

Cure shrinkage defects in epoxy resins

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The formation of shrinkage defects in eight epoxy compositions was investigated during isothermal cure in a constraining vessel. For an epoxy resin there may be three ranges of isothermal cure temperatures distinguished by the type of cohesive defects formed. The boundaries of the ranges are individual for each polymer. The mechanisms of shrinkage damage and type of defects are defined initially by gelation and vitrification processes. Dependence of the processes upon temperature leads to a dramatic change in the influence of the type of defect formation and defines the boundaries of the temperature ranges. The quantity of cohesive defects depends on temperature range to a large extent and polymer chemical composition to a lesser extent. Vitrification may be the cause of shrinkage defect formation in both network and linear polymers.

(Keywords: epoxy resin; curing; chemical shrinkage)

INTRODUCTION

A peculiarity of thermosetting polymers lies in their wide application in contact with another, usually more rigid, material. In this case typical dimensions of the polymer material are usually small and can reach hundreds of micrometres in adhesives, tens of micrometres in filled polymers, and just a few micrometres in continuous fibre reinforced composites. Such close contact increases the role of interaction between polymer and contacting material. Mechanical interaction can lead to stress arising in the polymer during processing.

There are two different ways that processing stress influences the ultimate properties of polymer-based materials: by means of residual stresses and processing defects. Residual stresses change the permissible operation load, and the change may potentially be either positive or negative. Formation of various defects usually decreases the finished material performance.

Considerable success has been achieved in the investigation of the first problem^{1–6}. This concerns a convenient method to measure residual stresses at standard conditions after processing. Furthermore, the residual stress calculation is facilitated by the fact that the main contribution of temperature stresses is at the cooling stage, when the change in polymer mechanical characteristics is relatively small. At that stage an adequate theoretical simulation is significantly easier than during the curing stage, when the changes in mechanical characteristics of the reacting system (viscosity, strength, etc.) reach some tens of orders of magnitude.

The complications of experimental investigations of the defect formation process in a layer of polymer

material as thin as a few micrometres, while it is curing, are extraordinarily large. A natural method is through experimental modelling⁷. An experimental model allowing reproduction of the behaviour of a polymer curing in contact with a rigid material has been proposed in refs 8 and 9. The model is a cylindrical tube filled with a curing system. From this model, it was discovered that defects conditioned by chemical shrinkage arose in epoxy resins that were cured under three-dimensionally constrained conditions. Visual observations of defect formation are possible in transparent glass vessels. Defects appear in the polymer as cohesive cracks and adhesive failures from the tube surface.

Two experimental parameters for estimation of shrinkage toughness, \bar{l} and \bar{L}_{\min} , have been previously suggested⁹. Parameter \bar{l} is the mean distance between cohesive defects appearing in the long specimens. In this case the polymer specimen length comes to approximately $(10–100)d$, where d is the internal diameter of the tube. Parameter L_{\min} characterizes the defect formation process in the short polymer specimens. This parameter is the length of the minimum specimen with a cohesive defect formed. The overbar means that these parameters are related to the internal diameter of the tube, $\bar{l} = l/d$, $\bar{L}_{\min} = L_{\min}/d$. Higher values of the parameters correspond to higher polymer resistance to cohesive shrinkage cracking. The influence of various factors on the defect formation process can be compared by means of these parameters as well as by fractography.

With the aid of the model the influence of the isothermal curing temperature on defect formation in resin a (*Table 1*) was investigated¹⁰. Three temperature ranges characterized by different types and quantity of defect formation have been discovered. In this work the influence of epoxy system composition on defect

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Table 1 Characteristics of the resins studied

Resin	Composition ^a	Ratio of components	α_{gel} (%)	$T_{g,x}$ (°C)	T_g^{gel} (°C)	T_{cure} (°C)	Defect type	\bar{L}_{min}	\bar{l}	\bar{L}_{min}^c	\bar{l}^c	\bar{l}/\bar{L}_{min}	
a	m-PhDA + DGER	Stoichiometric	87	133	36		1 (1)	100	7.5	–	–	1.5	
								90	6.2	–	–	1.2	
								80	6.2	–	–	0.8	
								70	7.5	–	–	0.9	
								60	15.0	–	–	2.0	
								50	15.6	–	–	1.3	
								40	16.0	–	–	1.0	
b	m-PhDA + DGEBA	Stoichiometric	72	150	52		1 (1)	110	7.0	–	–	0.5	
								2 (1)	90	13.2	6.2	13	1.1
									70	15.0	–	10	1.9
c	TGEDDDM + aniline	Stoichiometric	68	140	59		3 (1,2,3)	20	–	–	–	–	
								120	7.5	–	–	0.8	
								80	17.0	–	–	1.2	
d	TGEDDDM + TEAT	10/1	–	140	–	–	1 (1)	20	11.0	–	–	3.2	
								120	–	–	–	–	
e	DEG + TEAT	10/1	–	–18	–	–	1 (1)	5.0	12.5	2.5	–	2.5	
f	TGEDDDM + iso-MTHPhA	10/9	–	180	20		1 (1)	100	13.0	3.8	–	2.6	
								80	12.0	3.8	–	1.5	
g	Oligomers of DGEBA + aniline	Stoichiometric	No gel	80	–		3 (3)	120	– ^b	1.9	24	–	
								80	– ^b	2.5	21	–	
								20	7.0	–	–	–	
h	Oligomers of DGEBA + DEG + TEAT	10/1/1.1	38	80	–		1 (1)	160	11.0	3.1	–	2.2	
								130	16.0	3.1	–	3.7	
								100	8.0	–	–	–	
								80	8.0	–	–	–	

^aFor abbreviations, see Table 2^bDefects arise during cooling

formation during isothermal curing in the constraining vessel has been studied. The systems differed in chemical structures and functionalities of epoxide resins and curing agents. Glass transition temperature of completely cured polymer ($T_{g,x}$) and conversion at the gel point (α_{gel}) vary significantly, because they are supposed to be relevant to shrinkage cracking.

EXPERIMENTAL

We used five epoxy resins, DGEBA, DGER, DEG, oligomers of DGEBA and TGEDDDM, and four curing agents m-PhDA, aniline, iso-MTHPhA and TEAT (see Table 2 for structures and full names of polymers) to produce eight polymer composition. After stirring the initial substances, each polymer composition was degassed under vacuum. Then the quantity of the reacted epoxy groups in the composite was checked by chemical analysis.

Each composition was cured under isothermal conditions, as a rule, at a few temperatures, and shrinkage damage parameters, \bar{l} and \bar{L}_{min} , were defined. A glass tube

with internal diameter 1.6 mm was used as the constraining vessel. For better adhesion the glass tube was washed with chromic acid and then with water.

Isothermal calorimetry at different temperatures was used to measure the chemical kinetic curves. To calculate epoxy group conversion, the enthalpy of the epoxy cycle opening was supposed to equal 25 kcal mol⁻¹ (ref. 11). Thermomechanical analysis (t.m.a.) of the polymer samples was used for determination of the vitrification temperature (T_g). Specimens for t.m.a. were cured in an oven simultaneously with polymer samples used for determination of parameters \bar{l} and \bar{L}_{min} . The former specimens were removed one after another from the oven during the isothermal cure. Then conversions of all t.m.a. specimens removed were determined from the isothermal chemical kinetics known. The beginning of cohesive crack formation in the high-temperature range was assumed to correspond to polymer gelation¹⁰. The t.m.a. specimen was removed from the oven at this moment and its T_g was accepted as the temperature of the glass transition of polymer at the gel point (T_g^{gel}).

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