

Curing of vinyl ester resins. Rheological behaviour

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The paper reports the data on the curing reaction of bisphenol A vinyl ester resin in presence of styrene and a monomer based on turpentine, used as reactive diluents. Kinetics of the curing reaction was studied by means of viscometry at temperatures between 60 °C and 90 °C. The viscometric measurements were carried out on a RHEOTEST viscometer, using a cone and plate device at a constant shear rate. Effect both of the reactive diluents content and the temperature on the curing process were also investigated. Participation of the double bond to the curing reaction was proved by infrared spectroscopy (IR).

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1. Introduction

Vinyl ester resins (VERs) are one of the most important classes of thermosetting polymers used for obtaining of high performance composites with military, commercial and biomedical applications [1]. VERs also find multiple applications in optical fiber coatings, topcoats for metal containers, UV curing inks and in printed circuit boards due to their ability to constitute photocrosslinkable systems [2]. VERs have superior properties compared with other thermosetting polymers, such as unsaturated polyester resins, are less expensive and easier to process than epoxy polymers. From structural points of view, VERs are the addition reaction products between different epoxy resins and unsaturated monocarboxylic acids [2]. By means of the two terminal reactive double bonds, VERs can easily form crosslinked network structures by a free radical polymerization mechanism, with or without other comonomers. Due to the high viscosity of VERs, it is necessary to add some reactive diluents such as styrene, α -methyl styrene, methyl methacrylate, triethylene glycol dimethacrylate or epoxy-acrylic compounds during the crosslinking reaction [3-7]. VER copolymers diluted with reactive diluents are important matrix resins for thermoset matrix composites.

Because the reactive diluents are often toxic and volatile substances, we tried their substitution with a new monomer obtained from turpentine and maleic anhydride [8,9]. There are various methods that can be employed to follow the progress of the cure reaction of thermosetting materials [10]. Spectroscopic (IR and UV) and chemical methods examine the changes of concentration of the functional reactive groups during the chemical processes. Other important characterization methods are: differential scanning calorimetry (DSC) [10,11], rheological measurements [6,12], volume modifications measurements [13] and dielectric and electromagnetic changes [14].

This paper presents the results that were obtained on the cure reaction of the resin resulted from diglycidyl

ether of bisphenol A and acrylic acid, in presence of two reactive diluents: styrene and a turpentine-based monomer (TBM). The double bonds conversion was monitored by IR spectroscopy.

2. Experimental

2.1 Preparation of vinyl ester resin

The vinyl ester resin was synthesized starting from the Dinox epoxy resin, the latter being obtained from Bisphenol A and acrylic acid. Dinox resin was a commercial product supplied by Sintofarm-Bucharest, Romania. It has an epoxy equivalent of 0.54 and a number-average molecular weight of 500.

A mixture of 500g (1 mol) Dinox and 144.12 g (2 mol) acrylic acid was heated at 100-110°C by stirring under nitrogen, for a duration of 4 h. The reaction was carried out in presence of 4g (0.0175 mol) triethylbenzylammonium chloride (catalyst) and 0.065 mol hydroquinone (thermal polymerization inhibitor). The synthesized resin was purified by dissolution in toluene. The obtained solution was washed with sodium bicarbonate (30 wt% aqueous solution) in order to remove the traces of unreacted acrylic acid. It was then dried in anhydrous calcium chloride and distilled under vacuum. The final crude product was dried in the oven at 70 °C for duration of 72 h.

2.2 Preparation of TBM

The data referring to TBM synthesis, which was obtained from the reaction between the turpentine, glycerol and maleic anhydride, were reported elsewhere [8,9].

2.3. Resin-reactive diluent sample preparation

The reactive diluents, in proportion of 30%, were added to the resin dissolved in acetone. Benzoyl peroxide (2% by weight) and N,N-dimethylaniline (1% by weight) were mixed with sample solutions by stirring with a glass rod at room temperature. Acetone was completely removed at 50 °C.

2.4. Curing reaction

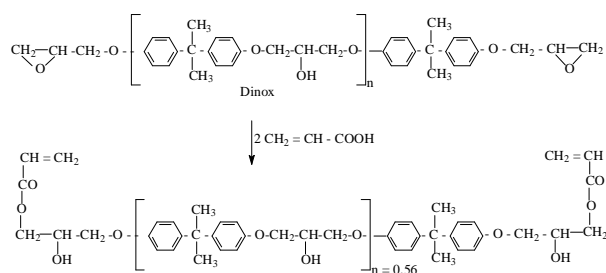
Kinetics of the curing reaction of the samples, in presence of benzoyl peroxide, was studied by means of viscometry at temperatures between 60 °C and 90 °C. The viscometric measurements were carried out on a coaxial cylinder RHEOTEST viscometer type 2.1 (Germany), using a cone-and-plate device at a constant shear rate (18 s⁻¹). The viscometer was connected to an ENDIM recorder type 621.02 (Germany) with the object of the graphic registration of the shear effort during the curing reaction. The apparent shear viscosity (α_{ap}) of the studied samples was evaluated by means of formula:

$$\eta_{ap} = \frac{\tau}{\dot{\gamma}}$$

where τ is the shear stress (Pa) and $\dot{\gamma}$ is the shear rate (s⁻¹).

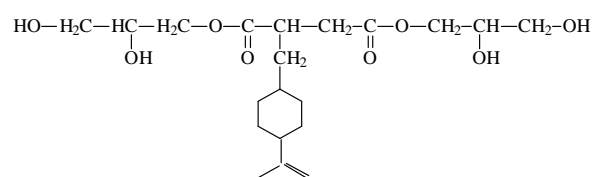
3. Results and discussion

The reactions used for the synthesis of VER resin are shown in Scheme 1.



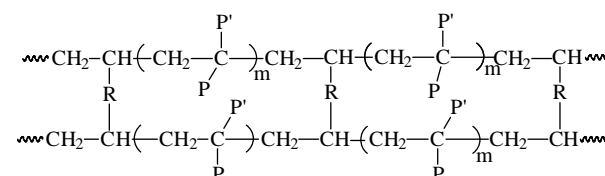
Scheme 1. Synthesis of VER resin

The chemical structure of TBM is shown in Scheme 2.

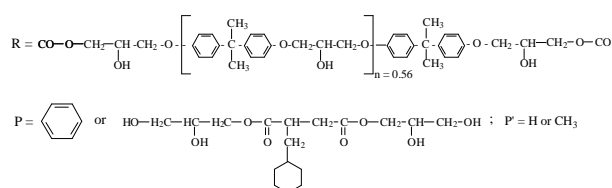


Scheme 2. Chemical structure of TBM

The structure of the network VER/reactive diluents, obtained through the free radical copolymerization mechanism, is presented in the Scheme 3.



where,



Scheme 3. The structure of the VER/reactive diluent network

The effect of temperature on the viscosity of VER resin is shown in Fig. 1.

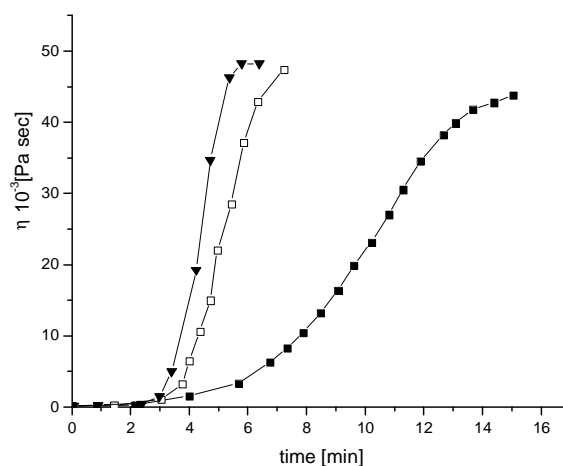


Fig. 1. Variation of viscosity versus curing time for VER: (■) 60 °C; (□) 75 °C; (▼) 90 °C.

Fig. 1 shows the increase of VER viscosity against the temperature, as well as the heating time. The shape of the curves starts with a very short induction period, which is characterized by the relative constant values of viscosity. The formation of microgels leads to a significant increase of viscosity in the second stage of the curing process [6,15]. In the third stage an outstanding increase of viscosity with time is remarked. Gelation occurs in course of this phase, at a specific inflection point of the curve viscosity versus cure time. We observed a significant decrease of the gel point with the increase of temperature.

For practical applications, the viscosity of VER must be very low to assure the efficient flow and intimate

contact with reinforced fibers. Fig. 2 shows the relation between the concentration of reactive diluents and the viscosity of VER.

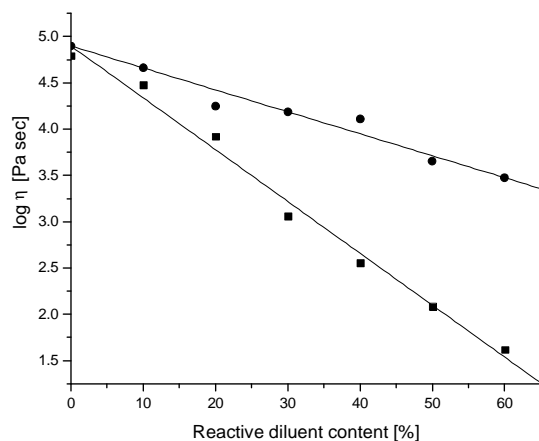


Fig. 2. Variation of viscosity of uncured VER versus reactive diluents content: (■) Styrene; (●) TBM at 30 °C.

$$\log \eta_1 = 4.90 - 0.056 [\text{St}\%] \quad (1a)$$

$$\log \eta_2 = 4.90 - 0.024 [\text{MBT}\%] \quad (1b)$$

The viscosity of VER decreases with the increase of the reactive diluents content. We found a linear correlation between the content of reactive diluent and the logarithm of viscosity. Thus, the viscosity of VER-reactive diluent systems can be calculated with the equations 1a and 1b, resulted from linear curves shown in Fig. 2. The relations 1a and 1b can be suitable for practical applications.

Fig. 3 shows the changes of VER viscosity in function of the used reactive diluent.

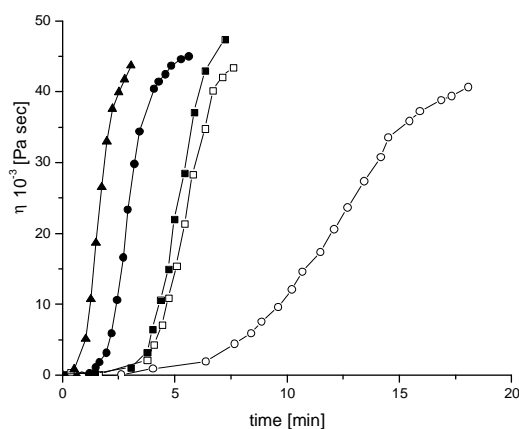


Fig. 3. Variation of viscosity versus curing time for the systems: (■) VER; (□) Styrene; (○) MBT; (▲) VER+30% styrene; (●) VER+30% TBM at 75 °C.

An acceleration of the cure reaction of VER took place in the presence of the reactive diluents (Table 1).

Table 1. The gel time of the studied sample.

Sample	Gel time at 75 °C (min)
VER	2.8
Styrene	3.5
TBM	5.3
VER+30%Styrene	0.9
VER+30% TBM	1.7

The diminution of the gel time of VER in the presence of diluting reagents can be observed.

The participation of the double bonds on the cure reaction was monitored by IR spectroscopy using the absorbances from 943 cm⁻¹, specific to the vinyl ester double bond backbone, and the absorbance from 830 cm⁻¹, characteristic to polyhydroxyether structure [16].

As an exemplification, the IR spectrum of VER is shown in Fig. 4.

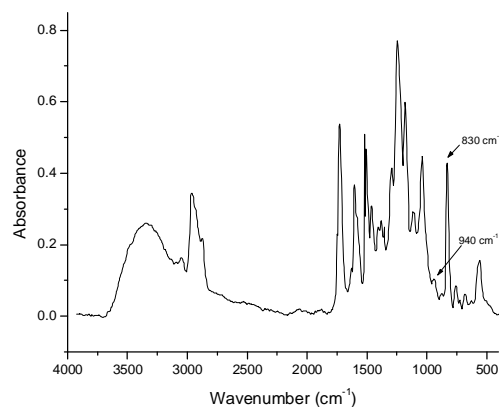


Fig. 4. Infrared spectrum of VER.

An exhaustive analysis of IR spectrum of VER was presented elsewhere [17]. In this study we observed a gradually diminution of the absorbance from 943 cm⁻¹, compared to the absorbance from 830 cm⁻¹ (Fig. 5).

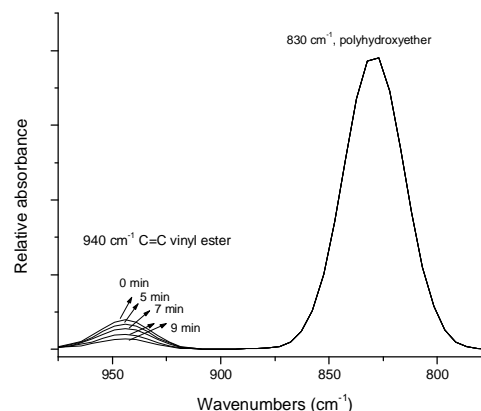


Fig. 5. Modification of the IR spectrum of VER during the cure reaction, at 90 °C.

The ratio of the absorbances from 940 cm^{-1} and 830 cm^{-1} can be used as a measure of the double bonds conversion.

4. Conclusions

Kinetic of curing reaction of a vinyl ester resins based on bisphenol A and acrylic acid, in presence of two reactive diluents, respective styrene and turpentine, was studied by means of viscometry.

The decrease of the gel point with the increase of temperature was observed in the case of VER.

There is a significant decrease of viscosity of VER-reactive diluent system with the increase of reactive diluent content. A linear correlation between the content of reactive diluent and the logarithm of viscosity was found.

The presence of reactive diluents leads to the acceleration of the cure reaction and the diminution of the gel-time.

Participation of the double bonds of VER to the curing process was proved by IR spectroscopy.

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