcing fillers and solid curatives. They are chemically stable at room temperature for extended time periods and are processed as pumpable liquids or pastes. The application performance of paste adhesives is strongly affected by many material and process variables, including paste viscosity, yield stress, flow rate, thermal stability, application temperature, and cure temperature and time. Since most commercial one-component epoxy adhesives contain not only epoxy resin with curatives but also fillers, plasticizers, rubber modifiers, pigments, and other additives, their rheological behavior is rather complicated. A characterization of the flow properties of typical commercially available epoxy adhesive pastes is a necessary first step in understanding and modeling the adhesive application process.

In this study, the flow characteristics of one-component epoxy adhesives were determined using both a controlled shear stress rheometer and a controlled shear rate rheometer. The flow measurements were conducted over a wide range of shear rates. Temperature dependence of the rheological parameters was also examined.

EXPERIMENTAL

Materials

Five convection-oven-curable and two induction-curable one-component adhesives were provided by their respective manufacturers. These adhesives are designed for semi-structural applications with standard industrial equipment. The manufacturer-supplied specifications of these adhesives are listed in Table I. The adhesives were stored under refrigeration to prolong their shelf life. Prior to rheological measurements, the adhesive samples were allowed to reach thermal equilibrium at room temperature (about 25°C).

Controlled shear stress rheometry

Flow curves of the one-component adhesives were generated with a Carri-Med Model 500 Controlled Stress Rheometer. Due to the presence of relatively large size filler particles in the adhesives, a parallel plate configuration with 40 mm diameter plates was employed for flow behavior studies. The apparent shear rate of the parallel plates was calculated at the edge of the plates, where maximum shear occurs. Gap size of the parallel plates was initially varied from 0.20 mm to 1.00 mm. It was found that the gap size did not affect the measured flow data and

TABLE I
Description of one-component epoxy adhesives

Adhesive sample	Manufacturer	Trade name	Filler wt %
ES-1	Ciba Geigy	XB-3131	25
ES-2	American Cyanamid	Cybond-4531	40
ES-3	American Cyanamid	Cybond-4551	30
ES-4	W. R. Grace	Terokal-3919-US	25
ES-5	Uniseal	AP-116 HY	40
ES-6	Widger Chemical Corp.	WC-2390	60
ES-7	Widger Chemical Corp.	WC-2290B	40

a 1.00 mm gap was then used for all measurements. Samples were subjected to a controlled shear stress, also calculated at the edge of the plates, that varied linearly with time according to a preset stress ramp rate. The rate of shear stress increase was approximately 12.5 Pa/sec. Data were collected at constant temperature for temperatures ranging from 5°C to 60°C. Data acquisition and analysis were accomplished with a manufacturer-supplied software package.

Controlled shear rate rheometry

A Rheometrics Mechanical Spectrometer Model RMS-800 was used to measure the flow characteristics of the one-component epoxy adhesives under constant shear rate. A 25 mm diameter parallel plate configuration with a 1 mm gap was used for all measurements. Rate sweep measurements were conducted from 0.001 to 0.1 $\sec^{-1}$ with five rate intervals per decade. The adhesives were subjected to steady shear for 300 seconds at the given shear rate prior to the measurements to minimize shear history effects. Isothermal rate sweep measurements were made at 5, 15, 25, 35, 45, and 55°C.

RESULTS AND DISCUSSION

Controlled shear stress rheometry

Room temperature (25°C) flow (shear stress *vs.* shear rate) curves of the one-component epoxy adhesives measured by the controlled-stress rheometer (Carri-Med) are shown in Figure 1. Also shown in the figure is the curve for pure Epon 828, a typical low molecular weight epoxy resin, for reference. The Epon 828 exhibits Newtonian flow behavior; *i.e.*, shear stress is proportional to shear rate ($\sigma = \eta\dot{\gamma}$, where σ is the stress, $\dot{\gamma}$ is the shear rate, and η is termed the (Newtonian) viscosity). As shown in the figure, all of the adhesive pastes studied clearly show strong deviations from simple Newtonian flow. The non-linearity in the low shear region of the paste flow curves indicates that a simple linear model such as the Bingham equation $\sigma = \sigma_y + \eta\dot{\gamma}$, where σ_y is designated as yield stress, is also not adequate for prediction of the flow behavior of the adhesives. Moreover, a comparison of data for the different adhesives indicates that the materials possess very different flow characteristics. The highest shear stress was observed from the ES-7 material. Three of the adhesive pastes: ES-1, ES-2, and ES-4 showed similar flow behavior represented by a linear shear stress-shear rate relationship at high shear rates and an apparent yield stress. The yield behavior in filled polymer systems is time or shear rate dependent, therefore, the apparent yield stress is not an intrinsic material property. The yield phenomenon is discussed in more detail in the next section of this paper. The ES-5 and ES-7 pastes exhibit much higher resistance to flow (as represented by the slopes of their flow curves) than do the other adhesive pastes. The ES-3 paste shows strong non-linearity in the low shear region and higher terminal viscosity in the

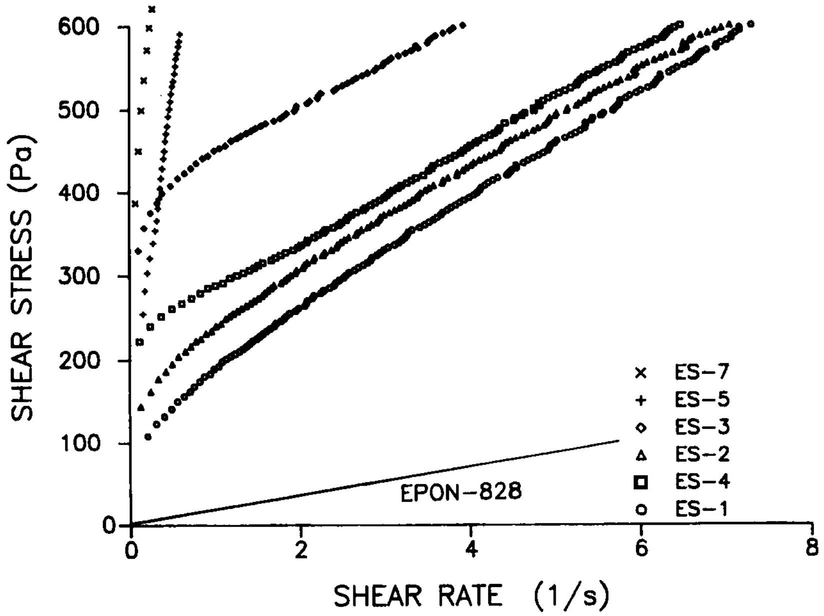

FIGURE 1 High shear rate flow curves of the one-component epoxy adhesive pastes.

Newtonian flow region. Microscopic examination of the adhesives indicates that the filler particle size in the ES-3 is about three times larger than that in other adhesives. More importantly, the fillers in ES-3 tend to form even larger (macroscopic) aggregates which can strongly affect the flow properties of the ES-3 paste.

It is well known that Newton's law of viscosity does not adequately describe the mechanical response of polymeric fluids such as filled polymer solutions.[1,2] The flow behavior of the adhesive pastes in the high shear rate region (when $\dot{\gamma} > 0.1\,\mathrm{sec}^{-1}$), however, can be represented empirically by the Casson equation:[3]

$$\sigma = (\sigma_0^{1/2} + (\eta\dot{\gamma})^{1/2})^2 \tag{1}$$

where σ_0 is the apparent yield stress and η is the plastic viscosity. Matsumoto *et al.*[4,5] and Bauer *et al.*[6] applied the Casson equation to fit high shear rate flow data in studies of suspensions of rigid particles in polymer solutions. They reported that the agreement between the Casson equation and the experimental data was generally very good. It is, however, difficult to extract a mechanistic description of the rheological behavior from the Casson equation. The rheological behavior of the adhesive pastes predicted by the Casson equation approaches that given by the Bingham equation at very high shear rates (higher than $10\,\mathrm{s}^{-1}$). This is an important point since many of the process engineering calculations at high shear rates could be accomplished by employing the mathematically simpler Bingham model. Figure 2 provides an example of fitting the Casson equation to the flow curve data of ES-1 at 25°C. Similar agreement between the Casson equation and

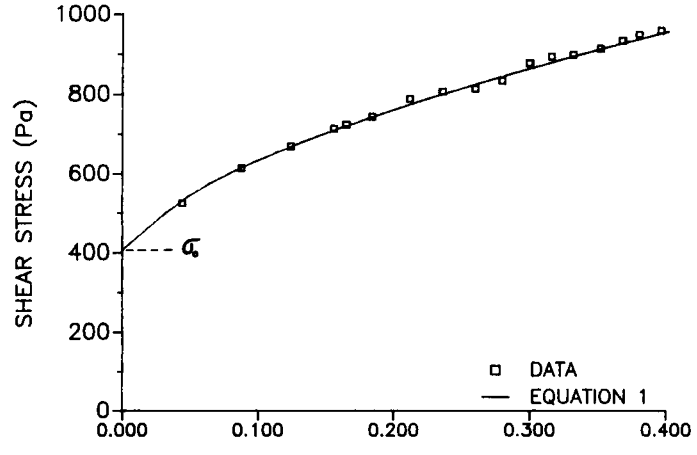

FIGURE 2 Representation of ES-4 flow data at 10°C fit by the Casson equation.

experimental data was found for other adhesive pastes in this study. The Casson parameters of the adhesive pastes are listed in Table II. The apparent yield stress σ_0 at room temperature varies from 56.2 Pa (ES-1) to 413 Pa (ES-7) while the plastic viscosity η ranges from 11.6 Pa · s (ES-3) to 329.5 Pa · s (ES-7). Since the Casson equation provides a very good representation of the flow properties of these adhesive pastes in the high shear rate region, the Casson parameters σ_0 and η can be useful for designing adhesive application processes. For instance, the shear rates typical to adhesive dispensing for automotive applications range from 5 to 100 s^{-1}. The flow properties could be easily represented or extrapolated using the Casson parameters due to the linear relationship between shear stress and shear rate in the high shear rate region.

TABLE II
Summary of processing properties of one-component epoxy adhesives

Adhesive sample	Yield stress[1] at 25°C (Pa)	Viscosity[2] at 25°C (Pa · s)	T_g °C	Activation Energies[2] E_η (kcal/mole)	E_σ
ES-1	56.2	39.5	−38	23.72	7.614
ES-2	97.1	30.2	−24	25.61	2.825
ES-3	313	11.6	−33	29.37	6.919
ES-4	144	22.5	−36	20.44	5.735
ES-5	174	155.2	−42	24.92	7.119
ES-6	273	22.1	−36	22.41	3.875
ES-7	413	329.5	−38	20.06	4.170
Epon 828[3]	0	15.7	−18	28.01	

[1] Apparent yield stress σ_0 and plastic viscosity η were calculated by fitting Casson equation to the flow curves of adhesive pastes.

[2] E_η and E_σ designate activation energies of viscosity and apparent yield stress respectively.

[3] The flow parameters of pure Epon 828 resin included here are for comparison purposes. These adhesives may or may not contain Epon 828 in their formulations.

Rheological properties of adhesives are important considerations in selection of adhesives for manufacturing processes. The apparent yield stress σ_0 is a significant parameter in determining the extent and stability of flow and can affect the quality of the final bond. The existence of an apparent yield stress and associated "shear thinning" typically make pumping and dispensing less reproducible and more difficult. Qualitatively, a low value of apparent yield stress can be expected to result in improved flow uniformity. For materials with high apparent yield stress, intermittent dispensing can result in unstable flow at the beginning and end of each application cycle. Moreover, the adhesive flow profile (velocity distribution) as well as the flow rate (dispensing output) are affected by the presence of an apparent yield stress. The ratio of the apparent yield stress to the pressure drop in a given flow path is an important parameter for the adhesive dispensing. A high yield stress at application temperatures can prevent the adhesive from fully wetting a rough adherend surface, and can thus interfere with establishment of intimate contact during bonding. On the other hand, the existence of a substanial yield stress contributes to good sag resistance during processing and improves resistance to adventitious displacement of the adhesive during subsequent stages of processing prior to cure. For example, a minimum yield stress of about 10 Pa is necessary to prevent a 1.0 mm thick layer (assuming a 2.0 g/cm^3 density) from sagging under gravitational stress. As shown in Table II, every sample of the one-component epoxy adhesive pastes examined possesses an apparent yield stress σ_0 higher than the estimated minimum yield stress of 9.8 Pa.

The second Casson parameter listed in Table II, the plastic viscosity, η, provides a convenient quantitative measure of the paste viscosity in the high shear rate region. Proper viscosity is required for each specific application of the paste. A paste with high viscosity may experience excessive viscous heating during pumping and high shear rate application. Since the filled adhesive pastes usually exhibit a yield phenomenon, they are forced to flow through the dispensing device in a so called "plug flow" fashion. The shear rate across the flow path is not uniform as in the case of a highly viscous Newtonian fluid. Thus the shear rate tends to be much higher near a solid boundary depending upon the relative contributions of yield and viscous components of the paste. A detailed treatment of viscous heating in non-Newtonian fluids is not within the scope of this study, but it should be noted that local viscous heating in the high shear region may occur when dispensing a non-Newtonian fluid at high volumetric flow rates. On the other hand, the filler particles may not be well suspended in the paste if the viscosity is not high enough to prevent settling. Most of the one-component epoxy adhesive pastes surveyed possess plastic viscosity ranging from 11.6 to 39.5 Pa · s. Two, ES-5 and ES-7, are five to ten times more viscous (see Table II).

Controlled shear rate rheometry

The flow behavior of filled polymer systems at low shear rates measured by controlled shear rate rheometry is usually different from that measured at high shear rates by a controlled stress method. Figure 3 shows steady state flow curves of ES-7 at low shear rates. Data were collected at constant shear rates ($\dot{\gamma}$ between 0.001 sec^{-1} and 0.1 sec^{-1}) at different temperatures. The well-known principle of time-temperature superposition[7] has been applied to the flow curves at different temperatures. Rong and Chaffy adopted this method for filled polymer systems.[8] According to the superposition procedure, flow curves such as those in Figure 3 are shifted horizontally along shear rate axis to an arbitrarily chosen reference temperature until they coincide with the curve measured at the specified reference temperature. A shift factor α_T, dependent only on temperature, is defined by $\alpha_T = \dot{\gamma}T_{\text{ref}}/\dot{\gamma}(T)$. The time or rate dependence of a relaxation phenomenon can be examined from the superposed curves. As shown in Figure 4, the master flow curve shows a good superposition of individual flow curves. The master flow curve also shows that the flow behavior of ES-7 at very low shear rates is Newtonian. Contrary to the flow characteristics measured by controlled stress rheometry at high shear rates, the master flow curve does not show an intrinsic yield stress. The absence of an intrinsic yield stress suggests that the apparent yield stress measured at high shear rates is a time (or shear rate) dependent phenomenon.[10]

Low shear rate flow data of other one-component adhesives were collected in the same fashion as for the ES-7 sample. Strong shear history effects on low shear rate flow curves were observed for ES-2 and ES-4 materials, and superposition of flow curves was not satisfactory. A complete characterization of the time and history effects on the flow properties is beyond the scope of this paper.

Figure 5 shows the flow behavior of ES-2 paste in an expanded shear rate

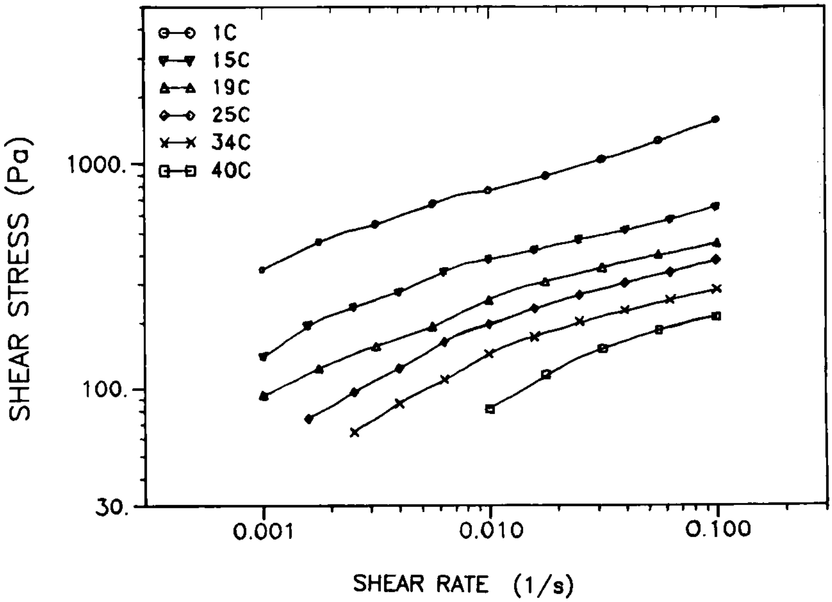

FIGURE 3 Steady state low shear rate flow data of ES-7 adhesive at different temperatures.

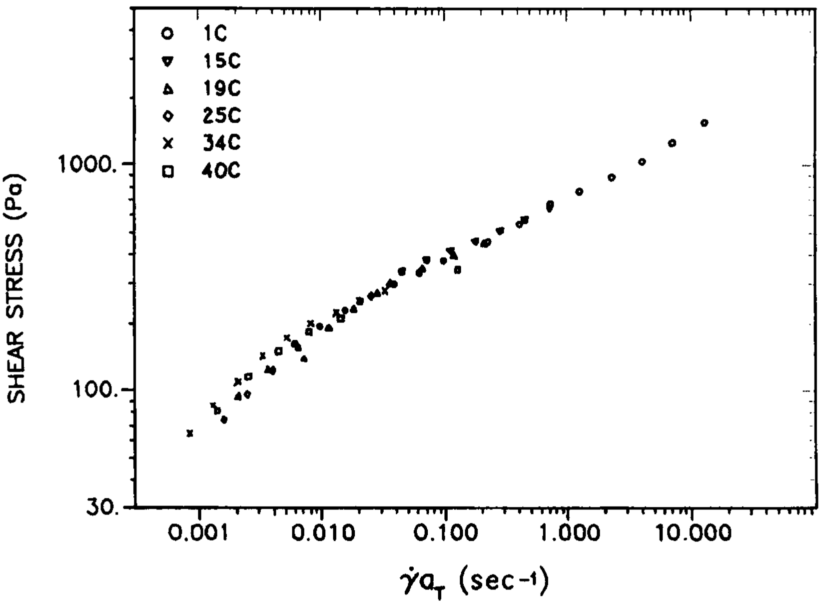

FIGURE 4 Master flow curve of ES-7 in the low shear rate region.

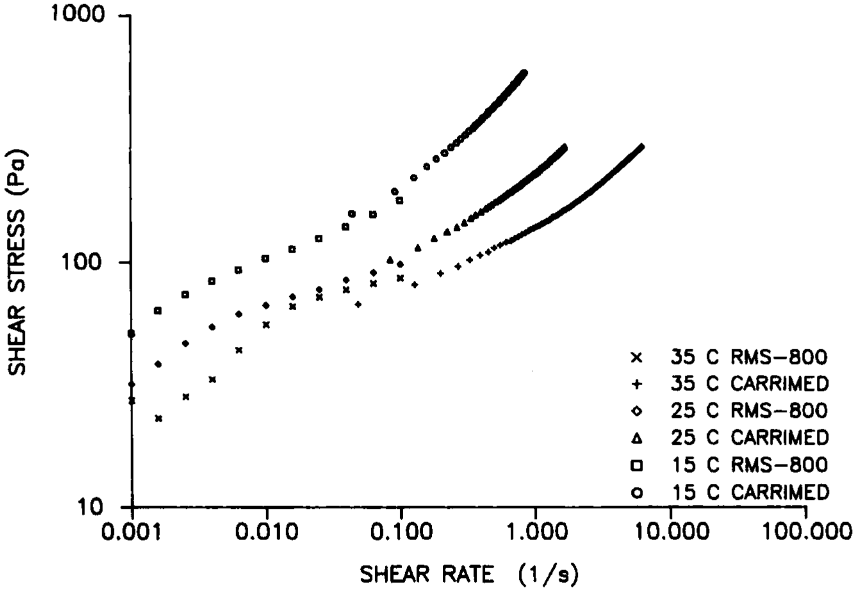

FIGURE 5 Flow characteristics of ES-2 over a wide range of shear rates. Both RMS-800 (low shear rate) and Carri-Med (high shear rate) data are shown.

region by plotting the low shear rate data ($\dot{\gamma} \leqslant 0.1\,\text{sec}^{-1}$) obtained from the controlled shear rate instrument (Rheometrics RMS-800) and the high shear rate data ($\dot{\gamma} \geqslant 0.1\,\text{sec}^{-1}$) measured from the controlled stress apparatus (Carri-Med Model-500) on a log–log plot. There are three characteristic regions in the flow curves of this material: a Newtonian region at extremely low shear rates, a plateau region where shear thinning or "apparent yielding" occurs, and another region of linear dependence of shear stress on shear rate at high shear rates. Similar to the flow behavior of ES-7 in Figure 4, ES-2 does not show an intrinsic yield stress as the stress decreases in the very low shear rate region. Flow curves of ES-7 in an extended shear rate range are illustrated in Figure 6. Other epoxy adhesive pastes also show similar flow behavior and are omitted here. As described in previous sections, the ES-7 material exhibits a very high value of apparent yield stress ($\sigma_0 = 413$ Pa at 25°C) when measured at high shear rates. Such high apparent yield stresses are reflected by the high plateau stresses in Figure 6. This material also does not possess an intrinsic yield stress; just as for ES-2, the stress decreases in the very low shear rate region. Such highly non-Newtonian rheological behavior has been observed and documented for filled polymer systems by Onogi *et al.*[9] and Matsumoto *et al.*[4,5] The non-linearity between observed shear stress and shear rate in filled systems is attributed to the particle–particle interactions as well as the formation of a three-dimensional structure in the filled fluids. At very low shear rates, local viscous forces are only sufficient to force the filler particles to move in concert with the resin medium. The observed shear stress is, therefore, proportional to shear rate. The

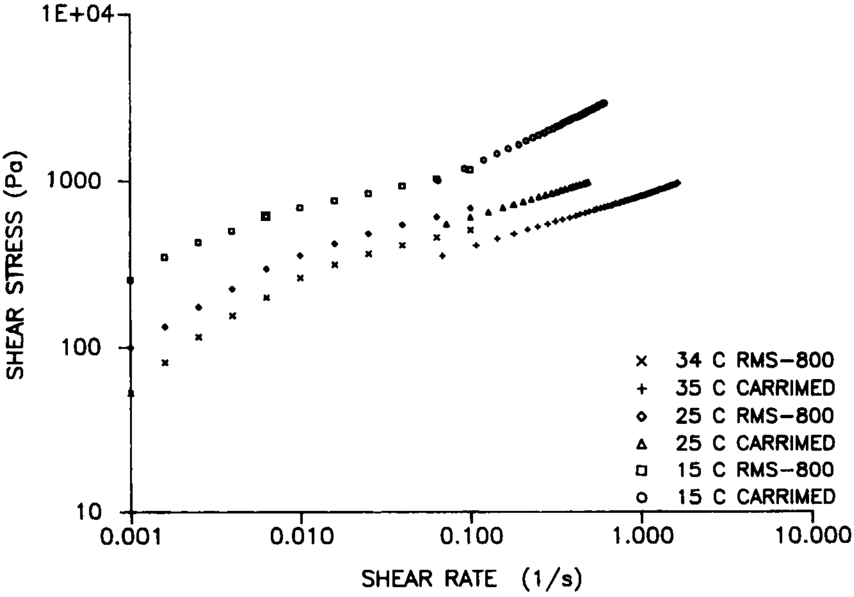

FIGURE 6 Flow characteristics of ES-7 over a wide range of shear rates. Both RMS-800 (low shear rate) and Carri-Med (high shear rate) data are shown.

interparticle three-dimensional structure in a filled fluid is due to van der Waals interaction. It is easily broken down, therefore, by the local viscous forces at higher shear rates. Layer formation or particle migration can occur at intermediate shear rates, leading to the development of a particle-free zone near the wall of the rheometer plates.[11] This effect greatly influences flow behavior of the pastes as the particle-free zone lowers the observed viscosity markedly.[11,12] "Shear thinning" (a decrease of viscosity with shear stress) occurs in this region of shear rates. It should also be pointed out that the observed apparent yield stress σ_0 from Figures 1 and 2 corresponds well with the shear thinning stress in the plateau region in Figure 5. The apparent yield stresses observed in Figures 1 and 2 cannot be interpreted as the intrinsic yield stresses of the filled paste. Rather, they are critical shear stresses at which the pastes just begin to flow under prescribed shear stress ramping rates. Since industrial adhesive paste application devices operate at high shear rates and high stress ramps at start-up, the apparent yield stress σ_0 is still a very useful parameter for designing adhesive application processes and for selecting application equipment.

An apparent yield stress observed in a fluid is generally interpreted in terms of some sort of macroscopic structure in the fluid. A minimum stress is required to break the structure in order to produce flow.[4,5,12] This weak three-dimensional structure undergoes some structural change under strain, as shown by shear thinning. Such a phenomenon can also be described in terms of the response of the three-dimensional structure to specific time dependent shear stress.[4,5,12]

Temperature dependence of rheological parameters

The flow properties of adhesive pastes are strongly termperature dependent. Figures 7 and 8 show representative flow curves of selected epoxy adhesive pastes measured at different temperatures ranging from 5 to 60°C. As discussed in the previous section, the Casson equation fits these flow curves well. The Casson parameters σ_0 and η obtained from curve fitting are used for the studies of the temperature dependence of adhesive rheological behavior. The activation energies of plastic viscosity, E_η, given by:

$$E_\eta = -Rd(\ln \eta)/d(1/T) \tag{2}$$

and of apparent yield stress, E_σ, given by:

$$E_\sigma = -Rd(\ln \sigma_0)/d(1/T) \tag{3}$$

can be found from the slope of the semi-log plots of the plastic viscosity η or the apparent yield stress σ_0 against the reciprocal of the absolute temperature T. R is the gas constant. Figures 9 and 10 show such plots. While $\ln \sigma_0$ *vs.* $1/T$ curves are straight lines in the temperature range examined, $\ln \eta$ *vs.* $1/T$ plots are slightly non-linear, indicating that there is a slight dependence of the activation energy on temperature. The slope of $\ln \eta$ *vs.* $1/T$ curve increases slightly at higher $1/T$ (lower temperature). Average values of E_η are reported in Table II to allow comparisons to be made between the adhesive pastes. Adhesive paste ES-3 shows

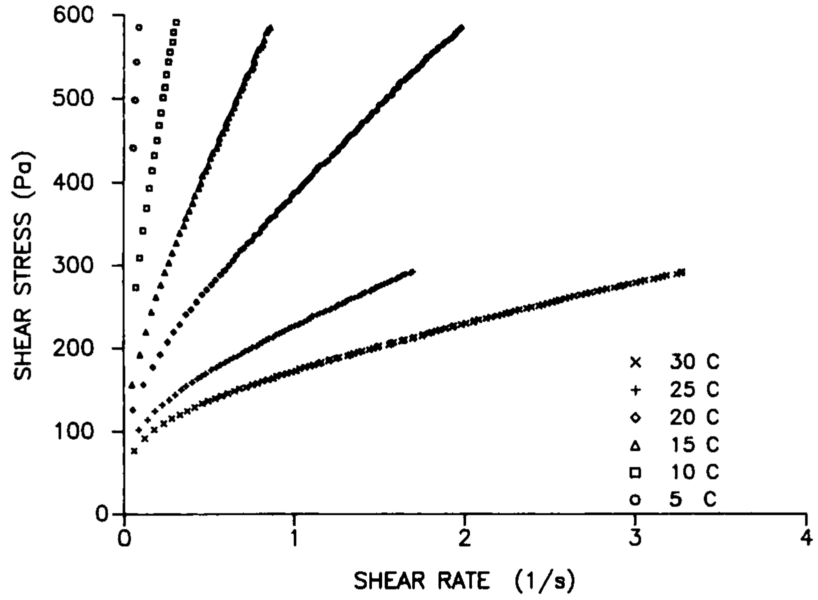

FIGURE 7 High shear rate flow curves of ES-2 at different temperatures.

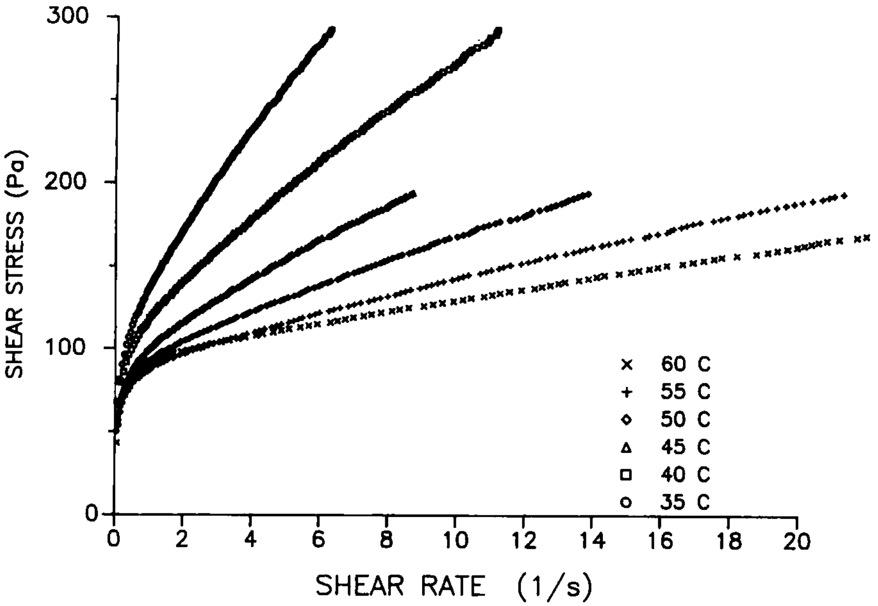

FIGURE 8 High shear rate flow curveof ES-4 at different temperatures.

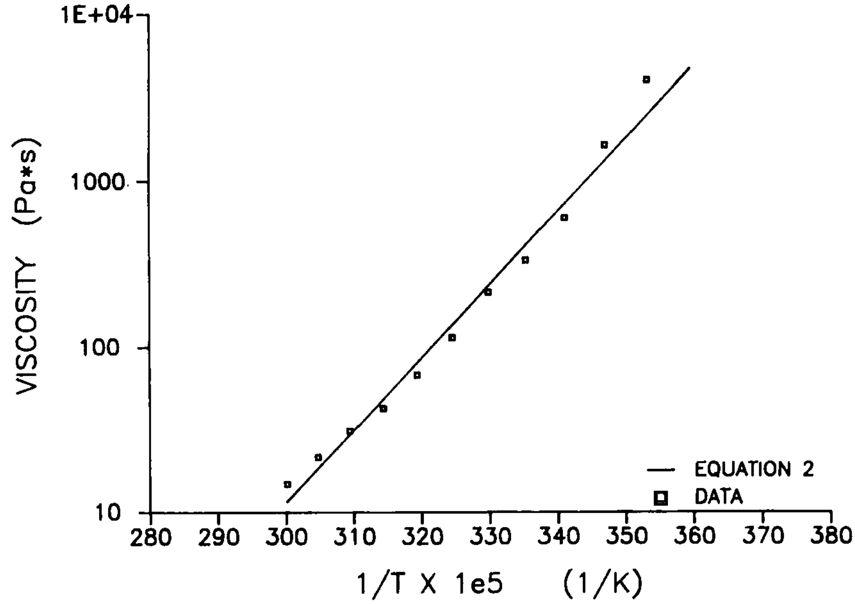

FIGURE 9 Temperature dependence of plastic viscosity (ES-7 adhesive).

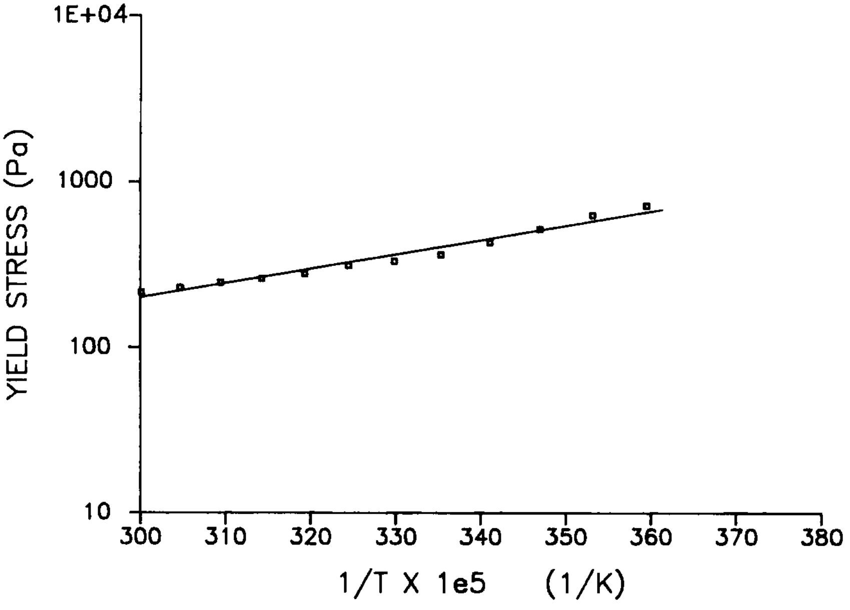

FIGURE 10 Temperature dependence of apparent yield stress (ES-7 adhesive).

the highest E_η while ES-7 is the least sensitive to temperature in terms of plastic viscosity. The measured activation energies of all of the filled epoxy pastes are lower than E_η for pure Epon-828 resin, as shown in Table II.

Matsumoto *et al.*[4,5] and Bauer *et al.*[6] found that the apparent yield stress, σ_0 is essentially independent of temperature. In our survey of the one-component epoxy adhesives, however, apparent yield stess, σ_0, decreases with increasing temperature. The apparent yield stress is not as sensitive to temperature as the plastic viscosity. The activation energy, E_σ, ranges from 2.825 kcal/mol for ES-2 to 7.614 kcal/mol for ES-1. Numerically, E_σ is less than one third of the value of E_η for each adhesive paste.

SUMMARY

Flow characteristics of seven one-component epoxy adhesive pastes were measured using a controlled shear stress rheometer and a controlled shear rate rheometer over a temperature range from 5°C to 60°C. The methodology presented here is generic and can be extended to other non-Newtonian adhesive pastes. The adhesive pastes studied exhibit a wide range of rheological behavior. Flow curves at high shear rates ($\dot{\gamma} > 1.0\,\mathrm{sec}^{-1}$), obtained using controlled shear stress rheometry, fit very well to the Casson equation. The two parameters of the Casson equation, plastic viscosity η and apparent yield stress σ_0, vary from 11.6 to 329.5 Pa · s and from 56.2 Pa to 413 Pa respectively. Controlled shear rate experiments at low shear rates reveal that the filled epoxy adhesive pastes do not possess true yield stresses. Combining data obtained from both controlled rate and controlled stress experiments of these adhesives, we observed a Newtonian region at very low shear rates, a plateau of "shear thinning" region at intermediate shear rates, and a second region of linear dependence of shear stress on shear rate at high shear rates. The shear stress in the shear thinning plateau correlates well with the apparent yield stress for each adhesive paste. The apparent yield stress was attributed to filler particle interactions and to the formation of interparticle structure in these filled systems. Flow behavior of these filled adhesives can be easily extrapolated using the reported Casson parameters when needed for high shear rate applications such as simulating the paste flow in a dispensing process. The temperature dependence of the rheological parameters of the one-component adhesive pastes was measured and reported as the activation energies, E_η and E_σ, of plastic viscosity and apparent yield stress respectively. The activation energy of plastic viscosity, E_η, varied from 29.37 kcal/mol (ES-3) to 20.06 kcal/mol (ES-7). The apparent yield stress for each adhesive paste was much less sensitive to changes in temperature than was the plastic viscosity. The relative contribution of the plastic viscosity and the apparent yield stress to the flow of adhesive, therefore, change with temperature. This suggests that the processing characteristics are likely to show qualitative as well as quantitative changes with temperature.

References

1. R. B. Bird, O. Hassager, R. C. Armstrong, and C. F. Curtiss, *Dynamics of Polymeric Liquids* (Wiley, New York, 1977).
2. W. H. Bauer and E. A. Collins, in *Rheology*, Vol. 4, F. R. Eirich Ed. (Academic Press, New York), p. 423; R. B. Bird *J. Rheol.* **26**(3), 277 (1982).
3. N. Casson, in *Rheology of Disperse Systems*, C. C. Mill, Ed. (Pergamon Press, London, 1959), p. 84.
4. T. Matsumoto, Y. Segawa, Y. Warashima and S. Onogi, *Trans. Rheol. Soc.* **17**, 47 (1973).
5. T. Matsumoto, C. Hitomi and S. Onogi, *Trans. Rheol. Soc.* **19**, 541 (1975).
6. D. R. Bauer, L. M. Briggs and R. A. Dickie, *I&EC Prod. Res. and Dev.* **21**, 686 (1982).
7. J. D. Ferry, *Viscoelastic Properties of Polymers* (Wiley, New York, 1980); R. A. Mendelson, *Polym. Engr. Sci.* **16**, 690 (1976).
8. S. Rong and C. E. Chaffy, *Rheol. Acta.* **27**, 179 (1988).
9. S. Onogi, T. Matsumoto, Y. Warashima, *Trans. Soc. Rheol.* **17**, 175 (1973).
10. H. A. Barnes and K. Walters, *Rheol. Acta.* **24**, 323 (1985).
11. D. J. Highgate and R. W. Whorlow, in *Polymer Systems, Deformation and Flow*, R. W. Wetton and R. W. Whorlow, Eds. (Macmillan, London, 1968), p. 251.
12. H. van Oene in *Polymer Blends*, Vol. 1, D. R. Paul and S. Newman, Eds. (Academic Press, New York, 1978), Chapt. 7, p. 296.