

Epoxy Resin/Polyurethane Functionally Graded Material Prepared by Microwave Irradiation

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ABSTRACT: The glass-transition temperature (T_g) and modulus (E) of graded material in a plastic-elastomer system prepared with layer-by-layer casting in connection with microwave curing were studied. Epoxy (EP) resin and polyurethane (PU) were selected as the plastic and elastomer components, respectively. The structure of the functionally graded material (FGM) was such that EP ($E = 3.2$ GPa, and $T_g = 162^\circ\text{C}$) and PU ($E = 0.069$ GPa and $T_g = -54^\circ\text{C}$) were both surfaces, with a stepwise gradient in EP and PU content existing between the two over a thickness of 9 mm. Fourier transform infrared spectroscopy and scanning electron mi-

croscopy were used to investigate the PU content and the morphologies of the FGMs separately. Finite element analysis (FEA) was used to simulate the temperature and thermal stress distribution along the graded direction under a steady-state, nonuniform temperature field. The results of FEA showed that the temperature and thermal stress distribution decreased along the graded direction. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 994–999, 2004

Key words: plastics; elastomers; processing

INTRODUCTION

Functionally graded materials (FGMs) are designed to reduce thermal stress and maintain high heat resistance and ductility. They possess a continuous concentration change of one or more components from the surface to the bottom. Metallic and ceramic FGMs have been actively developed as ultra-high-temperature-resistant materials for aircraft, space vehicles, and other engineering applications. However, there have been fewer studies on polymer FGMs. Among the few reports on polymer FGMs, most are related to biomedical^{1,2} or optical purposes.^{3–7} There are hardly any reports concerning thermal protection systems. In fact, synthetic polymers have great potential for thermal barrier material production because of their heat insulation. Some plastics, for example, epoxy resin (EP), have excellent high chemical and corrosion resistance and mechanical and thermal properties and outstanding adhesion to various substrates. Elastomers, such as polyurethane (PU), made from polyether and isocyanate, have good abrasion resistance and toughness, even at tens of degrees below zero centigrade. However, EP becomes very brittle at low temperatures, and PUs lose elasticity and decompose at higher temperatures. Both can be used only in a temperature range of

tens of degrees. Thermal barrier materials, for example, hot-substance transport pipes and other thermal protection systems, often work in nonuniform temperature fields; in this condition, the temperatures of the one surface and the other generally span from above 120°C to below -50°C . Neither EP nor PU can satisfy this demand. If an EP/PU elastomer FGM were processed, the problem would be resolved. The face of EP to high temperatures could provide heat and corrosion resistance, and the opposite face of PU to low temperatures would offer freeze resistance and toughness.

On the basis of the design of a metal/ceramic FGMs, EP and PU were selected as components of a FGM, with the addition of diaminodiphenyl methane (DDM) as crosslinking agent, both EP and isocyanate in PU could react with amino groups in DDM. However, the isocyanate reacted with amino groups much faster than the epoxy ring, which is an inconvenience during processing. To slow down the reaction rate of the isocyanate with amino groups, the isocyanate group in the urethane prepolymer was blocked with phenol; at a temperature of about 120°C , the amino group reacted with isocyanate by replacing the phenol.

Common steps for the production of metal/ceramic FGMs include two stages: first, a gradient structure is formed by methods such as vapor deposition, layer-by-layer casting, or powder metallurgy, and then, the green compacts are hot-pressed at a high temperature.

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Each layer is processed at the same temperature and for the same heating time.

The previous method is not suitable for the production of an EP/PU FGM. The viscosity of EP and PU decrease quickly with increasing temperature, and the graded structure would be destroyed before the curing of system because of the flowing of the components. A practical route for the fabrication of an EP/PU FGM is the following: a mixture of EP/PU/DDM is cast, followed by curing. Then, the cured film is submitted for the next casting. When the FGM is cured with conventional heating, the sample cast first is always exposed to high temperatures and suffers a longer heating time than those cast subsequently. It is well known that the properties of the polymer are related closely to the curing time; if the different parts in the FGM have different heating times, the mechanical properties of the FGM are affected by the diverse curing time.

However, this problem is prevented when the EP/PU FGM is processed by microwave irradiation. The microwave absorption of the polymer depends on the dielectric constant itself; when the first layer is cast and cured, the dielectric constant of the sample is reduced. The microwaves used to irradiate subsequent layers has little effect on it, so every layer in the FGM has equal microwave absorption. In addition, reports on the microwave curing of EP⁸⁻¹³ and PU¹⁴ have proven that microwaves can enhance the curing rate greatly and improve the mechanical properties of the samples; this will be of great benefit by shortening the processing time and improving the properties of the FGM.

The objective of this research was to apply microwave irradiation to the curing of an EP/PU FGM with layer-by-layer casting. The structure and the properties, including modulus (E), glass-transition temperature (T_g), and tensile strength throughout the FGM were investigated. Under a steady-state temperature field, the temperature distribution and thermal stress along the gradient direction were simulated.

EXPERIMENTAL

Materials

The initial materials consisted of bisphenol A and diglycidyl ether epoxy resin (E-51, with an epoxy equivalent of 185–210, Yueyang Resin Plant, Yueyang, China). Toluene diisocyanate (TDI; 80:20 an mixture of the 2,4 and 2,6 isomers) and trifunctional poly(ox propylene) glycol (PPG 330; number-average molecular weight = 3000) were purchased from Shanghai Reagent Co. (Shanghai, China). EP and PPG 330 were degassed at 80°C and 10 mmHg for 3 h to remove any absorbed water before use. The TDI (an 80:20 mixture of the 2,4 and 2,6 isomers) and DDM used in this study were standard laboratory reagents.

Preparation of phenol end-capped PU prepolymer

TDI was charged to a flame-dried, 500-mL, three-necked, round-bottom flask, equipped with a water-cooled condenser with a CaCl₂ drying tube, a N₂ inlet, a 200-mL addition funnel, and a mechanical stirrer, which was placed into an oil bath. PPG was added dropwise to the TDI (NCO/OH = 2:1) under a nitrogen atmosphere. The mixtures was stirred and held at 80°C for 3 h; then, phenol was added (OH/NCO = 1:1). The reaction temperature was raised to 110°C and maintained for 6 h.

Curing of EP/PU/DDM

Different mass ratios of EP and PU and a stoichiometric amount of DDM were mixed and stirred at 100°C until the mixture became uniform; the mixture was then poured onto the polytetrafluoroethylene (PTFE) mold. Microwave curing was conducted inside a multimode stainless steel cavity with dimension 302 × 221 × 318 mm connected by a wave guide to a 2.45-GHz magnetron powered by a variable power direct current. The PTFE mold was always placed in the center of the cavity to guarantee the same field strength every time. The thermal curing was conducted at 120°C.

Procedure for the preparation of the EP/PU FGM

Different mass ratios of EP and PU were mixed with a stoichiometric amount of DDM and dissolved in the dimethylchloride. A solution containing 65 wt % of the EP/PU/DDM mixture was poured on to the PTFE mold and was then irradiated at 200 W of microwave power for 20 min. The film was submitted for the next casting. Except for the bottom and top layers the amount of solution of every layer was same. After each layer was poured in, the layered sample was successively irradiated at 400 W for 30 min.

Measurements

Fourier transform infrared (FTIR) spectroscopy was recorded with a Testscan Shimadzu 8000 FTIR spectrometer (Shimadzu Ins., Kyoto, Japan). The morphology of the sample was taken with a Hitachi S-570 SEM scanning electron microscope (Hitachi Ins., Tokyo, Japan). The T_g values of the EP/PU/DDM system were determined with a PerkinElmer DSC-7 differential scanning calorimeter (Perkin-Elmer Co., Boston, MA, USA) at a heating rate of 20°C min. The midpoint of the change in slope of the heat capacity plot of the second scan was taken as the value of the T_g . The mechanical properties (tensile strength and E) of the system were measured by an Instron tensile tester (model 4204) (Instron Co., Canton, MA, USA). The

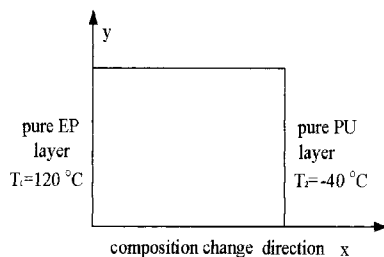


Figure 1 Boundary heat conditions in the FGM.

specimen gauge was set for 20 mm. The test were run at room temperature at a strain rate of 2 mm/min; E was reported at 0.1% strain. Five measurements were taken for each specimen.

Poisson's ratio (ν) was evaluated from the longitudinal and transverse strains in uniaxial loading. Transverse strain was measured with strain gage (YJB.1A; Dongnon Instrument Inc., Shanghai, China). The thermal expansion coefficient (α) was obtained with PZ-2 thermal expansion measurements (Shanghai, China). Thermal conductivity (λ) was measured with a transient thermal conductivity tester (KDR-I, Mingda Instrument Inc., Hefei, China).

Thermal analysis in the steady state

The 11-layer FGM plate was subjected to a steady-state, nonuniform heating, the pure EP surface of the FGM plate was kept at 120°C, the pure PU surface was subjected to a temperature of -40°C, the side surfaces were insulated, and the mechanical conditions were stress-free, as shown in Figure 1.

The temperature and the thermal stress distribution along the FGM plate were analyzed by two-dimensional finite element analysis (FEA) with a finite element package (ANSYS Inc., Canonsburg, PA, USA). The finite elements used in FEA were 4-node-isopara-

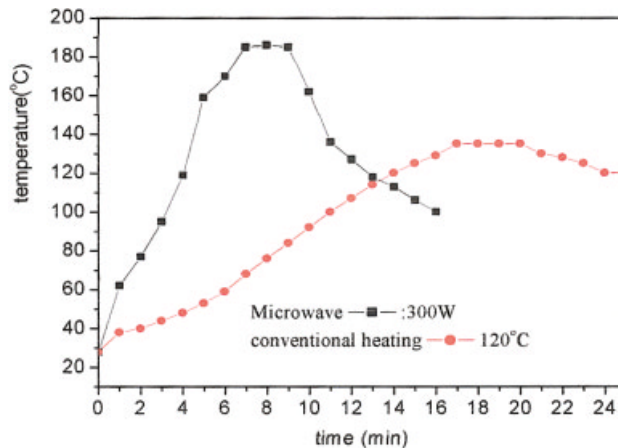


Figure 2 Specimen temperatures versus cure time during microwave and thermal curing for the EP/PU/DDM system (EP/PU = 10/10 w/w). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

metric elements. Material properties for analysis included λ , ν , E , and α , as listed in Table I. The layers were assumed to be isotropic and linear elastic; ν and E were assumed to be unchanged with temperature in calculation.

RESULTS AND DISCUSSION

Thermal behaviors and mechanical properties of EP/PU/DDM cured by microwave irradiation and conventional heating

The microwave curing of the EP/PU/DDM system investigated in detail in our laboratory. The specimen temperatures during microwave curing and conventional heating are shown in Figure 2.

When the sample was cured by microwave irradiation, the temperature increased to a maximum and

TABLE I
Relevant Properties of Specimens for FEA of EP/PU FGM

PU/EP (w/w)	E (Gpa)	ν	λ (w/mk)	α ($10^{-6}/^{\circ}\text{C}$)				
				-10°C	20°C	60°C	80°C	120°C
10/0	0.069	0.487 ^a	0.099	6.13	6.50	6.60	7.14	12.02
10/2	0.078	0.467	0.105	6.27	6.52	6.81	6.93	10.43
10/4	0.245	0.438	0.108		5.61	9.74	11.42	10.39
10/6	0.86	0.432	0.112		6.59	10.07	11.11	10.24
10/8	0.99	0.427	0.115		8.38	11.56	11.94	10.31
10/10	1.01	0.425	0.117		7.45	11.56	11.74	10.85
8/10	1.438	0.423	0.120		6.94	11.61	11.81	10.87
6/10	1.585	0.418	0.121		6.65	11.40	10.67	10.65
4/10	2.62	0.394	0.123		6.27	9.60	9.96	10.06
2/10	2.72	0.372	0.128		6.23	8.13	8.39	8.91
0/10	3.2	0.36	0.132		5.54	5.58	6.55	7.08

Microwave curing cycle: 200 W/20 min + 400 W/30 min.

^a Evaluated.

TABLE II
Mechanical Properties of the EP/PU/DDM System cured with Microwave Irradiation and Conventional Heating

Curing cycle	<i>E</i> (MPa)	Tensile strength (MPa)	Tensile strain (%)
Microwave			
200 W/40 min	782	19.2	4.3
200 W/60 min	783	19.4	4.4
200 W/120 min	782	19.3	4.3
200 W/20 + 400 W/30 min	1011	25.8	8.08
200 W/20 + 400 W/60 min	1013	25.2	8.06
Heating: 120°C/360 min	972	24.9	6.53

EP/PU = 10/10 w/w.

then dropped greatly within several minutes; compared to microwave curing, after the temperature of the sample cured with conventional heating reached a maximum, it decreased slowly and then stayed at 120°C.

The mechanical properties, including *E*, tensile strength, and tensile strain at fracture of the sample cured at different conditions, are listed in Table II.

The data in Table II indicate that the properties of the sample were only related to the microwave power setting; prolonging the irradiation time did not influence the properties. Compared to the sample cured with conventional heating at 120°C for 360 min, the

samples cure by microwave irradiation at 200 W for 20 min and at 400 W for 30 min had higher mechanical properties and shorter curing times. This indicated microwave irradiation was very efficient for curing the EP/PU/DDM system.

Structure and morphologies of the FGM produced by microwave irradiation

By adjusting the ratio of EP to PU, one can control the gradient profiles. In this study, the FGM had 11 layers, and the EP/PU mass ratio changed piecewise linearly from 10/0 to 0/10 through the thickness. The mass discrepancy of the components in adjacent layers was 2/10. The PU content variation could be determined with FTIR by analysis of the carbonyl groups in it. Figure 3 shows the FTIR spectra of the medial layers in the FGM. The mass ratio of the EP/PU ordered in layers was 4/10, 6/10, 10/10, 10/6, and 10/4. The characteristic peaks of the IR spectrum of carbonyl were at 1732 cm⁻¹; when the content of the PU decreased, the absorption at 1732 cm⁻¹ decreased correspondingly.

The profile of the FGM, the thickness and microstructure, were investigated with scanning electron microscopy (SEM). Figure 4 shows the profile of selected layers of the FGM. The sample was 13.2 mm thick, and the EP and PU layer was 2 mm thick. The

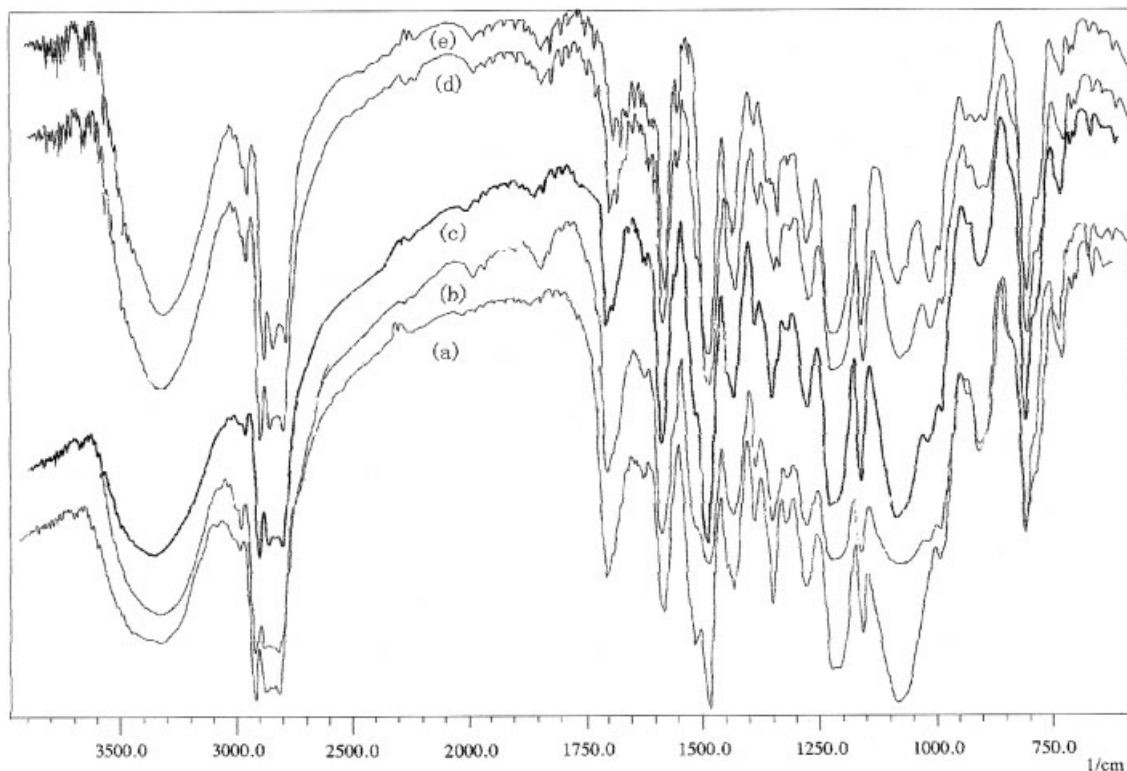


Figure 3 FTIR spectra of the FGM. (a) layer of EP/PU=4/10 w/w, (b) layer of EP/PU=6/10 w/w, (c) layer of EP/PU=10/10 w/w, (d) layer of EP/PU=10/6 w/w, (e) layer of EP/PU=10/4 w/w.

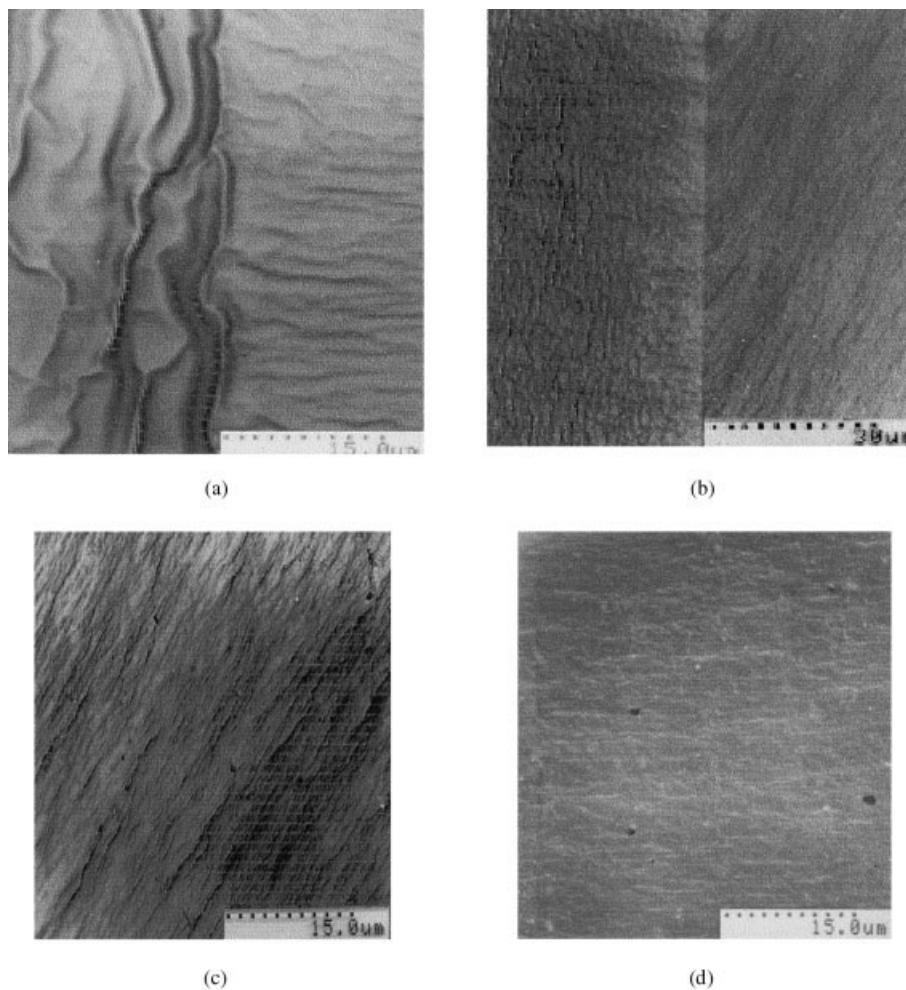


Figure 4 SEM micrographs of a selected layer in the FGM: (a) layers of EP/PU = 2/10 and 4/10 w/w, (b) layers of EP/PU = 8/10 and 10/10 w/w, (c) EP/PU = 10/10 w/w, and (d) EP/PU = 8/10 w/w.

other layers, were each approximately 1.0–1.2 mm thick. An interface was observed between the layers. The microstructure with individual layers; was uniform, and there were no defects at the interlayer boundaries.

Some property distributions in the direction of the composition change in FGM are listed in Table III; The mechanical properties including E , tensile strength, and T_g were varied gradually in the FGM. The top

layer was composed of pure EP; its T_g , E , and tensile strength were 162°C, 3.2 GPa, and 64.8 MPa, respectively. The bottom layer was composed of pure PU; its T_g , E , and tensile strength were -54°C, 0.069 GPa, and 4.65 MPa, respectively. The E value of the top layer, was 46 times as much as that of the bottom layer, and the T_g difference between them was about 220°C. A great discrepancy in T_g and E between the top and bottom layer was the aim of our FGM design.

TABLE III
Properties Along the Thickness Direction in the FGM

Layer	Thickness direction in the FGM										
	1	2	3	4	5	6	7	8	9	10	11
PU/EP (w/w)	10/0	10/2	10/4	10/6	10/8	10/10	8/10	6/10	4/10	2/10	0/10
Tensile strength (MPa)	4.65	5.84	11.6	15.2	20.8	25.8	27.4	32.5	45.8	75.9	64.8
T_g (°C)	-54	-9.3	25.4	45.7	83.2	99	109.2	113.2	139.6	145	162
E (GPa)	0.069	0.078	0.245	0.86	0.99	1.01	1.438	1.585	2.62	2.72	3.20

Microwave curing cycle: 200 W/20 min + 400 W/30 min.

Thermal stress of the EP/PU FGM produced by microwave irradiation

The variations in temperature and thermal stress distribution along the graded direction of the FGM analyzed by FEA are shown in Figures 5 and 6, respectively. The temperature in the FGM was distributed linearly through thickness; the temperature at the EP surface was 120°C, and it decreased gradually with increasing PU content. When we compared the data in Figure 6 and table III, we found that thermal stress distribution was consistent to strength change along the graded direction in the FGM; the layer with higher tensile strength underwent greater thermal stress. For example, the maximum thermal stress (27.8 MPa) occurred at the layer where EP/PU = 10/0, which had the highest tensile strength (64.8 MPa) in the FGM. In addition, the tensile strength was higher than the thermal stress in the same layer in the FGM. This implied the FGM could endure the thermal stress arising from the heating load.

CONCLUSIONS

In this study, a new type of polymer FGM was designed by changing the content of EP and PU. The FGM possessed a wide variety of T_g and E combinations and was expected to be used in nonuniform temperature field. FEA showed that under a steady-state, nonuniform temperature field, the thermal stress decreased from the EP side to the PU side, which corresponded to the variety of the strength obtained from the experiment. In addition, the higher strength than thermal stress in the same layer of the FGM indicated the FGM could well bear the thermal stress arising from the heating load.

More importantly, the FGM was produced by microwave assistance, which involved more uniform curing, energy saving, and rapid fabrication than ther-

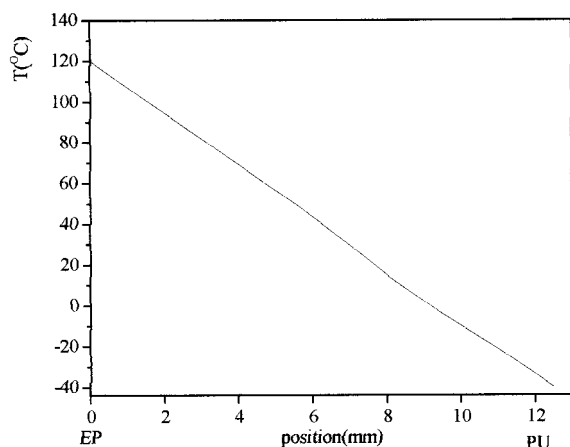


Figure 5 Temperature (T) distribution along the FGM.

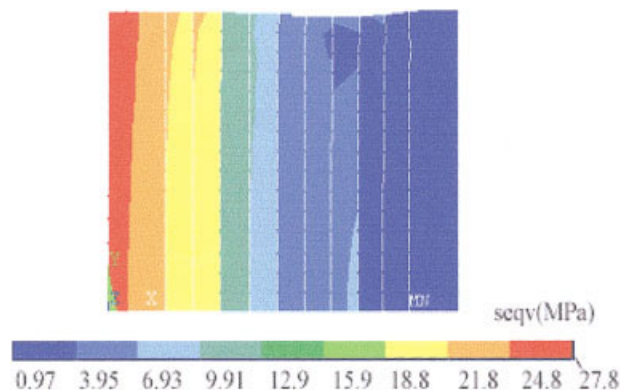


Figure 6 Thermal stress distribution in the FGM. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

mal processing. The system studied was EP/PU, but there is no reason why this process route should not be suitable for a wide variety of polymer/polymer and mineral filler/polymer combinations. Indeed, a thermal expansion coefficient graded material composed of SiO_2 and EP has also been successfully produced with same method in our laboratory. We envisage that a FGM consisting of a polymer component would probably easier to fabricate, and the problem arising because of different curing times in different parts of the FGM by thermal heating would be avoided.

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References

- Berry, G. C.; Dror, M. *Plast Prepr (Am Chem Soc Div Org Coat)* 1978, 38, 465.
- Predecki, P. *J Biomed Mater Res* 1974, 8, 487.
- Kosjakov, V. I.; Ginzburg, L. I. In *Diffusion Phenomena Polymers*; Chernogolovka: IKhF, Moscow, Russia 1985; p 86.
- Bukhbinder, T. L.; Kosjakov, V. I.; *Vysokomol Soedin Ser B* 1986, 28, 625.
- Krivchenko, E. I.; Ginzburg, L. I.; Nabatova, L. N. In *Synthesis and Properties of Styrene Polymer and Copolymers*; Leningrad; 1985; p 54.
- Ohtsuka Y. *Appl Phys* 1973, 23, 247.
- Krivchenko, E. I.; Matveenko, R. V.; Pavlova, V. N.; Budtov, V. P. *Plast Massy* 1988, 4, 26.
- Wei, J. H.; Hawley, M. C.; Delong, J. D.; Demeuse, M. *Polym Eng Sci* 1993, 33, 1132.
- Le Van, Q.; Gourdenne, A. *Eur Polym J* 1987, 23, 777.
- Mijovic, J.; Wijaya, J. *Macromolecules* 1990, 23, 3671.
- Jullien, H.; Petit, A.; Merienne, C. *Polym* 1996, 37, 3319.
- Jordan, C.; Galy, J.; Pascault, J. P. *Polym Eng Sci* 1995, 35, 233.
- Thuillier, F. M.; Jullien, H.; Loustalot, M. F. G. *Polym Commun* 1986, 27, 206.
- Jullien, H.; Valot, H. *Polym* 1985, 26, 506.