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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 modelling[7]. 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 suggested[9]. Parameter 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 investigated[10]. 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} (%)	$T_{g,\infty}$ (°C)	T_g^{gel} (°C)	T_{cure} (°C)	Defect type	$\bar{L}_{min}$	$\bar{l}$	$\bar{L}^c_{min}$	$\bar{l}^c$	$\bar{l}/\bar{L}_{min}$
a	m-PhDA + DGER	Stoichiometric	87	133	36	100	1 (1)	5.0	7.5	–	–	1.5
						90		5.0	6.2	–	–	1.2
						80		8.1	6.2	–	–	0.8
						70		8.1	7.5	–	–	0.9
						60	2 (1)	7.5	15.0	–	–	2.0
						50		12.0	15.6	–	–	1.3
						40		15.0	16.0	–	–	1.0
						20	3 (1)	3.7	–	–	–	–
						5		4.4	–	–	–	–
b	m-PhDA + DGEBA	Stoichiometric	72	150	52	110	1 (1)	14.0	7.0	–	–	0.5
						90	2 (1)	12.0	13.2	6.2	13	1.1
						70		8.0	15.0	–	10	1.9
						20	3 (1,2,3)	6.6	–	–	–	–
c	TGEDDDM + aniline	Stoichiometric	68	140	59	120	1 (1)	9.5	7.5	–	–	0.8
						80	2 (1)	14.0	17.0	–	–	1.2
						20	3 (2,3)	3.4	11.0	–	–	3.2
d	TGEDDDM + TEAT	10/1	–	140	–	130	1 (1)	6.2	6.9	–	–	1.1
e	DEG + TEAT	10/1	–	−18	–	130	1 (1)	5.0	12.5	2.5	–	2.5
f	TGEDDDM + iso-MTHPhA	10/9	–	180	20	100	1 (1)	5.0	13.0	3.8	–	2.6
						80	1 (1)	8.1	12.0	3.8	–	1.5
g	Oligomers of DGEBA + aniline	Stoichiometric	No gel	80	–	120	3 (3)	–[b]	–[b]	1.9	24	–
						80				2.5	21	–
						20		7.0	–			–
h	Oligomers of DGEBA + DEG + TEAT	10/1/1.1	38	80	–	160	1 (1)	5.0	11.0	3.1	–	2.2
						130	1 (1)	4.3	16.0	3.1	–	3.7
						100	1 (1)	–	8.0	–	–	–
						80	1 (1)	–	8.0	–	–	–

[a] For abbreviations, see *Table 2*

[b] Defects 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 ($T_{g,\infty}$) and conversion at the gel point (α_{gel}) vary significantly, because they are supposed to be relevant to shrinkage cracking.

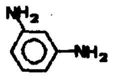
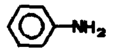
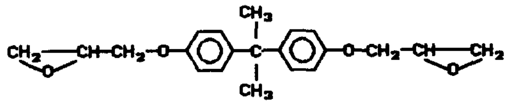
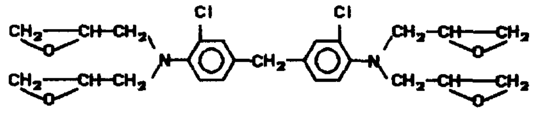
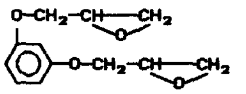
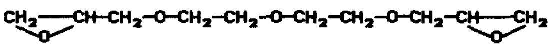
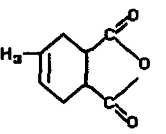
EXPERIMENTAL

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 gelation[10]. 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}).

Table 2 Chemical structures of the resins studied

Structural formula	Abbreviation	Polymer	Functionality	Amine or epoxide equivalent Real	 Pure chemical
	m-PhDA	m-Phenylenediamine	4	54	54
		Aniline	2	47	47
	DGEBA	Diglycidyl ether of bisphenol A	2	180	170
		Oligomers of DGEBA	2	215	170
	TGEDDDM	Glycidyl ether 3,3′-dichlor-4,4′-diaminebiphenylmethane	4	153	124
	DGER	Diglycidyl ether of resorcinol	2	122	111
	DEG	Diglycidyl ether diethylene glycol	2	123	112
	iso-MTHPhA	4-iso-1-methyltetrahydrophthalic anhydride	2		
$C_{24}H_{48}O_{12}N_4Ti_3$	TEAT	triethanolamine titanate			

In *Table 1* parameters $\bar{l}^c$ and $\bar{L}^c_{min}$ are given as well as $\bar{l}$ and $\bar{L}_{min}$. The former also include the defects arising from cooling. Clearly parameters $\bar{l}^c$ and $\bar{L}^c_{min}$ would be less than parameters $\bar{l}$ and $\bar{L}_{min}$ if defects are formed while cooling, in the opposite case values of parameters before and after cooling would be the same.

RESULTS AND DISCUSSION

Mechanisms of defect formation

Three cure temperature ranges distinguished by type and quantity of defects were noticed earlier[10] for resin a from *Table 1*. Similar ranges have been also observed for all other epoxy resins investigated, though temperature boundaries are different in each case. Cohesive defects appear as cracks intersecting the resin[9,10] in the high-temperature range (range 1 in *Table 1*) during isothermal cure. This type of defect will be labelled as 1(1). The first number is the number of the range, and the number in brackets is the number of defect types in the relevant range. When a cohesive crack has reached the tube walls, it continues to propagate along the internal surface of the tube as an adhesive failure[9]. In the intermediate range, the main type of defect is the sperical void with uneven surface[10], 2(1).

Three types of defects exist in the low-temperature range, 3. Damage to the resin during the curing process was discovered to occur mainly due to zigzag shrinkage cracks, 3(1), propagating along the tube axis (*Figure 1a*). The cohesive cracks of the second type, 3(2), intersect the tube with subsequent formation of large adhesive debonding from tube walls with an uneven surface (*Figure 1b*). The cohesive defects of the third type, 3(3), show multiple destruction surfaces (*Figure 1c*). Defects of the third type always arise a significant time after the development of the first type of defect. The formation of the second type of defect overlaps partly with the first type.

It was shown[10] that the role of gelation and vitrification in shrinkage defect formation changes dramatically at different temperatures for resin a. These phenomena under isothermal cure follow from the time–temperature–transformation cure diagrams developed by Wisanrakkit and Gillham[12].

For resins a, b, c, and probably for h, the condition $T_{cure} > T_g^{gel} + \Delta$ is valid for range 1, where Δ is $\geqslant$20–30°C.

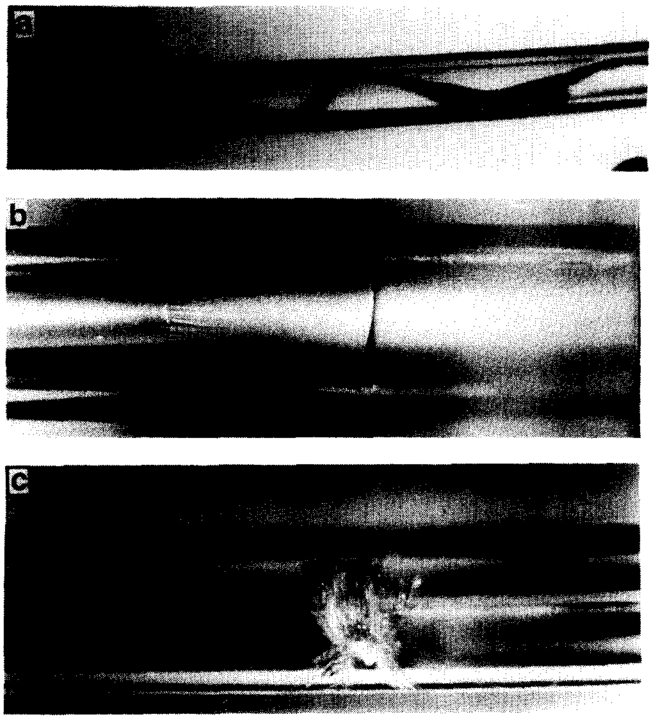


Figure 1 (a) Micrographs to show three types of shrinkage defect. Zigzag defect 3(1) arising during cure at room temperature (range 3) in epoxy resin a. (b) Cohesive defect of the second type 3(2) arising during cure at room temperature (range 3) in epoxy resin c. (c) Cohesive defect of the third type 3(3) arising during cure at room temperature (range 3) in epoxy resin c

So, in range 1, gelation precedes vitrification and it is gelation that is the cause of the shrinkage stress increase, preventing free volume shrinkage of the curing system. For resins a–d and f, $T_{cure} < T_{g,\infty}$, so vitrification occurs during cure. The vitrification time was observed to coincide with cessation of defect development. Therefore, in range 1 the vitrification hinders defect formation. This fact seems to be caused by an increase in toughness of the polymer network due to vitrification.

In the low-temperature range 3, the vitrification occurs before gelation. It is the factor preventing free shrinkage and increasing shrinkage stresses, with the non-network structure facilitating defect formation.

In the intermediate range 2, gelation and vitrification overlap, and vitrification suppresses defect formation from the beginning of its possible occurrence due to gelation. So, the cohesive defects in this range are poorly developed and their quantity is small.

We observe that the lower limit of range 2 is the vitrification temperature at the gel point T_g^{gel}, and the upper limit is defined by the temperature of isothermal cure at which the process of vitrification begins, at the moment of gel transition, $T_g^{gel} + \Delta$, where Δ depends upon the vitrification region width at the gel point.

Parameters of defect formation

The values of parameter $\bar{l}$ in range 1 and in range 2 are represented in *Figure 2*. It is obvious from *Figure 2* that the values of parameter $\bar{l}$ in range 1 fall into two groups. The first group corresponds to $\bar{l}$ values close to 8 (resins a, b, c, d and h) and the second group corresponds to $\bar{l}$ values of 12–18 (resins e, f and h). Analysing the experimental samples from the second group, the considerable adhesive debondings from tube walls were found to arise from the first cohesive defects. The adhesive debondings extend to the whole tube length for the short period of time of conversion, hindering subsequent cohesive defect formation. Few cohesive defects arise under such conditions and it corresponds to large values of parameter $\bar{l}$.

In *Figure 3*, the values of parameter $\bar{L}_{min}$ are represented for three temperature ranges. They have a considerable dispersion in all ranges. This is mainly caused by methodological difficulties in the determination of parameter $\bar{L}_{min}$ (ref. 9).

In confirmation of the conclusion that defect formation in range 3 is conditioned by polymer vitrification, the composition g (oligomers of DGEBA + aniline) with stoichimetric ratio of components was chosen. The functionalities of both components in this composite are 2, therefore a linear polymer is formed under curing.

The cohesive defects appeared during the cure process of this system at room temperature. The T_g of TMA specimens removed at the moment of defect formation was determined to be 20°C, and $T_g = T_{cure}$. The cohesive defects have a multiple surface of destruction 3(3) and

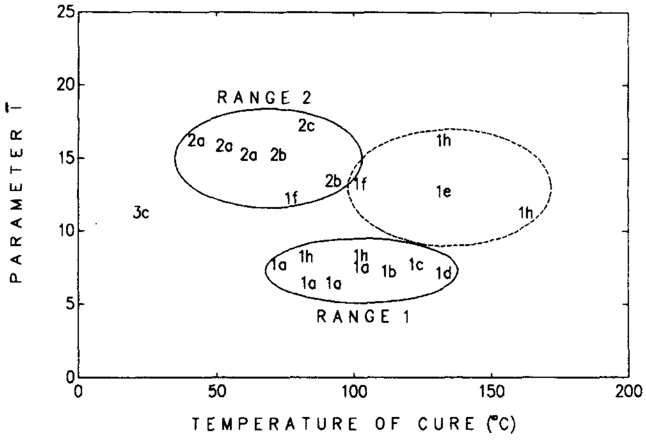


Figure 2 Correlation between parameter $\bar{l}$ and temperature of cure. Digits denote number of cure temperature range, and letters relate to epoxy resins from *Table 1*. The values of parameter $\bar{l}$ for specimens with considerable adhesive debondings are enclosed by a dashed line

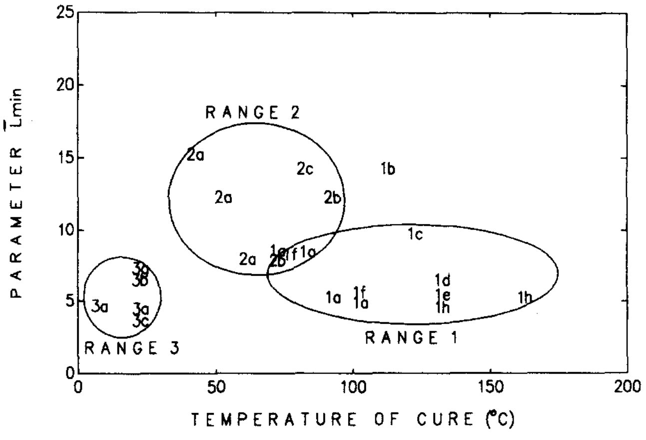


Figure 3 Correlation between parameter $\bar{L}_{min}$ and temperature of cure. Digits denote number of cure temperature range, and letters relate to epoxy resins from *Table 1*

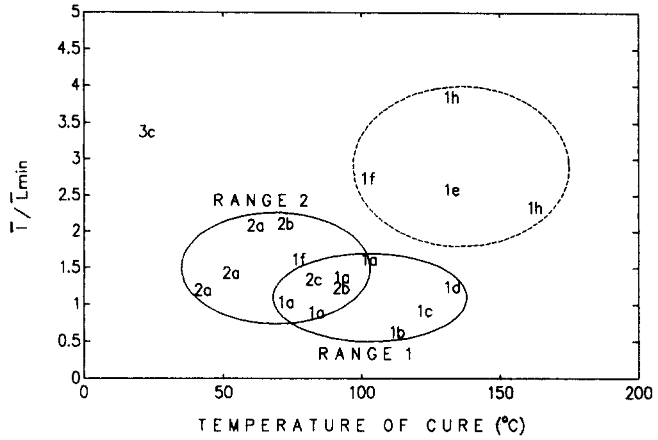


Figure 4 Correlation between $\bar{l}/\bar{L}_{min}$ and cure temperature. Digits denote number of cure temperature range, and letters relate to epoxy resins from *Table 1*. The values of the ratio $\bar{l}/\bar{L}_{min}$ for specimens with considerable adhesive debondings are enclosed by a dashed line

look like the defects in *Figure 1c*. The similar appearance emphasizes that the polymer destruction in range 3 is conditioned by vitrification, as in resins b and c.

Attention should be paid to the experiments on resin g cure under higher temperatures. Shrinkage defects did not arise during the cure, but strong sample cracking occurred under cooling. The values of $\bar{L}_{min}$ for the resin are the smallest seen on *Table 1*. The large values of parameter $\bar{l}$ here are caused by formation of large adhesive debondings. The apperance of the cohesive defects formed under cooling was identical to those formed under room temperature curing. This is connected with the fact that, since vitrification of polymer takes place during the cooling from high temperature ($T_{cure} > T_{g,\infty}$), vitrification is also the reason for considerable polymer fracture. Thus we may conclude that vitrification can be a reason for shrinkage defect formation in resins in which a three-dimensional network does not form.

Dependence of the $\bar{l}/\bar{L}_{min}$ ratio on cure temperature for the polymer systems investigated is shown in *Figure 4*. Two differences in defect formation in specimens for determination of $\bar{l}$ and $\bar{L}_{min}$ should be noticed before carrying out comparative analyses of these parameters. They are related to different manifestations of adhesion and cohesive mechanisms of shrinkage damage and with different averaging in the definition of the parameters. Parameter $\bar{l}$ depended inversely upon the resistance of the material to cohesive and adhesive shrinkage cracking. Parameter $\bar{L}_{min}$ characterizes only the cohesive damage. The magnitude of the $\bar{l}/\bar{L}_{min}$ ratio acts as an indicator of the activity of the adhesive damage mechanism.

Comparison of $\bar{l}/\bar{L}_{min}$ magnitudes of different resins can help to show which resins and conditions cause considerable adhesive debondings. Whether cohesive or adhesive shrinkage defects are more dangerous for polymer-based materials depends on the materials in question.

CONCLUSIONS

(1) In general, for a thermosetting epoxy resin there are three ranges of isothermal cure temperature distinguished by type of formation of cohesive defects. The boundaries of the ranges are individual for each polymer.

(2) The appearance of cohesive defects appearing in different resins but in the same temperature range is quite similar: cracks intersecting the specimen in the high-temperature range; uneven voids in the intermediate range; three types of defects in the low-temperature range. Hence, the failure mechanism is, mainly, determined by the current conversion and relaxation state of the curing system and not by its chemical composition.

(3) The mechanism of shrinkage damage and the type of defects are defined primarily by gelatoin and vitrification processes. The dependence of the processes upon temperature leads to dramatic change in the influence of these on the defect formation and defines the boundaries of the temperature ranges.

(4) The temperature boundary between ranges 2 and 3 is T_g^{gel} and the length of range 2 seems to be about Δ, where Δ is the length of the vitrification region at the gel point.

(5) The quantity of cohesive defects depends on the temperature range to a great extent and polymer chemical composition to a lesser extent.

(6) Vitrification may be the reason for shrinkage defect formation both in the network polymers (before the gel point) and in the linear polymers.

(7) The ratio $\bar{l}/\bar{L}_{min}$ is greater when more active formation of adhesive debondings occurs.

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