

DMTA Analysis of Glycerol Diglycidyl Ether Based Photocross-linked Polymers

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Abstract - In this paper, the effect of the amount and chemical structure of the structurally different alcohols on the rheological properties of the photocross-linked glycerol diglycidyl ether based polymers was investigated by dynamic-mechanical thermal analysis. The glass transition temperatures of photocross-linked polymers were determined from the onset point of storage modulus G' curve, maximum peak of loss modulus G'' curve and the maximum peak of the loss factor $\tan\delta$ curve. The lower concentration of alcohol was used in the batch the higher glass transition temperature and the increased height of the storage modulus G' curve was obtained as a consequence of the formed more rigid structure of polymers.

Keywords: photocross-linking, glass transition, dynamic-mechanical thermal analysis

1. Introduction

The glass transition temperature (T_g) is a key characteristic of plastics and often defines the temperature range in which the plastics may be used because it is a temperature at which material undergoes the transformation from rubbery to glassy state. The T_g is one of the most important and representative parameters of the chemical and physical properties of polymers [1,2]. In the highly viscous region above the T_g , polymeric materials are soft and rubbery, and below the T_g , polymers are hard and brittle [3]. In general, transitions in materials are associated with different localized or medium-to long-range cooperative motions of molecular segments. The glass transition is associated with cooperative motion among a large number of chain segments, including those from neighboring polymer chains [4]. When polymer chains are linked together by cross-links, they lose some of their ability to move. Cross-linking of polymers tends to increase T_g also increase rigidity [5].

Although there are several techniques available to make T_g measurements, by far the most sensitive and most used technique is dynamic-mechanical thermal analysis (DMTA). This method is relatively rapid and particularly suitable for quality control applications [6]. DMTA gives a number of measures of the glass transition temperature [7]. The onset point of the storage modulus G' as a function of temperature is the midpoint between the glassy and rubbery regions, and as such, is a measure of T_g . It occurs at the lowest temperature and relates to mechanical failure. The temperature at which the maximum peak of the loss modulus G'' curve appears is often used as well. The G'' modulus maximum peak occurs at the middle temperature and is more closely related to the physical property changes attributed to the glass transition in plastics. It reflects molecular processes and agrees with the idea of T_g as the temperature at the onset of segmental motion. The loss factor $\tan\delta$ is the ratio of the loss modulus and the storage modulus. The temperature at which the $\tan\delta$ maximum peak occurs is also a measure of the glass transition temperature, but is generally 10 °C or more higher than the loss modulus maximum peak or storage modulus onset point. The height and shape of the $\tan\delta$ peak change systematically with amorphous content [4].

In this study, four structurally different alcohols were chosen for the investigation of the effect of their chemical structure and amount on the glass transition temperature and rheological properties of the resulting photocross-linked polymers.

2. Experimental

2.1. Polymer preparation

The different compositions (**C1-C12**, see Table 1) were prepared by mixing of 0.2 g (0.98 mmol) glycerol diglycidyl ether with the different amounts (10, 20, or 30 mol.%) of structurally different alcohols, 1,4-cyclohexanedimethanol (**1**), 1,1,1-tris(hydroxymethyl)propane (**2**), hydroquinone (**3**), bisphenol A (**4**), using 3 mol% of photoinitiator, mixture of triarylsulfonium hexafluoroantimonate salts, and 0.1 ml of tetrahydrofuran. The composition without any alcohol (**C0**) was prepared for comparison. The components were stirred vigorously with a magnetic stirrer, poured on a plastic film, and kept at the room temperature under the Helios Italquartz UV lamp (model GR.E 500 W) with UV light intensity of $310 \text{ mW}\cdot\text{cm}^{-2}$ at the distance of 15 cm until the hard film was obtained (after (2–4) min). The thickness of the photocross-linked polymer films was 0.2 mm.

2.2. Dynamic-mechanical thermal testing

DMTA was performed in torsion mode using MCR302 rheometer from Anton Paar equipped with the plate/plate measuring system. The temperature was raised from $-20 \text{ }^{\circ}\text{C}$ to $45 \text{ }^{\circ}\text{C}$ at a heating rate of $2 \text{ }^{\circ}\text{C}/\text{min}$. The frequency of 1 Hz and the strain of 0.5 % was used in all cases. The T_g was defined by the onset point of the storage modulus G' curve, the maximum peak of the loss modulus G'' curve and the maximum peak of the loss factor $\tan\delta$ curve.

3. Results and discussion

The photocross-linking of the batches prepared from glycerol diglycidyl ether and structurally different alcohols resulted in the transparent polymer films. The T_g values of the photocross-linked polymers obtained from the batches **C0-C12** are presented in Table 1.

Table 1: Glass transition temperatures of the polymers obtained from the batches C0-C12.

Batch	Alcohol	Concentration of alcohol, mol. %	T_g^a , $^{\circ}\text{C}$	T_g^b , $^{\circ}\text{C}$	T_g^c , $^{\circ}\text{C}$
C0	-	-	5	8	13
C1	1	10	-1	2	11
C2		20	-2	1	8
C3		30	-3	0	7
C4	2	10	-1	3	10
C5		20	-4	-2	5
C6		30	-8	-6	0
C7	3	10	9	11	18
C8		20	8	10	16
C9		30	2	5	12
C10	4	10	9	12	18
C11		20	8	11	17
C12		30	6	9	15

^a - Glass transition temperature from the onset point of the storage modulus G' curve;

^b - Glass transition temperature from the maximum peak of the loss modulus G'' curve;

^c - Glass transition temperature from the maximum peak of the loss factor $\tan\delta$ curve.

The DMTA data confirmed that the photocross-linked polymers obtained from the batches **C0-C12** are amorphous materials. Only the glass transitions were observed in the DMTA curves of all the polymers prepared. The T_g 's of polymers obtained from the batches **C0-C12** recorded from the onset point of the storage modulus G' curves appeared at the lowest temperature (from $-8 \text{ }^{\circ}\text{C}$ to $9 \text{ }^{\circ}\text{C}$), the T_g 's registered from the maximum peak of the loss modulus G'' curves appeared at the middle temperature (from $-6 \text{ }^{\circ}\text{C}$ to $12 \text{ }^{\circ}\text{C}$) and the T_g 's recorded from the maximum peak of the $\tan\delta$ curves appeared at the highest temperature (from $0 \text{ }^{\circ}\text{C}$ to $18 \text{ }^{\circ}\text{C}$). The T_g values of the polymers obtained from the batches **C7-C9** with the aromatic alcohol **3**, as well as of the polymers obtained from the batches

C10-C12 with the aromatic alcohol **4** were higher than those of the polymers obtained from the batches **C1-C3** and **C4-C6** with the fragments of the aliphatic alcohols **1** and **2** due to the lower chain mobility caused by the steric hindrance of the aromatic fragments of the alcohols **3, 4** molecules [8]. The T_g values of the polymers obtained from the batches **C4-C6** with aliphatic alcohol **2** with three hydroxyl groups were lower than those of the polymers obtained from the batches **C1-C3** with the fragments of the aliphatic alcohol **1** with two hydroxyl groups due to proton-trapping effect. The T_g values of the polymers obtained from the batches **C10-C12** with more aromatic fragments were higher than the polymers obtained from the batches **C7-C9** due to more rigid macromolecular chains.

The storage modulus G' curves of the polymers obtained from the batches **C10-C12** with different concentrations (10, 20, 30 mol.%) of the alcohol **4** are presented in the Figure 1.

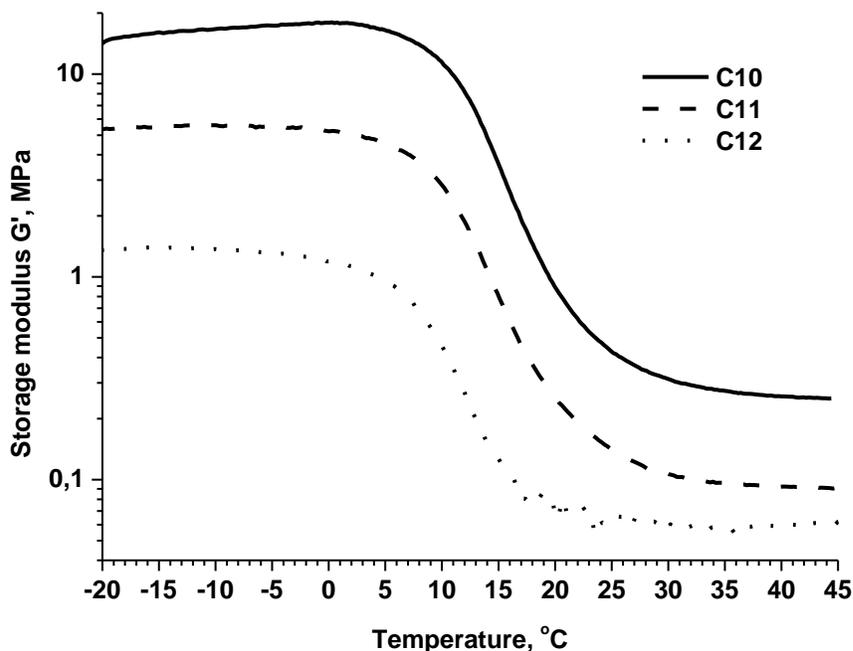


Fig. 1: Storage modulus curves of the polymers obtained from the batches **C10-C12** with different concentrations (10, 20, 30 mol.%) of the alcohol **4**.

The lower concentration of alcohol was used, the higher T_g value was observed and the height of the storage modulus curve was increased. The last observation suggests that the large number of protons released are trapped by alcohol molecules, and can not continue the chain growth reaction, resulting in a decreased T_g value [8]. As a result of this, the more rigid structures of polymers were formed when the lower amounts of alcohol were used in the batch.

The DMTA curves of the polymer obtained from the batch **C1** with 10 mol.% concentration of the alcohol **1** as a function of temperature are presented in Figure 2.

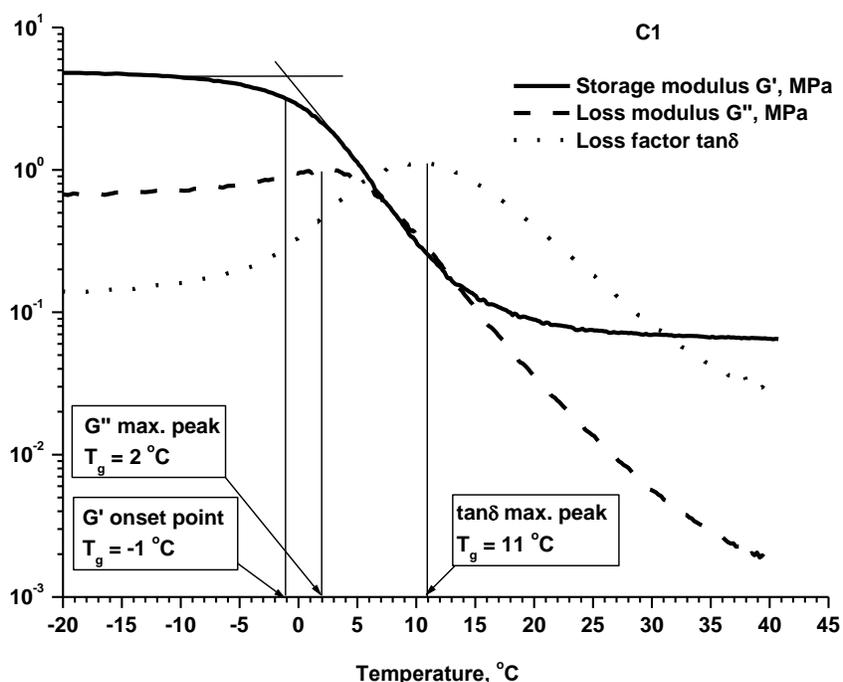


Fig. 2: DMTA curves of the polymer obtained from the batch **C1** with 10 mol.% concentration of the alcohol **1**.

At low temperatures (from -20 °C to -1 °C), the molecules are motionless and are unable to resonate with the oscillatory loads and remain rigid. The rigidity of thermosetting resin is indicated by the storage modulus [9]. The polymer is in the glass state or energy elastic state at the low temperatures. The macromolecular segments can not change shape, especially through rotation about C–C bonds, and so the molecular entanglements act as rigid cross-links. Storage modulus decreases as the molecules gain more free volume resulting in more molecular motions when temperature increases [10]. The glass state changes into the rubber-elastic state. The step of the storage modulus directly preceding the drop corresponds to the $T_g = -1$ °C (Fig. 1). The loss modulus, which is a measure of the dissipated energy, reaches the maximum at 2 °C (Fig. 1). The definition of the T_g as the temperature at which $\tan\delta$ reaches the maximum is the most frequently cited in the literature, because the $\tan\delta$ curves with the maximum peak are easier to evaluate than the step curves. The loss factor $\tan\delta$ curve of the polymer obtained from the batch **C1** reached maximum peak at $T_g = 11$ °C (Fig. 1). The polymer transits to the rubber state (from 11 °C to 45 °C). The DMTA curves of the other photocross-linked polymers were in the same character (storage modulus G' onset point occurred at the lowest temperature, loss modulus G'' maximum peak occurred at the middle temperature and finally the loss factor $\tan\delta$ maximum peak appeared).

4. Conclusion

The dynamic-mechanical thermal analysis indicated that the rheological properties of the photocross-linked polymers of glycerol diglycidyl ether and the structurally different alcohols were affected by chemical structure and amount of the used alcohol. The structural characteristics of the different alcohol molecules, e. g. steric hindrance and proton-trapping effect determine the glass transition temperature of the photocross-linked polymers of glycerol diglycidyl ether and structurally different alcohols. The higher concentration of alcohol was used in the batch the lower glass transition temperature of the resulting polymer was obtained due to the association with the proton. The amount of alcohol had the crucial influence on the rheological properties of the obtained photocross-linked polymers.

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