Effect of Additives on the Rheological Properties of Fast Curing Epoxy Resins

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Abstract

Rapid Resin Transfer Molding (RTM) process is suitable for high-throughput manufacturing of complex-shaped composite parts. Ideally the epoxy system should exhibit low viscosity and long gel time at room temperature for quick mold filling, and very fast curing once the resin is inside the heated mold. The present research was performed on different epoxy formulations by varying the concentrations of diluent and catalyst. Rheological studies were carried out to measure the flow viscosity and to determine the gel time at different temperatures. It is noted that the addition of diluent effectively decreases the viscosity of formulation, and the addition of imidazole affects the rate of epoxy cure. Several epoxy resin formulations were studied and compared with the commercially available infusion-grade epoxy system of Araldite LY 8601/Aradur 8602. The results show that epoxy systems such as that containing 5% imidazole and 10% reactive diluent are suitable for the rapid RTM process with balanced flow and cure characteristics.
Keywords: epoxy, composites, processing, curing
Kulcsszavak: epoxi, kompozitok, feldolgozás, utókezelés

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1. Introduction

Epoxy resins are widely used as matrix material for advanced composites, which offer superior strength-to-weight and modulus-to-weight ratios, fatigue strength, damage tolerance, tailored coefficient of thermal expansion, chemical resistance, weatherability, temperature resistance, among others. Many products for wind energy, ground transportation, marine, and recreational applications, for instance, are made by the resin infusion process using epoxy and other resins [1]. For some high volume applications such as automotive components, high throughput, fast processing is necessary, and rapid Resin Transfer Molding (RTM) is regarded as one of the most promising technologies for such applications. Epoxy resin used in rapid RTM process should exhibit low viscosity and low cure rate at room temperature for fast infusion into mold cavity and effective impregnation of the reinforcing fabrics. After the resin is injected into the preheated mold the resin must cure rapidly (i.e. rapid increase in viscosity) at the processing temperature. In this study the effect of additives to the epoxy resin such as diluents and reaction accelerators is analyzed which could be used to guide the development of epoxy formulations for rapid resin infusion process of composites.

Epoxy resins show viscoelastic behavior during the curing process. The liquid resin starts to form a network of molecules with molecular weight approaching infinity as the crosslinking reaction proceeds, and this is referred to as the gel point [2, 3]. Eventually the molecular chains become close packed and there is insufficient volume for cooperative chain motion to occur, and this stage is known as vitrification [4]. Rheology is widely used to study gel times, vitrification times and other viscoelastic parameters [5-9].

2. Experimental

2.1 Materials

Diglycidylether of bisphenol A (DEGBA) based epoxy resin (D.E.R.™ 331™) and Triethylene-tetraamine (TETA) (D.E.H.™ 24, an aliphatic polyamine curing agent) were supplied by the Dow Chemical company. 1-Benzyl-2-methylimidazole (90% purity) was purchased from Sigma-Aldrich®. Diglycidyl ether of 1,4-butanediol (Epodil® 750) used as a reactive diluent in the study was supplied by Air Products and Chemicals. The other epoxy system used was Araldite® LY 8601 (resin) / Aradur® 8602 (hardener), a low-viscosity two-component epoxy system provided by Huntsman Advanced Materials. Araldite® LY 8601 is a blend having major portion of bisphenol A resin.

Different compositions were formulated to study the effect on the rheological properties of the epoxy resin with diluent and imidazole. Detailed formulations are given in *Table 1*.

Sample code	D.E.R.™ 331™ (Epoxy)	D.E.H.™ 24 (Hardener)	Epodil® (diluent)	Imidazole (catalyst)
DD	100.00	13.00	0	0
DD/10E	100.00	15.21	10.00	0
DD/5I	100.00	12.14	0	5.00
DD/5I/10E	100.00	14.51	10.00	5.00
	Araldite®LY 8601 (Epoxy)	Aradur® 8602 (Hardener)		
AA	100.00	25.00		

Table 1. Details of different compositions (mass ratios)
1. táblázat Az egyes összetételek részletei (tömegarányban)

2.2 Rheological measurements

For the rheological measurements, parallel plate AR 2000ex TA instrument was used. All the experiments were carried out with 25 mm steel plates at an air pressure of 200 kPa under isothermal conditions. Preliminary frequency and strain sweeps were carried out to determine the optimum experimental conditions. The test fixture was preheated to the desired isothermal cure temperature and the plate spacing was zeroed. The chamber was then opened, the plates separated and the resin sample was rapidly inserted. The plates were then brought back together to a gap of 1.0 mm. Excessive resin was scraped out carefully before starting the test.

The following two test methods were used: (1) steady state flow tests to measure the viscosity of sample formulations at room temperature at different shear rates from 0.1/s to 100/s, and (2) time sweep experiments to determine gel time based on viscoelastic parameters like shear storage modulus G´, shear loss modulus G″, and tan δ as a function of time at three different temperatures (60, 80, and 100 °C) for 20 minutes at four different frequencies (5, 10, 15 and 20 Hz) at a constant 20% strain.

3. Results and discussions

3.1 Steady state flow tests

To evaluate the effect due to the addition of diluent in the resin matrix, steady state flow tests were performed to determine the viscosity of the formulation at room temperature at different shear rates, and the results are given in *Fig. 1*. At any shear rate it can be observed that the highest viscosity is shown by the pure epoxy and amine system (DD) and the least viscosity is shown by the commercially available epoxy system (AA). The addition of diluent effectively reduces the visosity of the resin and hence increases its flow behavior. Imidazole used in the study, such as DD/5I/10E, was a low visocity liquid, and a decrease in the viscosity is observed. Along with any constant shear rate it was also observed that with increase in shear rate the viscoscity of each formulation also increased, due to the cure reaction progress. With the increase in shear rate, molecular mobility increases and hence the cure reaction leads to an increase in visocity.
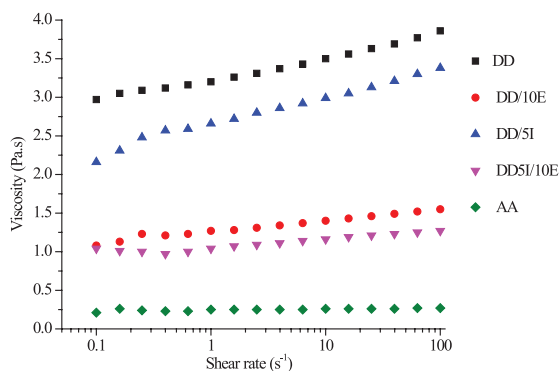

Fig. 1. Graphical representation of viscosity of all the formulations at different shear rates at room temperature obtained from steady state flow tests

1. ábra A vizsgált összetételek viszkozitásának grafikus megjelenítése különböző nyírási sebesség mellett szobahőmérsékleten végzett állandósult folyási vizsgálatból

3.2 Gel time determination (time sweep tests)

The gel time (t_{gel}) of the sample has been evaluated by different methods in the literature [10]. In this paper the crossover of G´ and G″ (i.e. G´ = G″ and tan δ = 1) was used to evaluate the gel time [11, 12].
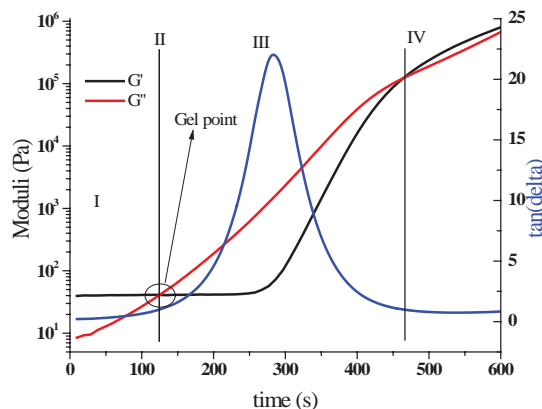

Fig. 2. A representative time sweep test curve for the determination of gel point, G´ and G″ values for DD at 80 °C

2. ábra Gélpont meghatározása a G´ és G″ keresztezési pontok alapján; DD összetétel, 80 °C hőmérsékleten

Formulation	t_{gel} (s)				
	60 °C	70 °C	80 °C	90 °C	100 °C
DD	375	222	125	84	26
DD/10E	566	398	279	107	37
DD/5I	419	306	218	118	40
DD/5I/10E	500	378	232	123	49
AA	1038	810	530	360	232

Table 2. Gel times calculated from time sweep tests at G´ and G″ crossover for all the formulations at different temperatures

2. táblázat Számított gélidők a G´ és G″ keresztezési pontok alapján, különböző hőmérsékleteken

Fig. 2 shows a representative response of the time sweep tests for the DD formulation. The plot can be divided into four regions. In the first region, the loss modulus (G″) keeps increasing with time, indicating the increase of viscosity and the structural growth of polymer molecules. By contrast, the storage modulus (G´) almost stays constant, indicating that no significant growth of elastic structures due to crosslinking reaction occurs. The second region represents a point where crossover of G´ and G″ takes place, and the sample shows similar elastic and viscous behavior. This point is considered as the time where gel formation takes place. In the third region of this plot the shear storage modulus, initially lower than the loss modulus, starts to grow. This indicates that more elastic structure due to crosslinking reaction takes place and the sample becomes semi-solid. The fourth region of the graph represents the sample in solid state where vitrification has occurred. All the samples at different temperatures in this study showed similar type of characteristic curves. *Table 2* shows the data of t_{gel} obtained from the time sweep tests for all the formulations at different temperatures. It can be observed that with increase in processing temperature the gel time is reduced for all the formulations. At any particular temperature it can be observed

that the longest time is shown by AA formulation and shortest for DD formulation. Adding 10% diluent increases time to attain gel point because dilution increases molecular mobility and a long time is required for the formulation to become gelled. A similar effect is observed with adding 5% imidazole.

4. Conclusions

In this study, different formulations of DGEBA based epoxy system D.E.R.™ 331™ were developed by varying diluent and catalyst concentration for rapid RTM process. To modify the D.E.R.™ 331™ epoxy system, Epodil® was used as epoxy based reactive diluent and 1-Benzyl-2-methylimidazole was employed as catalyst for the formulation. Rheological studies were carried out to determine the resin viscosity at room temperature and the gel time (t_{gel}) at different temperatures for all the formulations. The unmodified D.E.R.™ 331™ epoxy system gels, and thus cures, fast at processing temperature around 100 ℃, but it exhibits high viscosity at room temperature. The epoxy system for resin infusion processing (Araldite® LY 8601/Aradur® 8602) has very low viscosity but it is slow to gel and cure at processing temperature. It was found that the addition of diluent effectively decreases the viscosity of the formulation and improves the resin flow behavior. Although this also increases the gel time, the rate of curing remains fast enough to allow for rapid processing. When better flow characteristics and fiber wetting are desired, compositions with combined addition of imidazole and diluents, such as the DD/5I/10E formulation, could be a good choice, offering good processing characteristics for fast RTM molding.

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