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Study of the influence of a reactive diluent on the rheological properties of an epoxy-diamine system

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Abstract The rheological behaviour of the materials diglycidil ether of bisphenol A ($n = 0$), 1, 2 diamine-cyclohexane and the epoxy reactive diluent vinylcyclohexane dioxide have been studied both separately and mixed before the beginning of the curing reaction. Different kinds of tests such as: preshear and time sweep, flow curve and stress sweep experiments were carried out. From these experiments, interesting information about: viscosity-shear stress and viscosity-shear rate dependences, storage modulus and the linear viscoelastic region were found out. Relationships between concentration of diluent and the final viscosity of the mixed sample and also between percentage of diluent and storage modulus were studied.

Keywords Epoxy · Reactive diluent · Rheology

Introduction

Epoxy resins are widely used mainly because of the versatility of their polymerization reactions. An adequate choice of resin, modifying materials and crosslinking agent allows the design after curing of the final properties at the end products. This enormous versatility becomes a key factor for the increasing development of epoxy derived materials [1].

In recent years and for different reasons, a new method of applied research dealing with reactive diluents was developed [2–7].

In previous reports, the curing process of this kind of materials was studied [8]. However, as far as we know, the rheological behaviour of these materials previous to cure was not investigated in great detail. In our opinion, a study of this type becomes of great importance since the knowledge of physical properties such as viscosity during the processing previous to the chemical reaction plays a key role. Some features such as storage or application, have a great influence on this processing.

In previous articles our research group has reported on different studies on the epoxy systems DGEBA ($n = 0$)/1, 2 DCH and DGEBA ($n = 0$)/1, 2 DCH/vinilcyclohexane dioxide [9–21] during the curing process using different experimental techniques (DSC, MDSC, DMA, DEA and rheology). In those studies these systems were well characterized during the curing process, determining the glass transition temperature, the extent of conversion or the vitrification through isothermal and dynamic experiments. However, it is considered of key importance the determination of the viscoelastic properties of these materials at the stages previous to the curing process.

Experimental

Materials and sample preparation

The epoxy resin was diglycidyl ether of bisphenol A (DGEBA $n = 0$) (Resin 332, Sigma Chemical Co., St. Louis, MO) with an epoxy equivalent between 172 and 176. The curing agent was 1, 2-diaminocyclohexane (DCH) (Fluka, Switzerland) 98% pure with an amine

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hydrogen equivalent weight of 28.5 and a viscosity of around 900 mPa s at room temperature. The reactive diluent was vinylcyclohexane dioxide (VCHD). These three materials were used as received.

Rheological measurements

The rheological measurements were carried out using a TA Instruments AR2000 stress control. The cooling system was a Peltier device that assures the value of 15 °C throughout the whole experiment. A geometry of cone and plate with a diameter of 40 mm, an angle of 1° and a truncation of 30 μm was employed. Preshear experiments were carried out at a shear rate of 50 s^{-1} for 3 min. Time sweep experiments were carried out with a sinusoidal wave of 1 Hz and a constant amplitude selected from stress sweep experiments in the linear viscoelastic region. Flow curve experiments were carried out in a ramp mode with stress values in the range from 0.033 to 150 Pa, for 10 min. A previous analysis with a calibrating oil, assured that the effects of geometry and simple inertia were negligible within the experimental time chosen for the analysis. Stress sweep experiments were carried out with a sinusoidal wave of 1 Hz and amplitude values between 0.1 and 100 Pa. Samples were prepared in an air chamber at 15 °C, as at this temperature, the system does not undergo any cure reaction.

Results and discussion

Results of preshear and time sweep experiments for each of the three components are shown in Fig. 1. As it can be observed, the epoxy resin and the reactive diluent samples do not memorize the forces previously applied on them. However, in the case of 1, 2 DCH a slight recovery of the initial structure is observed after 4 min. This is the reason why, for this material, it is necessary to perform a preshear and also 4 min wait, after loading of the sample, previous to any experiment. Owing to this particular behaviour of 1, 2 DCH, all the systems containing this component should be submitted to a similar procedure to assure a negligible influence of the sample recovery after loading on the rheometer.

Figure 2 shows the flow curves for the DGEBA ($n = 0$), 1, 2 DCH and VCHD. In this figure, plots of viscosity versus shear stress are shown. As it can be seen, both DGEBA ($n = 0$) and VCHD show a pure newtonian behaviour as their viscosity depends neither on the shear rate nor on the shearing time. However, in the case of 1, 2 DCH, viscosity shows a dependence on the shear stress. Because of this, it is said that 1, 2 DCH shows a pseudoplastic behaviour, that it would be transferred to the systems containing this component.

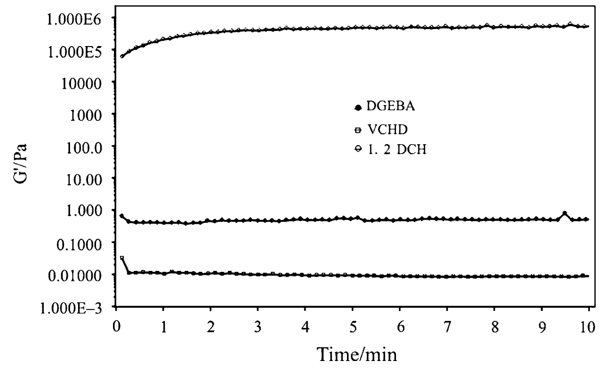

Fig. 1 Storage modulus G′ versus time for the three materials, DGEBA, VCHD and 1, 2 DCH, after preshear

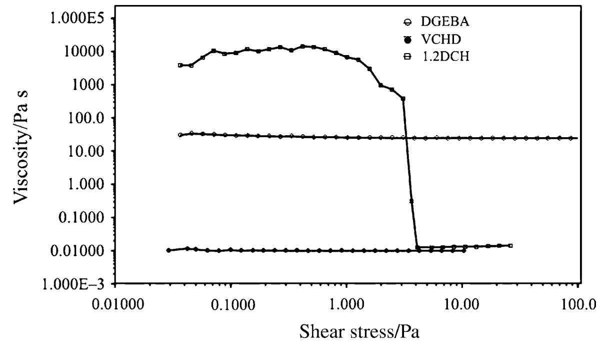

Fig. 2 Flow curves for the three materials DGEBA, VCHD and 1,2 DCH

Table 1 Newtonian and apparent viscosities (at low and high shear stresses, respectively) for the three systems

	Low stress viscosity (Pa s)	High stress viscosity (Pa s)
DEGBA ($n = 0$)	25	
VCHD	0.01	
1,2 DCH	1,300	0.013

Table 1 lists values of Newtonian viscosities for the DGEBA ($n = 0$) and VCHD and also of apparent viscosity for 1, 2 DCH, at lowest and highest stress values.

A further step in this work was the study of the composed system consisting of a homogeneous mixture of these three components. In a first stage, DGEBA and 1, 2 DCH were mixed at stoichiometric ratio. This proportion assures the highest $T_{g\infty}$ value after the curing process. Then, different amounts of the reactive diluent were added to the stoichiometric mixture to achieve final samples containing a concentration of diluent in the range from 0 to 25% in mass of the total mass. Viscosity versus shear stress curves for the neat system (0% VCHD) and for the systems containing 5, 10, 15, 20 and 25% of diluent are presented in

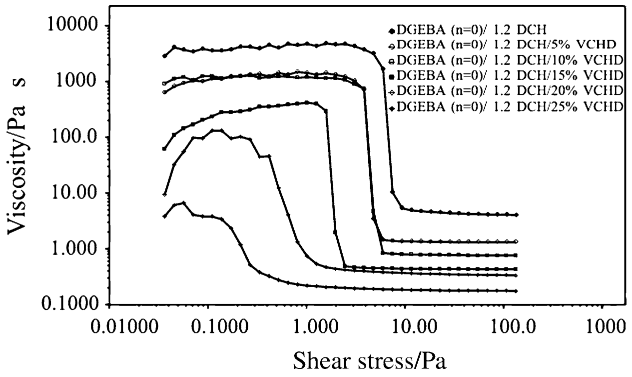

Fig. 3 Flow curves for the three component system at different concentrations of diluent

Fig. 3. As it was expected, the viscosity decreases with the increasing in VCHD concentration.

The flow curves were analysed through the Cross model [22]:

$$\frac{\eta-\eta_0}{\eta_0-\eta_\infty}=\frac{1}{1+\left(K\dot{\gamma}\right)^n} \qquad (1)$$

where η is the viscosity of the mixture, η_∞ and η_0 are the apparent viscosity at infinite and zero shear rate respectively, K is the consistency, γ is the shear rate and n is the rate index. Apparent viscosity is the ratio of stress to rate of strain. If the liquid is actually non-Newtonian, the apparent viscosity depends on the type and dimensions of the apparatus used. η_0 is the limiting viscosity at zero shear rate, and η_∞ the limiting viscosity at infinite shear rate. Values of η_∞, η_0, K, and n were obtained through the fitting of the experimental data to this model. Table 2 shows values of η_∞, η_0, K, and n calculated from the curves shown in Fig. 3, and also values of the yield stress σ_Y, corresponding to the different mixtures studied. These last values were calculated as those corresponding to the highest stress of the first Newtonian plateau. For a better understanding of the influence of VCHD (%), these values are also shown in Figs. 4, 5, and 6 as η_∞ and η_0, or K and n, or σ_Y versus VCHD (%), respectively.

As it can be seen in Fig. 4, both η_∞ and η_0 decrease with an increase in the percentage of diluent, as expected.

Table 2 η_0, η_∞, K, n y σ_Y values obtained from the flow curves (Fig. 3)

	η_0 (Pa s)	η_∞ (Pa s)	K (s)	n	σ_Y (Pa)
0%	4,270	3.98	296.6	1.25	4.55
5%	1,303	1.25	115.6	1.31	2.39
10%	1,217	0.71	105.2	1.26	2.55
15%	354.7	0.43	15.8	1.97	0.76
20%	160.6	0.34	29.9	1.00	0.44
25%	6.1	0.18	23.4	1.09	0.17

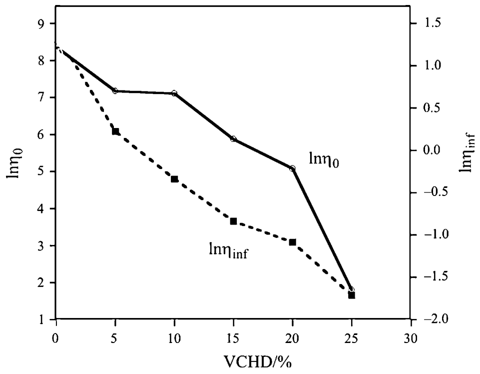

Fig. 4 η_0 and η_∞ versus the percentage of diluent

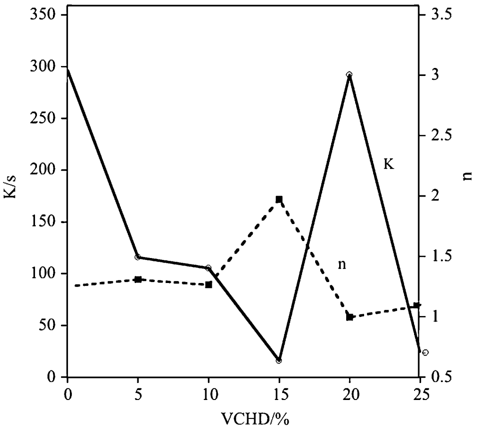

Fig. 5 K and n versus the percentage of diluent

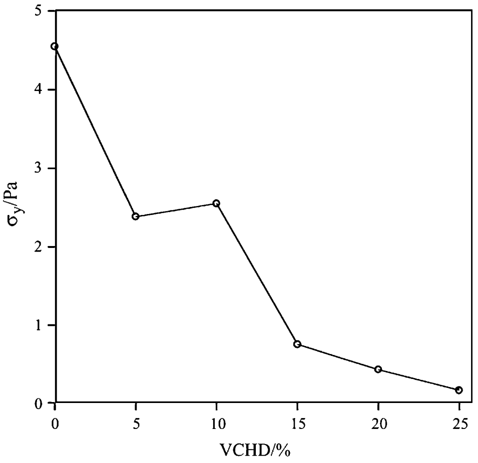

Fig. 6 σ_Y versus the percentage of diluent

Table 3 shows relative ratios of decrease for consecutive increases in diluent percentage. As it can be seen both η_∞ and η_0 show a significant decrease with the addition of 5% of diluent. This decrease is again significant for η_0 and σ_Y in the change from 10 to 25% of VCHD. However, for the step from 5 to 10% of diluent, the values of the parameters studied are reasonably close.

Table 3 Ratios of η_∞, η_0, σ_Y values between different concentrations of diluent (x/y)

	$\eta_{\infty x}/\eta_{\infty y}$	η_{0x}/η_{0y}	σ_{Yx}/σ_{Yy}
0%/5%	3.18	3.28	1.91
5%/10%	1.76	1.07	0.93
10%/15%	1.65	3.43	3.36
15%/20%	1.28	2.21	1.76
20%/25%	1.87	26.64	2.51

The knowledge of the behaviour in η_∞, σ_Y and K is very important from the technological point of view, since they are related to phenomena such as: sedimentation, sagging or levelling [23]. High values of η_0 indicate good anti-sedimentation and no sagging properties, but bad levelling if the value is too high. Also, high values of σ_Y before application, yields a good anti-sedimentation behaviour. In this work, values of these three parameters for different concentrations of the reactive diluent are reported. For a good application of the material, values of layer thickness, adherence or surface porosity must be known.

Table 2 and Fig. 4 show that viscosity at infinity shear rate changes in soft way with concentration of diluent, which is different of the η_0 behaviour. This can be related to the fact that the dependence of η_∞ on the molecular mass is different that of η_0. The molecular mass has a great influence on η_0 values. However, this is not the case for viscosity values at high rate of strain (power law region). In the present study, as the concentration of one of the monomers was changed in a linear way, η_∞ values change also linearly with diluent percentage. This behaviour is different from that shown by η_0. From a technological point of view, it must be pointed out that viscosity at infinity shear rate is related to the viscosity during application. The rate index parameter decreases very gently with an increase in diluent concentration. Owing to this nearly constant value, it can be said that the addition of diluent has only a small influence on the way of falling of the viscosity with the shear stress.

Stress sweep experiments

Oscillatory experiments can be very helpful for a better understanding of the rheological behaviour of the three-component systems when the diluent content is changed. For this reason, experiments at a constant frequency of 1 Hz and variable stress amplitude were carried out on the different systems. From these experiments, the linear viscoelastic regions also with the values in these regions of the storage and loss moduli, and loss factor were determined.

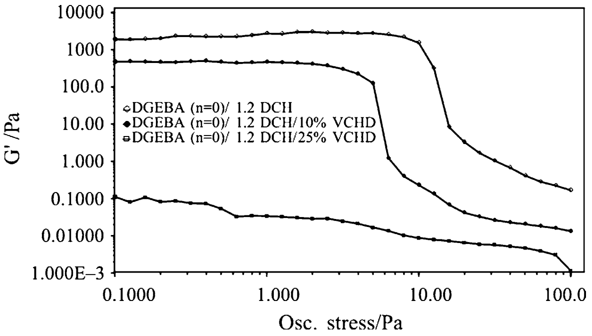

Fig. 7 G′ versus oscillation stress amplitude for the three component systems at the diluent concentrations 0, 10 and 25%

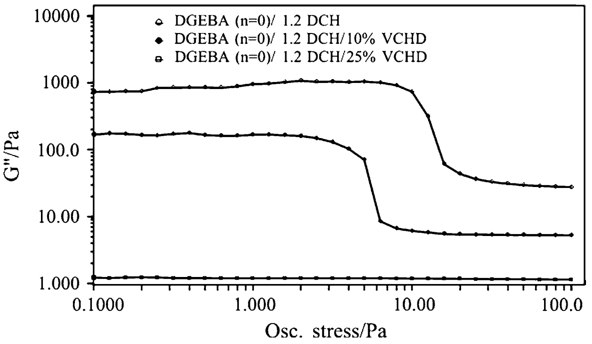

Fig. 8 G″ versus oscillation stress amplitude for the three component systems at the diluent concentrations 0, 10 and 25%

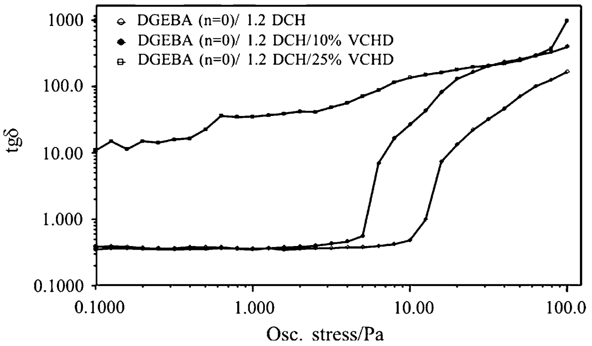

Fig. 9 Tan δ factor versus oscillation stress amplitude for the two component and three component systems at the diluent concentrations 0, 10 and 25%

Figures 7, 8 and 9 show plots of storage modulus, loss modulus and loss factor versus stress respectively for the two component system without diluent and for the three component system with diluent concentrations of 10 and 25%. These systems were chosen for our study because they show the strongest differences among all the systems studied.

Values of the highest oscillation stress in the linear viscoelastic region (calculated as the onset in the experimental curves), and values of G′ and G″ in this linear region for the three systems are listed in Table 4.

From Figs. 7 and 8 and values in Table 4 it can be seen that both, the storage and loss moduli, and also the extent of the linear viscoelastic region decrease with an increase in the percentage of diluent. As it is shown in Table 4, from

Table 4 Highest LVR stress values and G′ and G″ values

% de VCHD	Max. osc. stress (Pa)	G′ (Pa)	G″ (Pa)
0	9.1	1100	1000
10	5.3	118	100
25	–	0.1	0.1

the values of G′ and G″, the linear viscoelastic region practically disappears for the 25% of diluent system. From this behaviour and that observed in the flow curves it can be said that at concentrations of diluent higher than 25%, the material loses its pseudoplastic properties. This can also be observed in Fig. 9 where curves for the 10 and 25% of diluent systems are shown.

Conclusions

Preshear, time sweep, flow curve and stress sweep experiments have been carried out on the 1, 2 DCH, DGEBA, and VCHD systems, and also for the three-component system, at different concentrations of diluent. It has been observed that the epoxy resin DGEBA and the epoxy reactive diluent VCHD show a newtonian behaviour, but the curing agent, 1, 2 DCH, shows pseudoplasticity. For this reason it can be concluded that the diamine gives the pseudoplasticity properties to the three-component system.

Respect to η_0, K y σ_Y values, the three-component system shows a remarkable lack of discontinuity when they are represented versus the percentage of diluent between the concentrations of 0 and 5%, between 10 and 15%, and between 20 and 25%. However, the behaviour is more regular in the case of the η_∞ value. In all cases, these magnitudes decrease with the percentage of diluent.

The same tendency is observed with the stress-sweep experiments, where G′ and the LVR decrease as the percentage of diluent increases. It can be concluded that the solid and pseudoplastic behaviour introduced through the diamine is diminished with the effect of the diluent addition until the case of 25 or even 20% of diluent concentration where the three-component system trends to a newtonian behaviour. So we can conclude that a very careful selection on the concentration of diluent must be done, especially in the case of high concentrations of diluent.

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