

Rheological characterization of the curing process for a water-based epoxy added with polythiol crosslinking agent

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Abstract

This work presents a rheological investigation of the curing process of a water-based epoxy system by characterizing the efficiency of polythiols as crosslinking agents. Measurements using an oscillatory rheometer equipped with a parallel geometry determined that the rheological profiles (e.g. storage modulus and sol-gel transition - aka gelation, etc.) of the epoxy resins were affected by the number of thiols and the concentration of the added crosslinking agents. A strong correlation between the number of thiols and the storage modulus of the epoxy material was observed. These results enable improvement in epoxy curing process by providing a thorough understanding of the interrelationship of these variables.

Keywords: rheology, curing, epoxy, gel time

Kulcsszavak: reológia, utókezelés, epoxi, gélesedési idő

1. Introduction

Network materials based on crosslinked polymers (thermosets) are specific materials of interest from both basic and applied points of view. A common example of thermosets is epoxies [1-5]. We usually know epoxies as adhesives. A usual chemistry would involve the reaction of 1 mole of amine with 2 moles of epoxides. This will form three-dimensional crosslinks, and the degree of crosslinking determines the curing process (*Fig. 1*).

Usually comprised of a group of crosslinkable resin (epoxide) that when reacted with a curing agent - sometimes referred to as the hardener - resulted in a cured thermoset [6-11]. Combining the epoxy resin and hardener initiates a chemical reaction that converts the initially low molecular weight liquid resin into its thermoset form (solid) characterized by highly crosslinked network structure. This process is called curing [12-15]. The time it takes for this conversion from liquid to solid is called gel time [4, 16-18]. Understanding the curing reaction is very important in the safe and efficient utilization of epoxies as commercial and technological products.

Introduced in the 1940s, the combination of valuable properties of epoxies such as high toughness [19-23], good adhesion to many substrates [24-29] and remarkable chemical resistance [30-33] and low shrinkage [34-37] and their good processing characteristics had led to their wide utilization in the coatings industry. They are extensively used in plant maintenance, automotive primers, can and drum coatings, appliance finishes, pipe coatings and trade-sales paints [38-48].

A good majority of epoxy materials require high temperature conditions to effect curing. If epoxies are not heated enough, chemical, mechanical and heat-resistance properties of which epoxies are known for consequently suffer [49-52]. It is therefore desired to achieve ease with which the curing process can be fine tuned to suit the fabricating process.

In this work, we used rheology to characterize the curing reaction of an epoxy-amine system modified with polythiol agents. The rheological properties as affected by change in the number of thiol groups as well as varying concentrations were investigated.

2. Experimental methods

Our material of interest is a two-part water-based epoxy system provided by Chemrez, Inc. We decided to add polythiols into the system to give an opportunity to have more crosslinking points that may significantly affect the curing process. Polythiol crosslinking agents having (a) three thiol groups, represented here as $R(SH)_3$; (b) four thiols, $R(SH)_4$ and (c) six thiols, $R(SH)_6$ were used. These thiols are commercially available and hence, from an industrial point of view, are more practical to be used. Thiols were chosen because they are known to react with a lot of functional groups like epoxides inducing a curing reaction [53-57], and we can use a rheometer to follow this curing behaviour [58-63] (*Fig. 2*).

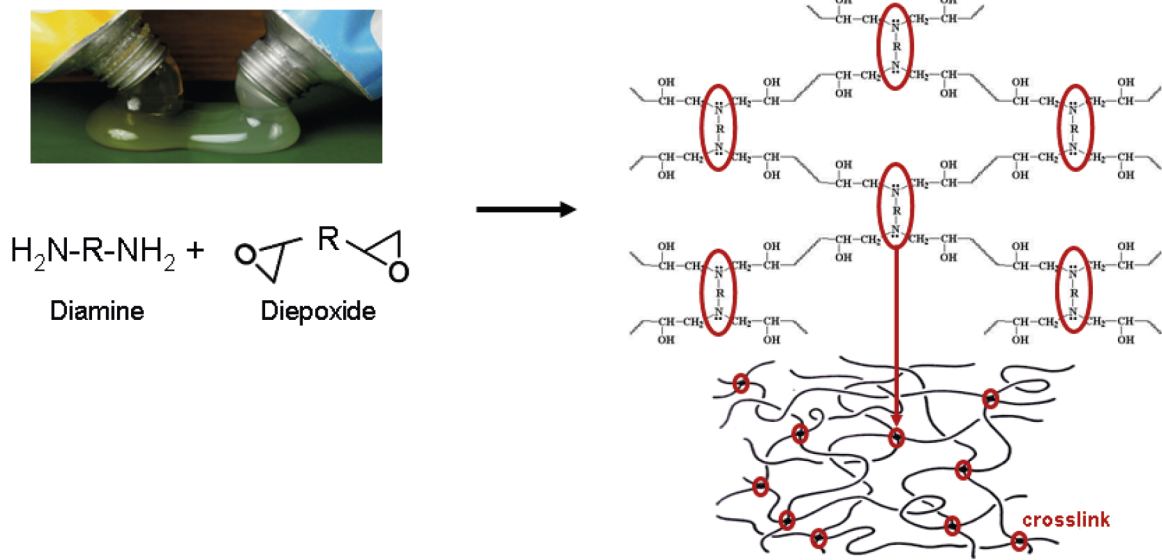


Fig. 1 An illustration of the formation of a network system from the crosslinking reaction involving an epoxy-amine system
 1. ábra Epoxi-amin rendszert tartalmazó térhálósodási reakcióból létrejövő hálózati rendszer kialakulásának illusztrációja

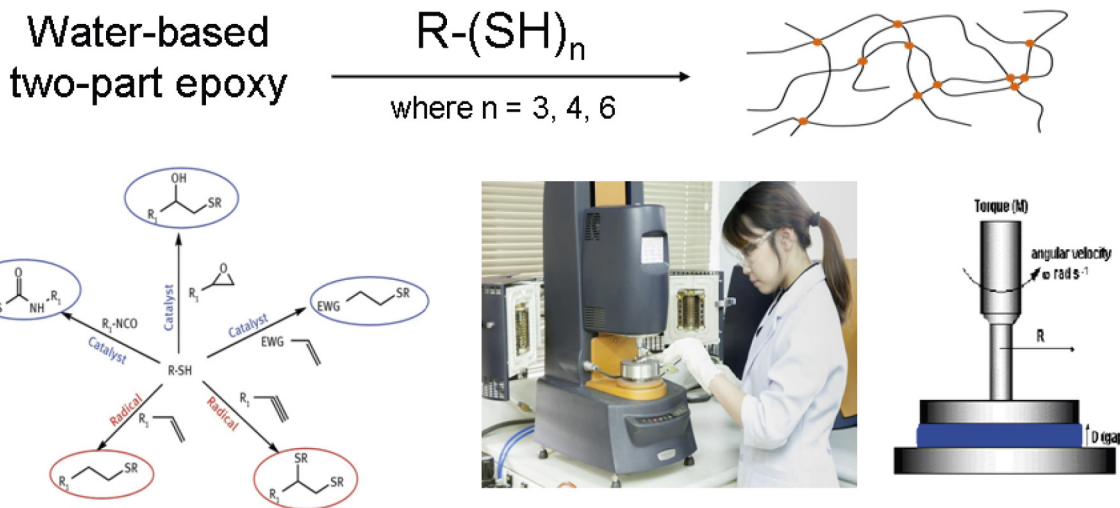


Fig. 2 Rheological study of the curing process of a water-based epoxy with polythiol additives using a rheometer
 2. ábra Víz alapú epoxi politioil-adalékanyagokkal való kezelési folyamatának reológiai vizsgálata reométer segítségével

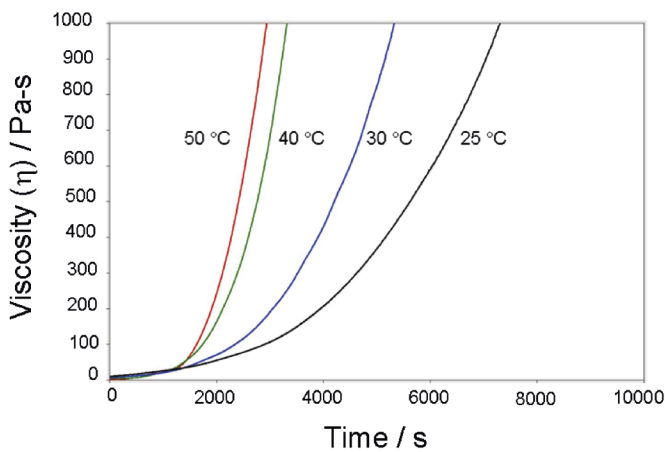


Fig. 3 Plot of viscosity (η), in Pa·s, vs time, in s, of the epoxy samples at different temperature conditions
 3. ábra Az epoxi minták viszkozitása (η) [Pa·s] az idő [s] függvényében különböző hőmérsékleteken

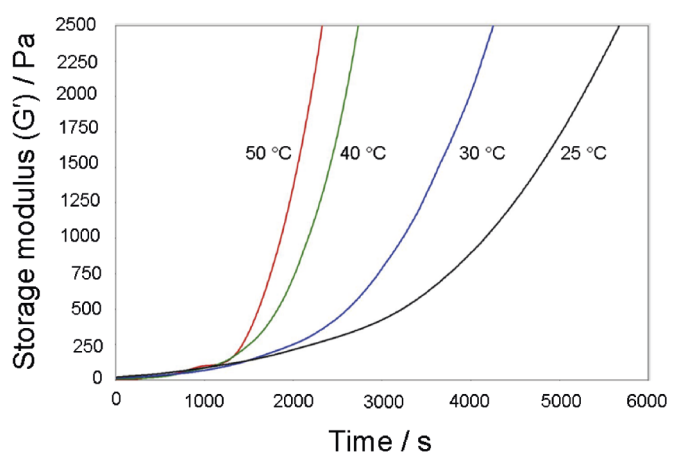


Fig. 4 Plot of storage modulus (G'), in Pa, vs time, in s, of the epoxy samples at different temperature conditions
 4. ábra Az epoxi minták tárolási modulusa G' [Pa] az idő [s] függvényében különböző hőmérsékleteken

Basically, we sandwiched the samples in between two plates. The samples were then subjected to oscillations and mechanical responses during this process were obtained using TA AR3 Hybrid Rheometer. From these measurements, mechanical properties such as viscosity (η) and storage (G') and loss (G'') moduli were extracted. In utilizing rheology to follow the curing process, we rely on the change of these viscoelastic parameters: G' , G'' and η when the material of interest is subjected to oscillations. η is the ability of the epoxy to resist flow, in a way reflects the fluidity of the epoxy material [64-65]. G' represents the elastic character (solid-like behavior) of the epoxy material and is a measure of the energy that can be recovered. On the other hand, G'' reflects energy loss by the material through dissipation and represents the viscous part (liquid-like behavior) of the epoxy [4, 16, 66-69].

3. Results and discussion

To characterize the curing reaction of the epoxy material, a sinusoidal shear strain or stress is applied to the sample sandwiched between two parallel plates and the response is monitored and finally recorded: viscosity (η) and storage (G') and loss (G'') moduli. We initially monitored the effect of different temperature conditions: 25, 30, 40 and 50°C on the η values of the two-part epoxy system over a period of time. As shown in Fig. 3, higher temperature results in a faster gelation as reflected in higher η values recorded over a shorter period of time. A case in point for instance is the higher slope of the η vs. time plot observed at 50°C than at 25°C.

Plotting G' against time – instead of η (Fig. 4) shows that the solid-like property of the material increases with increasing temperature. The change in these rheological parameters reflects the progress of the epoxy curing reaction: at the early stage, the epoxy resin behaves like a liquid. As the curing progresses, a crosslinking reaction occurs and this initiates network formation. This is known as the gel point [70]. During this time, epoxy behavior changes from being liquid-like to solid-like and is characterized by a significant change in η (gelation) denoting the formation of a highly crosslinked system [70]. This has a great impact on the application process of the epoxy material. However, in actual applications, increasing the temperature to hasten the curing is not very practical especially when in very wide spaces. So we came up with a solution to employ polythiol additives, in lieu of heating the epoxy to induce epoxy curing – and investigate its effect on the curing process.

At 1 %wt loading, different types of polythiol additives namely: (a) three thiol groups, represented here as $R(SH)_3$; (b) four thiols, $R(SH)_4$ and (c) six thiols, $R(SH)_6$ were used as shown in Fig. 5. A negative control – without $R(SH)_n$ – was also included for comparison. The polythiol with the most number of thiol reactive sites, $R(SH)_6$, exhibited the highest G' values, suggesting faster curing rate than the other polythiols used. Obviously, more reactive sites for the epoxides to crosslink offer the fastest gelation behavior the treatments considered.

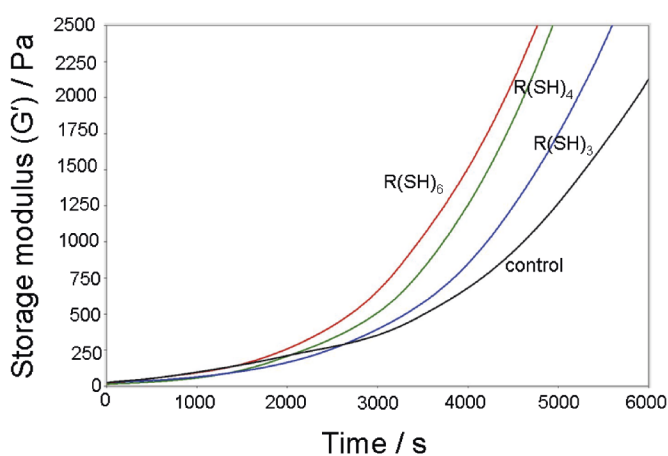


Fig. 5 Plot of storage modulus (G'), in Pa, vs time, in s, of the epoxy samples having different types of polythiol additives - $R(SH)_n$ where $n=3,4,6$ at 1 wt% loading - as compared to control (no additive)

5. ábra Az epoxi minták tárolási modulusa G' [Pa] az idő [s] függvényében különböző típusú politiol adalékszerekkel - $R(SH)_n$, ahol $n=0,3,4,6$

After identifying the polythiol additive that can provide the highest increase in G' at the shortest time, here in this case, $R(SH)_6$ – we varied the additive loading concentration: 1, 2, 3, 5 and 10 %wt. Increasing the concentration also results in a faster gelation, as observed in the significant change in G' values in much shorter time periods (Fig. 6).

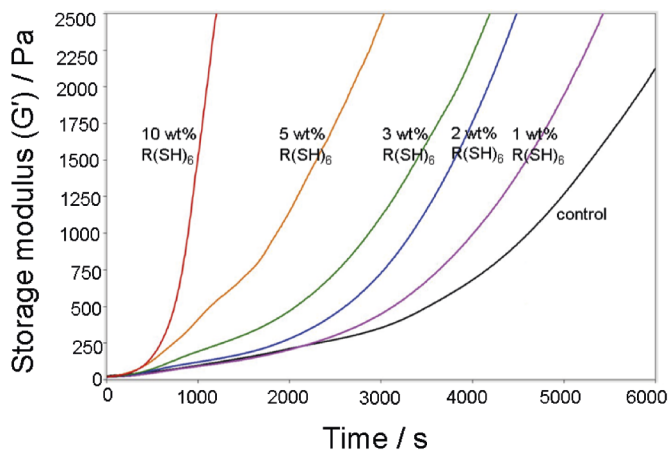


Fig. 6 Plot of storage modulus (G'), in Pa, vs time, in s, of the epoxy samples having different concentrations of $R(SH)_6$ additive as compared to control (no additive)

6. ábra Az epoxi minták tárolási modulusa G' [Pa] az idő [s] függvényében különböző koncentrációjú $R(SH)_6$ adalékszerekkel

We also determine the gel point. To do this, plot of G' and G'' versus time, the time correlating to the crossover point of G' and G'' corresponds to the gel point as shown in Fig. 7. During the initial cure period, the loss modulus is greater than storage modulus. What this means is during this stage, the liquid-like (viscous) behavior of the epoxy dominates over the solid-like (elastic) character. The crossover point is when $G'=G''$, suggesting that a crosslinking reaction between the epoxy resin and the hardener had initiated. This is known as the gel point. This is also characterized by a significant jump in η values. In the final cure stage, G' is much greater than G'' meaning the epoxy had become mostly an elastic solid.

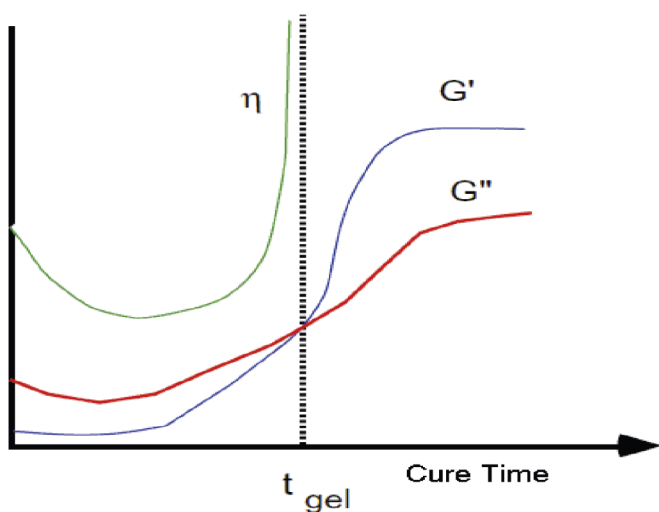


Fig. 7 Gel point is determined as the crossover point of G' and G'' in the plot of these moduli values against time

7. ábra A gélpont meghatározása a G' és G'' keresztelési pontjaként az idő függvényében

Getting the gel point which is the crossover points of the G' and G'' at various concentrations of the $R(SH)_6$ added to the epoxy matrix tells us that increasing the additive concentration led to faster gelation (shorter gel point) as shown in Table 1.

Crosslinking agent	Gel point, seconds
Without (control)	4.3×10^3
Added with 1 %wt $R(SH)_6$ crosslinking agent	4.7×10^3
Added with 5 %wt $R(SH)_6$ crosslinking agent	2.2×10^3
Added with 10 %wt $R(SH)_6$ crosslinking agent	0.7×10^3

Table 1 Gel points in case of different amount of crosslinking agents

1. táblázat Gélpontok kialakulási időpontja különböző térhálósító szerek esetén

4. Conclusions

In this study, we investigated the curing of a water-based two-part epoxy system modified with polythiol additives. As shown, the curing process can be effectively characterized using rheology. By varying the type of thiol agents as well as the concentration, rheological properties such as viscosity (η), storage modulus (G'), loss modulus (G'') and gel point can be fine tuned. Increasing the thiol functional groups for the added crosslinking agent and its concentration result in a faster gelation, as observed in the significant change in G' values in much shorter time periods. Also, getting the gel point which is the crossover points of the G' and G'' at various concentrations of the $R(SH)_6$ added to the epoxy matrix tells us that increasing the additive concentration led to faster gelation (shorter gel point). Understanding the interrelationship of these variables is vital in epoxy formulation efforts.

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