

CURE KINETICS MODELLING AND CURE SHRINKAGE BEHAVIOUR OF A THERMOSETTING COMPOSITE

Nuri Ersoy , Mehmet Tugutlu
Bogazici University, Mechanical Engineering Department
34342 Bebek, Istanbul, TURKEY
Nuri.Ersoy@boun.edu.tr

SUMMARY

Cure kinetics and through-the-thickness cure shrinkage of a carbon fibre-epoxy composite (AS4/8552) were studied. Differential Scanning Calorimeter (DSC) scans were performed to develop a new cure kinetics model. The coefficients of thermal expansion (CTEs), the glass transition temperatures (T_g), and the cure shrinkage strains of composite samples were measured by using a Dynamic Mechanical Analyzer (DMA).

Keywords: Cure Kinetics, cure shrinkage, thermosetting resins

I. INTRODUCTION

Due to the orthotropic nature of the fibre reinforced composites, high temperature processing results in shape distortions. The through-the-thickness thermal expansion coefficient of continuous fibre composites is much higher than the in-plane expansion coefficients. Composite parts with curved geometry spring-in as they come out of the mould. The through-the-thickness thermal and shrinkage strains are the main contributors to the spring-in phenomenon [1-5]. This makes measurement of the thermal expansion coefficient and cure shrinkage strains during the process cycle extremely important. Hence necessary tool compensations can be made by using models to predict the shape distortions.

During processing of thermosetting composites, the resin transforms from a viscous fluid of monomers to first a rubbery and then to a cross linked network. During this process, the free space occupied by the polymer molecules reduces and this causes a chemical shrinkage which is usually referred as cure shrinkage.

In order to investigate the cure development numerically, cure kinetics models specific to the resin system used in the composite were developed. The extent of the cure reactions is usually described by the degree of cure, α , which is quantified as the fraction of heat generated to that point relative to the total heat generated through the complete cure. The degree of cure can easily be determined using standard heat flow measurements in a Differential Scanning Calorimeter (DSC) by integrating the exothermic DSC peak. The cure kinetics models developed in the literature for the 8552 resin system are usually phenomenological and do not reveal the actual mechanism taking place during curing [4, 6-11].

The cure shrinkage of epoxy resins and composites were either measured directly by volumetric dilatometer [12-15], by density change techniques [16-18], by Thermo-Mechanical Analysis (TMA) [19, 20] or by indirect methods by curing additional layers of prepreg on already cured layers [20-22]. All of the direct measurement methods use small amounts of material to fit into the dilatometer or TMA cell and the material usually requires some kind of confinement such as a quartz dilatometer cell, and volumetric strains can be measured instead of orthotropic or through-the-thickness strains. Furthermore, the small size (usually a few millimetres) of the samples does not allow the isolation of edge effects in layered composites. Recently Garstka et al. [23] developed a method that allows direct monitoring of through-the-thickness strains in composite parts. This method utilizes a special tool to pressurize and to heat the sample and an optical system to measure the through-the-thickness strains.

In this study a series of thermal scans of curing prepreg samples were carried out in order to develop a cure kinetics model. Furthermore the relationship between degree of cure and the through-the-thickness cure shrinkage strains and coefficient of thermal expansion of partially cured composites were determined by using standard polymer laboratory equipment such as DSC and DMA. The method used in this paper for cure shrinkage measurements is inspired from the work of Garstka et al. [23], however does not require any special equipment and allows the measurement of cure shrinkage by conventional Dynamic Mechanical Analyzer (DMA) in compression mode. Furthermore the sample size used is large enough (a few centimetres) so that the edge effects do not affect measurements done.

II. EXPERIMENTAL

2.1 Material and Manufacturer's Recommended Cure Cycle (MRCC)

The prepreg used in this study is a unidirectional carbon/epoxy, produced by Hexcel Composites with a designation of AS4/8552. The nominal thickness of the prepreg is given as 0.184 mm. The MRCC consists of a first ramp of 2°C/min up to 120 °C and a first hold at 120 °C for 60 min, a second ramp of 2°C/min up to 180 °C and a second hold at 180 °C for 120 min. A pressure of 0.7 MPa is applied throughout the cycle.

2.2 Differential Scanning Calorimeter

Modulated DSC (MDSC) Q200 produced by TA Instruments was used to perform the dynamic and isothermal experiments to provide a database for calculating parameters in the model equations that describes the cure kinetics over a wide range of different conditions.

Dynamic experiments were performed by heating from -35 to 300°C at 1, 2, 3, 4 and 5 °C/min. Isothermal experiments were performed by heating from 25°C to 120°C, 140°C, 160°C, 180°C at 5°C/min, then holding at the specified temperature; 120°C for 360 min., 140°C for 240 min, at 160°C for 180 min, at 180°C for 120 min. After the isothermal run, the samples were cooled 50°C below the isothermal hold temperature and reheated to 300°C at 5°C/min to find the residual heats. Dynamic scans were performed by

modulation of temperature of $\pm 0.5^{\circ}\text{C}$. Mass of prepreg samples that were used in the experiments were around 6 grams.

2.3 Coefficient of Thermal Expansion and Cure Shrinkage Measurements

Five unidirectional (UD) and five cross-ply (XP) samples were prepared for the through-the-thickness strain measurements. Each sample was 26 layers and nominally 5 mm thick. These samples were then cured in a home-made fast response autoclave which can be programmed for the desired temperature and pressure. .

The temperature program followed the MRCC up to the end of the first dwell at 120°C . All samples were heated from room temperature to 120°C at a rate of $2^{\circ}\text{C}/\text{min}$, and kept at 120°C for one hour. Then in order to obtain the equilibrium asymptotic degree of cure attainable at a specific processing temperature, the samples were heated from 120°C to the desired temperature at a rate of $2^{\circ}\text{C}/\text{min}$ and kept at this temperature for a time sufficient to attain the equilibrium asymptotic degree of cure. This hold duration was determined by the isothermal DSC experiments. The hold durations for the second dwell at the specified temperature is listed in Table 1. The samples were then fast cooled to room temperature in the autoclave.

Table 1. Durations of the second isothermal holds

Temperature	($^{\circ}\text{C}$)	120	140	160	180
Hold duration	(mins.)	360	240	180	120

The samples thus manufactured were cut into 25×25 mm squares by a precise diamond cutter cooled by liquid coolant. To overcome the temperature gradient between specimen and DMA equipments measuring thermocouple, the samples were drilled a 1 mm diameter hole at the corner to accommodate the DMA equipment's control thermocouple.

TA Instruments Q800 Dynamic Mechanical Analyzer was used in compression mode with the appropriate compression clamps. The sample was placed on the flat surface of the fixed bottom clamp and the moving top clamp was pressed until touching the sample. Moving clamp applied a very small force (0.1 N) on the sample not to allow disengagement of the sample from the clamp, so measures dimensional changes of the sample as displacement. Nitrogen was used as purging gas and liquid nitrogen was used to get a controlled cooling. Regarding the temperature cycle, two sets of experiments were performed. Partially cured samples were heated from room temperature to 250°C and cooled back to room temperature at a rate of $2^{\circ}\text{C}/\text{min}$.

III. RESULTS AND DISCUSSION

3.1 Cure Kinetics Modeling

The Modulated Differential Calorimeter enables one to distinguish between non-reversing heat flow curve (which corresponds to the heat extraction during curing) and

reversing heat flow curve (which corresponds to the heat capacity of the sample). Figure 1 shows these two curves for a typical dynamic scan for a virgin prepreg sample, together with the baseline. The exothermic direction is up. A straight baseline between the onset and end of the reaction exotherm is used in this study. The glass transition temperature reveals itself as a step change in the reversing heat flow curve around -4°C . The heat of reaction is the total heat found by integrating the exothermic peak. It should be kept in mind that this is the heat of reaction of the composite and should be corrected for the resin content to find the total heat of reaction of the resin.

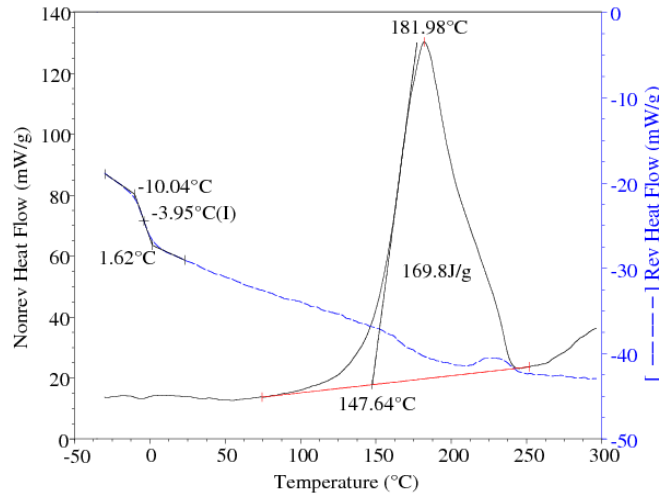


Figure 1. Reversing and non-reversing heat flow curves.

A model which includes two parallel single-step reactions is used in this study. These reactions were assumed to be of n -th order, autocatalytic Prout-Tomkins type with diffusion control. These reactions types are proved to be well suited for cure kinetics modeling of other types of epoxy resins [24, 25]

$$\frac{\partial \alpha}{\partial t} = k_1 \alpha^{n_1} (1 - \alpha)^{a_1} + k_2 \alpha^{n_2} (1 - \alpha)^{a_2} \quad (1)$$

where $k_{1/2}$ are the temperature dependent rate constants, $n_{1/2}$ and $a_{1/2}$ are freely selectable temperature independent exponents. Although physical interpretation of phenomenological models should be avoided, Eq. (1) can be thought as describing a reaction that proceeds along two parallel branches with two different rates, resulting in the same product, and the rates depend on the temperature as well as the degree of cure, α . The kinetic reaction equation takes into account the fact that for some conditions the glass transition temperature of the polymer increases faster than the program temperature for the dynamic tests, or the glass transition temperature rises above the isothermal hold temperature for the isothermal holds. After the partial or complete freezing of the reaction mixture the reaction is no longer controlled by the kinetics of the chemical reaction, but by the diffusion processes.

If diffusion hindrances must be considered, the Rabinowitch equation [26] can be used for calculation of the overall rate constants $k_{1/2}$:

$$\frac{1}{k_{1/2}} = \frac{1}{k_{1/2}^{chem}} + \frac{1}{k_{1/2}^{diff}} \quad (2)$$

where $k_{1/2}^{chem}$ are the chemical reaction rates, $k_{1/2}^{diff}$ are the diffusion rates.

The chemical rate constant is described in the form of Arrhenius equation:

$$k_{1/2}^{chem} = A_{1/2} \exp\{-\Delta E_{1/2}/RT\} \quad (3)$$

where $A_{1/2}$ are the pre-exponential factors, $\Delta E_{1/2}$ are activation energies, R is the universal gas constant, and T is the absolute temperature in degrees Kelvin.

The concrete form of the temperature function for $k_{1/2}^{diff}$ is absolutely unimportant. However, it should be such that the experimental input necessary for the calculation of the selected function is the easily accessible glass transition temperature. Therefore, for temperatures above the glass temperature T_g ($T > T_g$) the WLF equation can be used as proposed by Wise et al. [27]:

$$k_{1/2}^{diff}(T) = K_{1/2}^{diff} \exp\left\{\frac{C_1(T - T_g)}{(C_2 + T - T_g)}\right\} \quad (4)$$

Below T_g ($T < T_g$) dependence is according Arrhenius equation as proposed by Flammersheim and Opfermann [24, 25]:

$$k_{1/2}^{diff}(T) = K_{1/2}^{diff} \exp\left\{-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_g}\right)\right\} \quad (5)$$

with

$$\frac{E}{R} = \frac{C_1 \cdot T_g}{C_2} \quad (6)$$

where $K_{1/2}^{diff}$ and C_1 and C_2 are the model parameters to be found. At $T = T_g$ both formulas are continuous up to the first derivative.

For the fit of reaction curves, it is postulated that $k_{1/2}^{diff}$ may be different for each diffusion controlled reaction, but C_1 and C_2 are global, which means that they are valid for all reactions steps/branches.

An additional function of $T_g(\alpha)$ is needed for the kinetic evaluation of the diffusion controlled systems. T_g as a function of degree of cure is found by fitting the data to the following equation proposed by Heskamp [28]:

$$T_g(\alpha) = T_g(0) \cdot \exp\left\{\frac{g_1 \cdot \alpha}{g_2 - \alpha}\right\} \quad (7)$$

The constants g_1 , g_2 , and $T_g(0)$ can be found to be 0.9914, 2.616 and -2.05°C respectively by a least square fit of the T_g vs. α data, as in Figure 2.

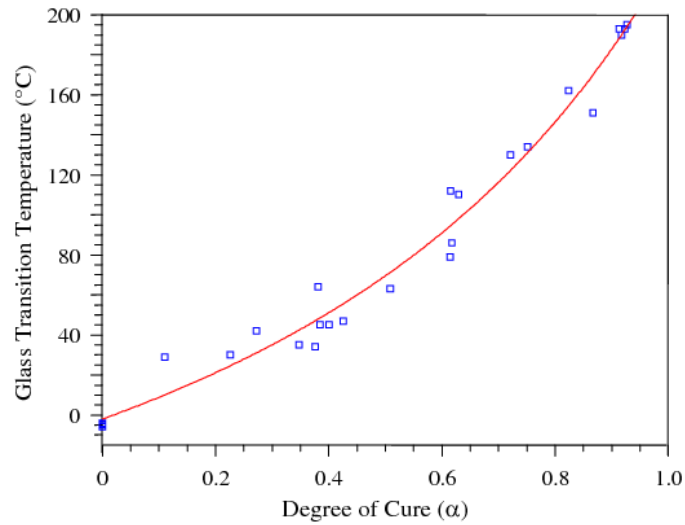


Figure 2. Glass transition temperature versus degree of cure

The parameters of the model listed in Table 2 were found using the NETZSCH Termokinetics Software [29] which utilized a multivariate non-linear regression scheme. Figure 3 shows the predictions of the model together with the original non-reversing heat flow curves. The model fits the experimental data very well as can be seen from this figure.

Table 2. Cure kinetics model parameters

Parameter	$\log(A_1)$	E_1	n_1	a_1	$\log(k_1^{diff})$	$\log(A_2)$	E_2	n_2	a_2	$\log(k_2^{diff})$	C_1	C_2
Unit	s^{-1}	kJ/mol		$\times 10^{-4}$	s^{-1}	s^{-1}	kJ/mol			s^{-1}		K
Value	10.1	125	0.338	5.53	-4.35	4.94	65.8	1.41	0.473	-4.94	8.40	31.6

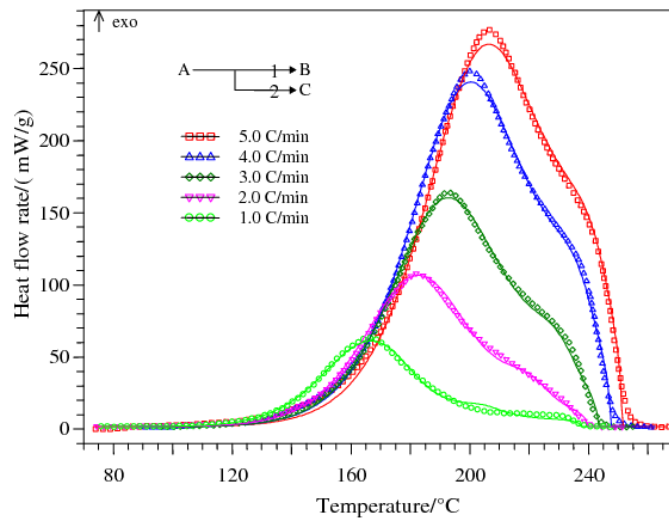


Figure 3. Measured and model fitted heat flow curves

3.2 Thermal expansion and cure shrinkage

It has been found that the thermal expansion of the clamp is significant during the measurement of thermo-chemical strain response of the composite, so the response of the samples should be corrected by using the clamp response as a baseline. The baseline corrected response of the crossply specimen precured at 160°C is shown in Figure 4. Here several features of the thermal strain response of the composite can be distinguished: During heating the partially cured composite expands due to increasing temperature and then undergoes a glassy-to-rubbery transformation (T_g (heating)); it then continues to expand in the rubbery phase with a greater CTE until the cure shrinkage starts to compete with the expansion. The reaction ends and since increasing temperature keeps the composite in the rubbery state, the composite continues expanding with almost the same rate as before the cure reaction. Cure shrinkage strain can be found by extrapolating the expansion response before cure shrinkage and subtracting from this the thermal response after cure reaction as shown in Figure 4. Upon cooling, the composite undergoes a glass transition at around T_g of fully cured composite.

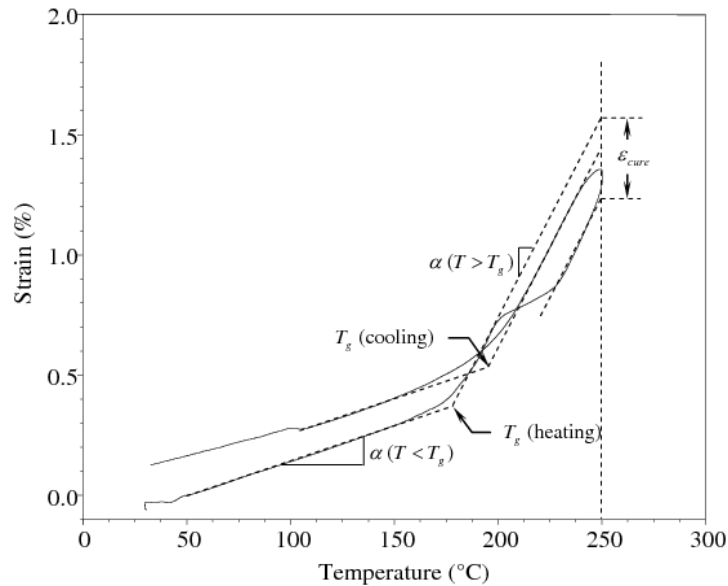


Figure 4. Baseline corrected thermal strain response of crossply specimen.

The thermal strain responses of composites with different initial degrees of cure are compared in Figure 5 for unidirectional and crossply composites during the heating stage. Different degrees of cure are obtained by precuring the composites at various isothermal temperatures at which the composite cures up to an equilibrium degree of cure as explained in the experimental part. It can be seen that as the degree of cure increases, the glassy-to-rubbery transformation temperature is shifted to higher temperatures, and the cure shrinkage strain decreases. The measured transition temperature for unidirectional and crossply samples is almost the same, however the CTEs before and after T_g and the cure shrinkage strains are larger for crossply samples.

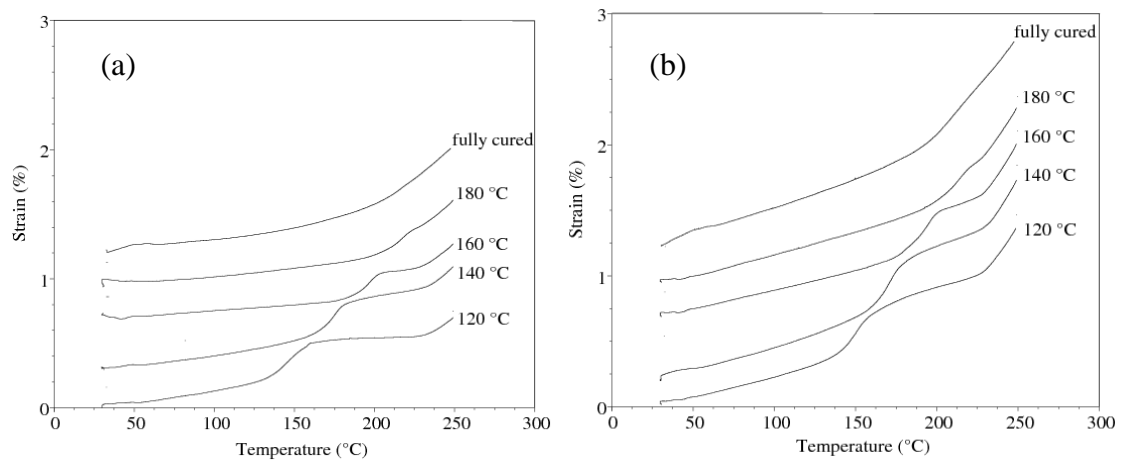


Figure 5. Thermal strain response of (a) unidirectional and (b) crossply samples precured at different temperatures.

The CTEs at the glassy and rubbery states as well as T_g during heating and curing are given in Table 3. It can also be seen from Table 3 that the cure shrinkage strains of the crossply samples are almost twice of CTEs of unidirectional samples. The T_g measured during curing is almost the same as the value reported in the manufacturer's data sheet [30]. The CTE increases dramatically upon glass transition and the rubbery CTEs are 4-5 larger than the glassy CTEs.

Table 3. Properties of the composite measured from the thermal strain response.

Precure T	Lay-up	$\alpha (T < T_g)$	T_g (heating)	$\alpha (T > T_g)$	T_g (cooling)	ϵ_{cure}
°C		$\mu\text{m}/(\text{m}\cdot^\circ\text{C})$	°C	$\mu\text{m}/(\text{m}\cdot^\circ\text{C})$	°C	%
120	UD	17.99	131.74	84.80	205.95	0.64
	XP	34.37	138.58	158.1	200.85	0.97
140	UD	18.83	162.22	91.44	198.84	0.42
	XP	38.47	158.50	166.4	196.84	0.78
160	UD	19.37	186.54	81.26	198.27	0.22
	XP	29.88	175.38	163.0	197.09	0.40
180	UD	12.50	201.13	101.4	195.64	0.04
	XP	35.00	197.92	155.7	200.85	0.11
fully cured	UD	16.73	193.36	97.47	-	-
	XP	42.89	190.02	147.0	-	-

IV. CONCLUSION

The cure kinetics of the epoxy resin was successfully modeled by a rate equation describing a reaction that proceeds along two parallel branches with two different rates, resulting in the same product, and the rates depend on the temperature as well as the degree of cure. The proposed model enables to capture all features of the reaction exotherm and the freezing of reaction as the glass transition of the resin approaches the process temperature and the reaction shifts from autocatalytic to diffusion controlled.

A method has been proposed that allows the measurement of through-the-thickness cure shrinkage strains during curing of the composite by using a compression clamp in conventional DMA equipment.

The thermal response of the partially cured composite samples shows that the resin undergoes a transition from glassy to a rubbery state, which shifts to higher temperatures depending on the degree of cure. The coefficients of thermal expansion in the through-the-thickness direction is found to be relatively independent of the degree of cure, however, they increase considerably after glassy-to rubbery transition. Further curing takes place at the rubbery state causing cure shrinkage strains that are inversely proportional to the previous degree of the cure of the resin.

The through-the-thickness cure shrinkage strains in crossply laminates are measured to be about twice of the strains in unidirectional laminates, because the fibers provide a constraint for shrinkage in both in-plane directions in crossply laminates whereas only in one direction in unidirectional laminates.

ACKNOWLEDGEMENTS

The authors acknowledge the support of Bogazici University Research Fund under project code 09A601P.

References

1. D.W. Radford, T.S. Rennick, *J. Reinf. Plast. Compos.*, **19**, 621–41 (2000).
2. D. A. Darrow, Jr. and L. W Smith, *J. Compos. Mater.* , **36**, 2407-2419 (2002).
3. C. Albert, G. Fernlund, *Compos. Sci. Technol.* , **62**, 1895–912 (2002).
4. N. Ersoy, K. Potter, M.R. Wisnom and M.J. Clegg, *Composites Part A*, **36**, 1700-1706 (2005).
5. M.R. Wisnom, N. Ersoy, K.D. Potter, *J. Compos. Mater.* , 41, 1311-1324 (2007).
6. M. Buczek, D. Mason, C. W. Lee, A. Saunders, Proactive control of curing composites, *Proceedings of the 44th International SAMPE Symposium*, Long Beach, CA, May 1999.
7. J. Player, M. Roylance, W. Zukas, D.K. Roylance, UTL consolidation and out-of-autoclave curing of thick composite structures, *32nd International SAMPE Technical Conference*, Boston, MA, USA; 5-9 Nov. 2000, 757-767.
8. P. Hubert, A. Johnston, A. Poursartip, K. Nelson, Cure kinetics and viscosity

models for Hexcel 8552 epoxy resin, *International SAMPE Symposium and Exhibition (2001)*, 46 (2001: A Materials and Processing Odyssey, Book 2), 2341-2354.

9. L. Sun, S.-S.Pang, A.M. Sterling, I.I. Negulescu, M.A. Stubblefield, *J. Appl. Polym. Sci.*, **83**, 1074-1083 (2002).
10. L. Sun, S.-S. Pang, A. M. Sterling, I.I. Negulescu, M.A. Stubblefield, *J. Appl. Polym. Sci.*, **86**, 1911-1923 (2002).
11. V. Antonucci, M. Giordano, S.I. Imparato, L. Nicolais, *Polym. Compos.*, **23**, 902-910, (2002).
12. B. Yates, B.A. McCalla, L.N. Phillips, D.M. Kingston-Lee, K.F. Rogers, *J. Mater. Sci.*, **14**, 1207-1217, (1979).
13. J.D. Russell, *SAMPE Quarterly* 24, 28-33 (1993).
14. P. Prasatya, G.B. McKenna, S.L. Simon., *J. Compos. Mater.* , **35**, 826-48 (2001).
15. M. Zarrelli, *Cure Induced Property Changes and Warpage in Thermoset Resins and Composites*, PhD thesis, Cranfield University, School of Industrial and Manufacturing Science, Advanced Materials Department (2003).
16. M.A. Stone, B.K. Fink, T.A. Bogetti, J.W. Gillespie Jr., *Polym. Eng. Sci.* , **40**, 2489-97 (2000).
17. F. Flores, J.W. Gillespie Jr., T.A. Bogetti, *Polym. Eng. Sci.* , **42**, 582-90, (2002).
18. C. Li, K. Potter, M.R. Wisnom, *Compos. Sci. Technol.* , **64**, 55-64 (2004).
19. B. Bilyeu, W. Brostow, K.P. Menard, *Polimery*, **46**, 799 (2001).
20. A.A. Johnston, *An integrated model of the development of process-induced deformation in autoclave processing of composite structures*, PhD thesis, University of British Columbia, (1997)
21. I.M. Daniel, T.-M. Wang, D. Karalekas, J.T. Gotro, *J. Compos. Tech. Res.* , **12**, 172-6 (1990).
22. T. Igarashi, S. Kondo, M. Kurokawa, *Polymer*, **20**, 301-710, (1979).
23. T. Garstka, N. Ersoy, K. Potter, and M.R. Wisnom, *Composites Part A*, **38**, 2517-2526 (2007).
24. H.J. Flammersheim, J. Opfermann, *Thermochim. Acta*, **337**, 141-148, (1999).
25. H.J. Flammersheim, J. Opfermann, *Macromol. Mater. Eng.* . **286**, 143-150 (2001).
26. E.Rabinowitch, *Trans. Faraday Soc.* **33**, 1225, (1937).
27. C.W.Wise, W.D.Cook, A.A.Goodwin, *Polymer*, **38**, 325 (1997).
28. D.Hesekamp, *Chem. Eng. Technol.*, **21**, 2 (1998)
29. NETZSCH Thermokinetics, *Instrument Manual*, NETZSCH Gerätebau
30. HexPly 8552 Data Sheet, Hexcel Corporation, Stamford, Connecticut. (2007)
31. N. Ersoy, K. Potter, M. R. Wisnom, M. J. Clegg, *Composites Part A*, **36**, 1536-1544 (2005).