

Thermal and Mechanical Properties of Fiber-Forming Poly(urethane semicarbazide)s

ARUNA PALANISAMY,¹ VENKATESHWARLU UMMADISETTY,² GANGA RADHAKRISHAN¹

¹ Advanced Centre in Polymers, Central Leather Research Institute, Adyar, Chennai 600 020, India

² Shoe Design and Development Centre, Central Leather Research Institute, Adyar, Chennai, 600 020, India

Received 19 December 2000; accepted 25 April 2001

ABSTRACT: Fiber-forming poly(urethane semicarbazide)s were prepared with poly(butylene adipate)glycol as soft-segment domains and hexamethylene diisocyanate/terephthalic dihydrazide as hard-segment domains. The hard-segment content was varied via variations in the polyol/isocyanate molar ratio, and the films were characterized by Fourier transform infrared spectroscopy and thermogravimetric analysis. The effect of the hard-segment-content variation on the properties was studied by differential scanning calorimetry, stress–strain analysis, and dynamic mechanical testing. Differential scanning calorimetry showed that the samples exhibited a very low level of hard/soft-segment phase mixing. The stress–strain analyses revealed that the elongation at break decreased with an increase in the hard-segment content and that the mechanical property depended on the overall crystallinity of the samples. Dynamic mechanical tests revealed a high glassy-to-rubbery state modulus and a high degree of phase separation between the hard and soft segments. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 86–93, 2002

Key words: poly(urethane semicarbazide); phase separation; hard-segment content; crystallinity; dynamic mechanical analysis; fibers; modulus

INTRODUCTION

Thermoplastic urethane elastomers are a class of segmented block copolymers consisting of sequences of soft segments and hard segments that are thermodynamically incompatible and may present, because of their chemical linkage, a phase separation.¹ Because of the polar nature of the urethane group in hard segments and the ability to form hydrogen bonds, the hard segments are capable of intermolecular association and possible domain segregation.² It is desirable

to have the highest degree of phase separation that provides for the elastomeric or apparent crosslinked nature of these polymers.^{3–5} Aliphatic hard segments lead to a more complete phase separation due to the increased mobility.

Polymer structures with a high concentration of amide groups can be made with the addition of hydrazine or a diacid hydrazide to a diisocyanate. Polyureylenes⁶ are structures prepared by the addition of hydrazine to a diisocyanate, and if dihydrazides are used instead of hydrazine, the polymer formed is a polysemicarbazide.⁷ Poly(urethane semicarbazide)s are a class of segmented block copolymers prepared by the reaction of a polyol, a diisocyanate, and a dihydrazide. The aim of this work was to prepare fiber-forming poly(urethane semicarbazide)s with a large number of polar groups in the hard-segment region and to

Correspondence to: G. Radhakrishnan (clrieco@md3.vsnl.net.in).

Contract grant sponsor: Council of Scientific and Industrial Research (India).

Journal of Applied Polymer Science, Vol. 83, 86–93 (2002)
© 2002 John Wiley & Sons, Inc.

Table I Polymer Codes, Compositions, and Differential Scanning Results

Code	Number of Moles			Hard Segment Content (%)	T_g (°C)	$T_{m,h}$ (°C)
	HMDI	Polyol	Terephthalic Dihydrazide			
PBA 11	1.5	1	0.5	26	-41.3	264
PBA 12	2	1	1	35	-37.7	269
PBA 13	3	1	2	47	-38.8	275
PBA 14	4	1	3	56	-41.5	280

study their thermal, stress-strain, dynamic mechanical, and structural properties.

EXPERIMENTAL

Materials

Poly(butylene adipate)glycol (PBA) with a molecular weight of 1000 (PBA 1000) was supplied by Bayer Sanmar (I) Ltd. (Mumbai, India). The polyol was dried and degassed at 90–100°C *in vacuo* for 6–7 h before use. Hexamethylene diisocyanate (HMDI) and dibutyltin dilaurate (Aldrich, Milwaukee, WI) were used as received. Terephthalic acid (Sisco Research Laboratories, Mumbai, India) and hydrazine hydrate (99%; s.d. fine chemicals, ltd., Boisar, India) were used as received. Dimethylsulfoxide (Ranbaxy Laboratories Ltd., SAS Nagar, India) was stored over calcium hydride overnight and purified by distillation under reduced pressure.

Synthesis of Terephthalic Dihydrazide

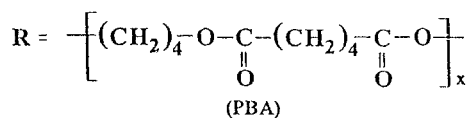
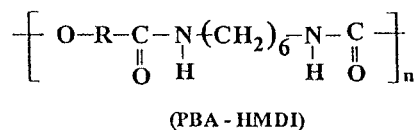
Terephthalic acid was converted to dimethyl terephthalate by a procedure reported elsewhere.⁸ The dimethyl terephthalate thus prepared was recrystallized from methanol for further use. One mole of recrystallized dimethyl

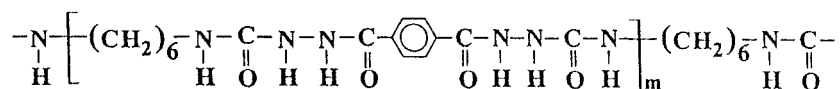
terephthalate was refluxed with 2 mol of hydrazine hydrate for 5 h in methanol.⁹ The resulting mixture was filtered when hot and washed several times with methanol, and the off-white powdery compound was dried in an oven at 70°C for 2 days and stored in a desiccator.

Preparation of Poly(urethane semicarbazide)

Prepolymers were prepared by the reaction of HMDI with PBA 1000 at 75°C under a nitrogen atmosphere. The reaction was monitored by di-*n*-butylamine titration, and when the theoretical NCO content was reached, the temperature was reduced; a drop of catalyst was added, followed by dropwise addition of a chain extender suspended in dimethyl sulfoxide. The temperature was slowly raised, and the chain-extension step was carried out at 60°C for 6 h until the reaction was complete [confirmed by the disappearance of the —NCO peak in Fourier transform infrared (FTIR)]. The polymer solutions, when precipitated in water by being forced through an ordinary hypodermic syringe, gave highly elastomeric fibers. Films were cast on a silicon mold and dried overnight at 70°C. The films were further dried at 60°C under vacuum for 2 days. Table I shows the basic formulation for preparing samples with various hard-segment contents. The polymers have the following general chemical structures:

Soft Segment :



Hard Segment:

(HMDI - TDH)

Measurements

FTIR spectra was recorded with a Nicolet Avator 360 FTIR spectrophotometer with an attenuated total reflection accessory. Thermogravimetric analysis was done with a DuPont 951 thermogravimetric analyzer at a heating rate of 20°C/min under a nitrogen atmosphere (flow rate = 50 mL/min). Differential scanning calorimetry (DSC) was carried out under a nitrogen atmosphere with a DuPont differential scanning calorimeter at a heating rate of 10°C/min. The samples were first heated to 200°C to erase the thermal history, then quenched to -80°C, and finally scanned up to +300°C. Microtensile specimens (40 mm × 10 mm) were conditioned in a desiccator before testing, and the stress-

strain analysis was carried out at room temperature with an Instron universal testing machine at a crosshead speed at 100 mm/min. Dynamic mechanical analysis (DMA) was carried out with rectangular specimens (20 mm × 10 mm × 2 mm) with a DMA 2980 dynamic mechanical analyzer (TA Instruments) at a 1-Hz frequency in the temperature range -100 to +100°C under a strain amplitude of 20 μm.

RESULTS AND DISCUSSION**FTIR Spectroscopic Analysis**

A representative FTIR spectrum of the polymers is given in Figure 1. All the polymers exhibit

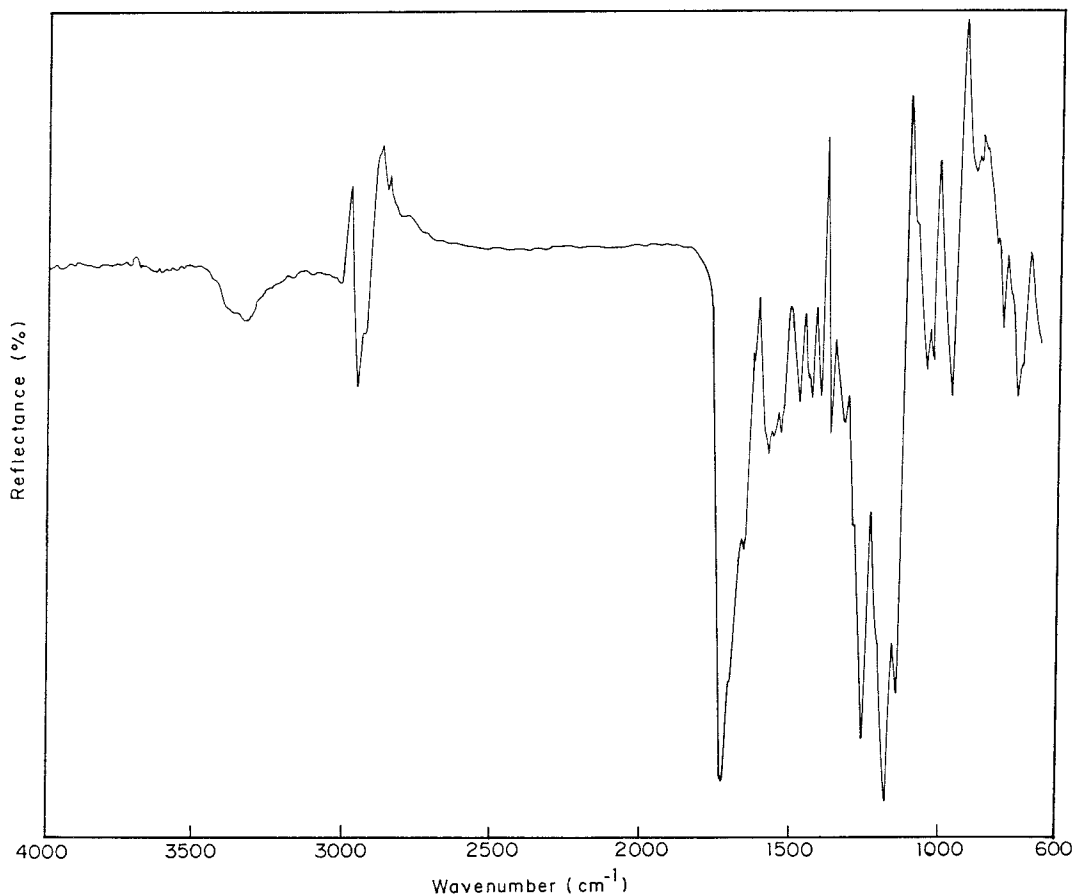


Figure 1 Representative FTIR spectrum of poly(urethane semicarbazide) PBA 11.

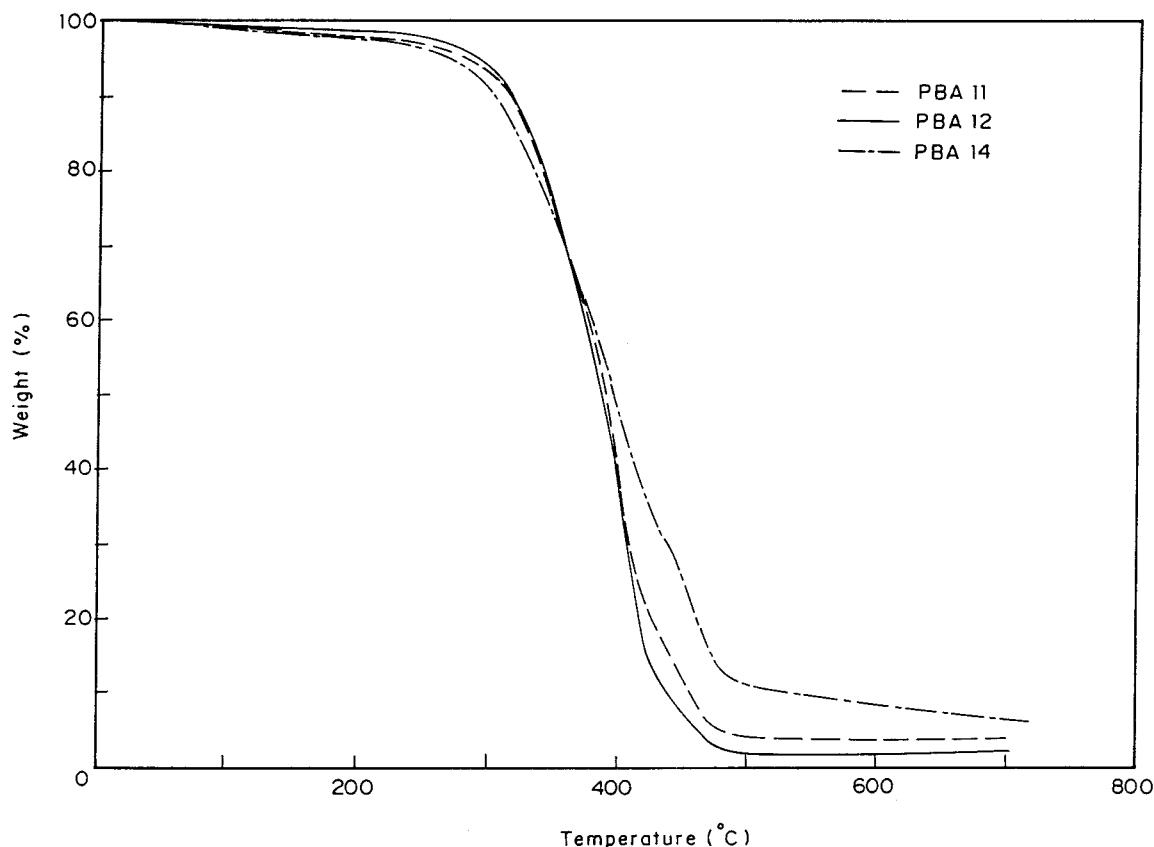


Figure 2 Representative thermogravimetric curves of poly(urethane semicarbazide)s heated at 20°C/min.

characteristic peaks around 3300 and 1750 cm^{-1} corresponding to the $>\text{NH}$ and $>\text{CO}=\text{}$ stretching of the urethane linkage. The peak around 2950 cm^{-1} is due to the stretching of aliphatic $>\text{CH}_2$ groups, and that around 3000 cm^{-1} is due to the aromatic $>\text{CH}$ stretching, confirming the incorporation of the chain extender.

Thermogravimetric Analysis

The thermal stability of the poly(urethane semicarbazide)s was evaluated by the determination of the weight change with temperature, and the initial decomposition temperature was taken as the point of onset. All four compositions exhibited stability up to 300°C, and the weight loss was observed around 300–310°C. The large number of amide linkages in the hard-segment domains may have led to a slight enhancement in the thermal stability in comparison with conventional polyurethanes.¹⁰ Representative thermograms of poly(urethane semicarbazide)s are given in Figure 2.

DSC

DSC traces of poly(urethane semicarbazide)s are shown in Figure 3. Data summarizing the glass-transition temperature (T_g) of the soft segment and the melting temperature of the hard segments ($T_{m,h}$) are given in Table I. The results indicate that all the materials have identical T_g 's (as observed in DMA); in other words, the soft-segment T_g was rather insensitive to changes in the hard-segment content, indicating that the soft-segment domains had a fairly lower degree of phase mixing.¹¹ An increase in the hard-segment content increased the size and peak position temperature of the soft-segment melting endotherm because longer hard segments produced better phase-separated systems that were more readily crystallizable.

Stress-Strain Properties

The stress-strain behavior of samples with various hard-segment contents is shown in Figure 4. It can be observed from Table II that the

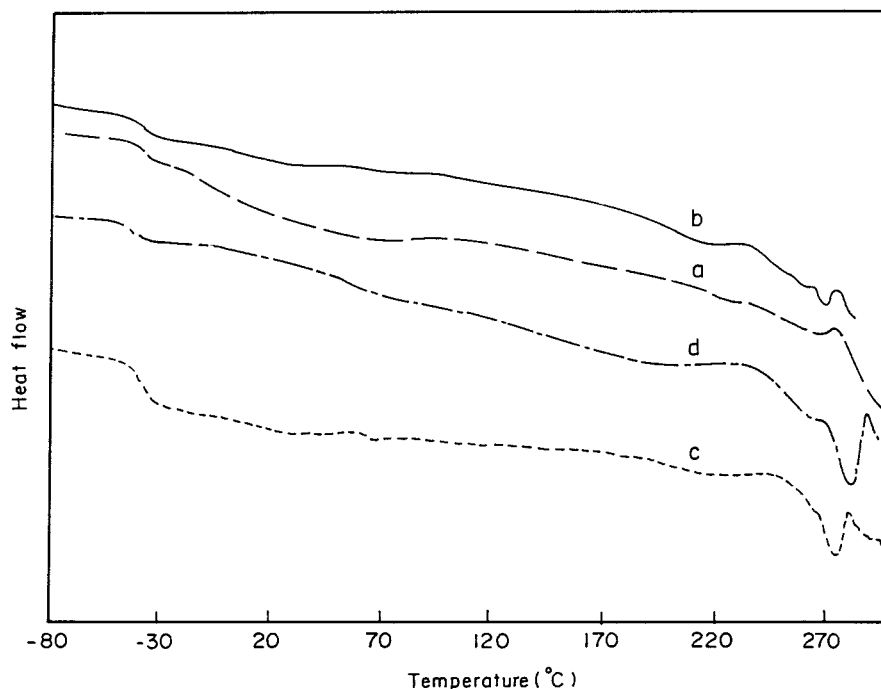


Figure 3 DSC thermograms of (a) PBA 11, (b) PBA 12, (c) PBA 13, and (d) PBA 14.

tensile strength increased and the elongation at break decreased with increasing hard-segment content. The higher elongation for PBA 11 is an indication of a greater extent of phase segregation, and the mechanical behavior can be explained on the basis of an alteration in the overall crystallinity of the samples. During the stretching process, the crystalline phases became oriented parallel to the stretching direction (a phenomenon called strain hardening), leading to increased elongation. As the hard-segment content increased, the amount of soft-segment crystallites decreased, and so there was a decrease in the elongation at break.

DMA

The dynamic mechanical spectrum of the samples with various hard-segment contents is shown by the dependence of $\tan \delta$ and the dynamic modulus (G') on the temperature in Figures 5 and 6, respectively. The spectra in Figure 6 show two distinct peaks, one in the low-temperature region and the other above ambient temperature. The $\tan \delta$ peak of higher intensity (relaxation) accompanied by a sudden drop in G' with increasing temperature was due to T_g of the soft segments. T_g increased from -39.2 to -33.9°C as the hard-segment content increased from 26 to 56%. One can observe from Table II that the $\tan \delta$ value

corresponding to relaxation increased from 0.12 to 0.37 as the hard-segment content decreased from 56 to 26%. Moreover, the peak intensity of relaxation became lower and broader. The transition at higher temperatures can be attributed to the crystalline nature of the soft segment. The crystallites in the soft segments melted, giving rise to transitions at temperatures denoted T_m .¹² The ratio of G' at temperatures below and above T_g ($T_g - 20^\circ\text{C}/T_g + 20^\circ\text{C}$) decreased with an increase in the hard-segment content. The tendency of the material to deform easily at high temperatures and exhibit large deformation resistance at low temperatures decreased with increasing hard-segment content. The high elastic modulus at temperatures below T_g was due to the energy elasticity of the crystal and a glassy-state non-crystal, whereas the low-temperature elastic modulus at temperatures higher than T_g was due to the entropy elasticity based on the micro-Brownian motion of the soft segment in the molecular chain.

CONCLUSION

A series of segmented poly(urethane semicarbazide)s with various hard-segment contents were synthesized with PBA as the soft segment and

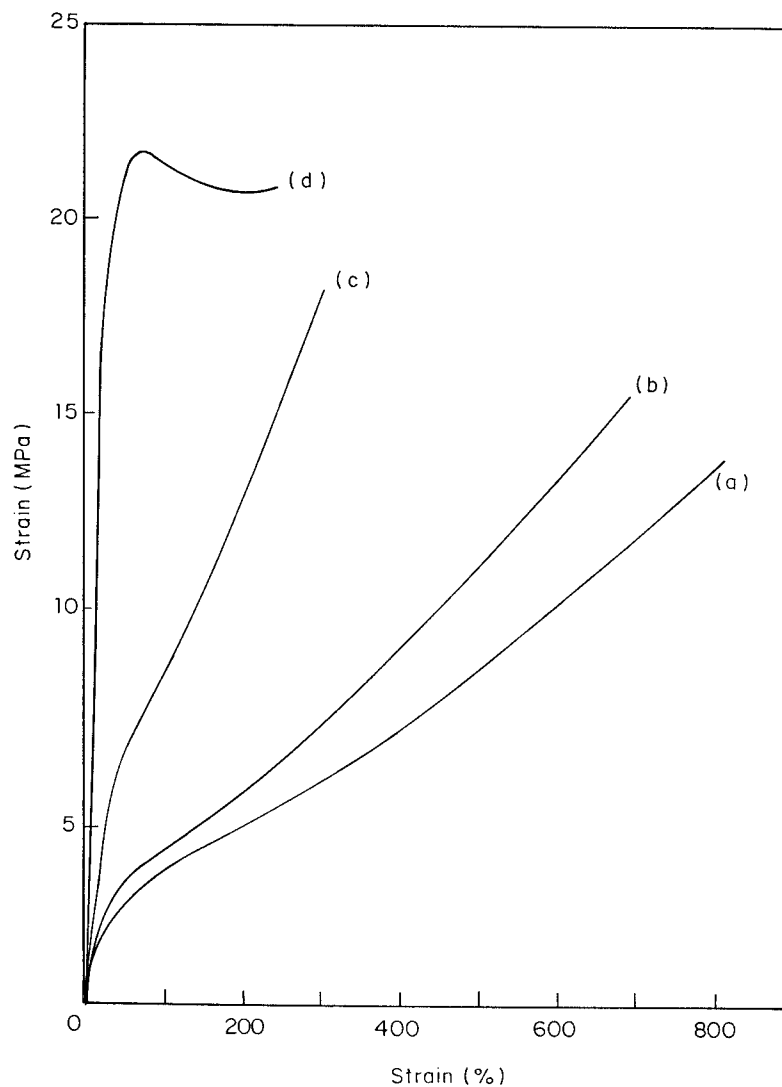


Figure 4 Stress-strain curves of (a) PBA 11, (b) PBA 12, (c) PBA 13, and (d) PBA 14.

HMDI and terephthalic dihydrazide as the hard segment. All the compositions had a fiber-forming tendency, and the structures of the polymers were confirmed by FTIR. The thermal and

mechanical properties revealed enhanced thermal stability and a high degree of hard/soft-segment phase separation for all the compositions.

Table II Stress-Strain and Dynamic Mechanical Data of Poly(urethane semicarbazide)s

Polymer Code	Tensile Strength (MPa)	Elongation (%)	T_g (°C)	$\tan \delta$	Storage Modulus Ratio ^a	T_m (°C)
PBA 11	14.1	816	-39.2	0.37	21.6	14.9
PBA 12	15.6	689	-35.0	0.36	7.8	21.5
PBA 13	18.2	296	-34.6	0.17	6.6	— ^b
PBA 14	20.8	238	-33.9	0.12	3.7	— ^b

^a Storage modulus ratio defined as $E'/T_g - 20^\circ\text{C}/E'/T_g + 20^\circ\text{C}$.

^b Crystallisation peaks could not be set accurately.

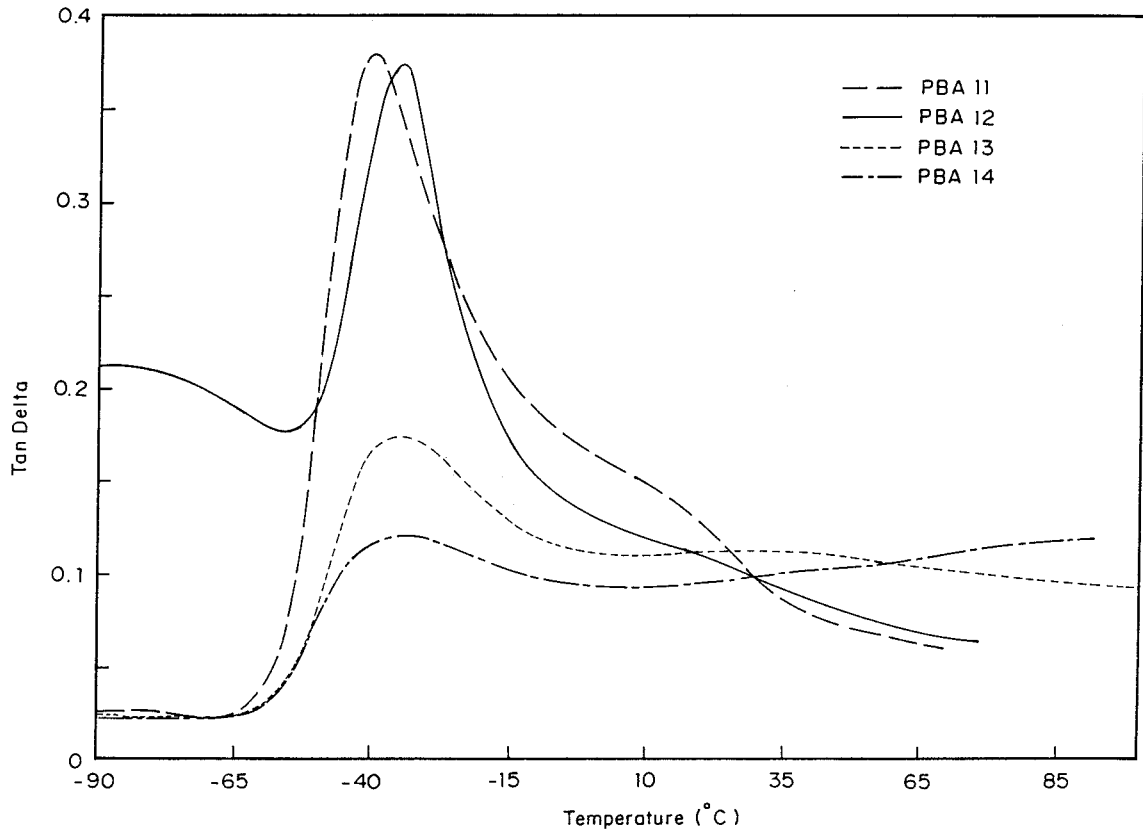


Figure 5 Damping ($\tan \delta$) curves of poly(urethane semicarbazide)s.

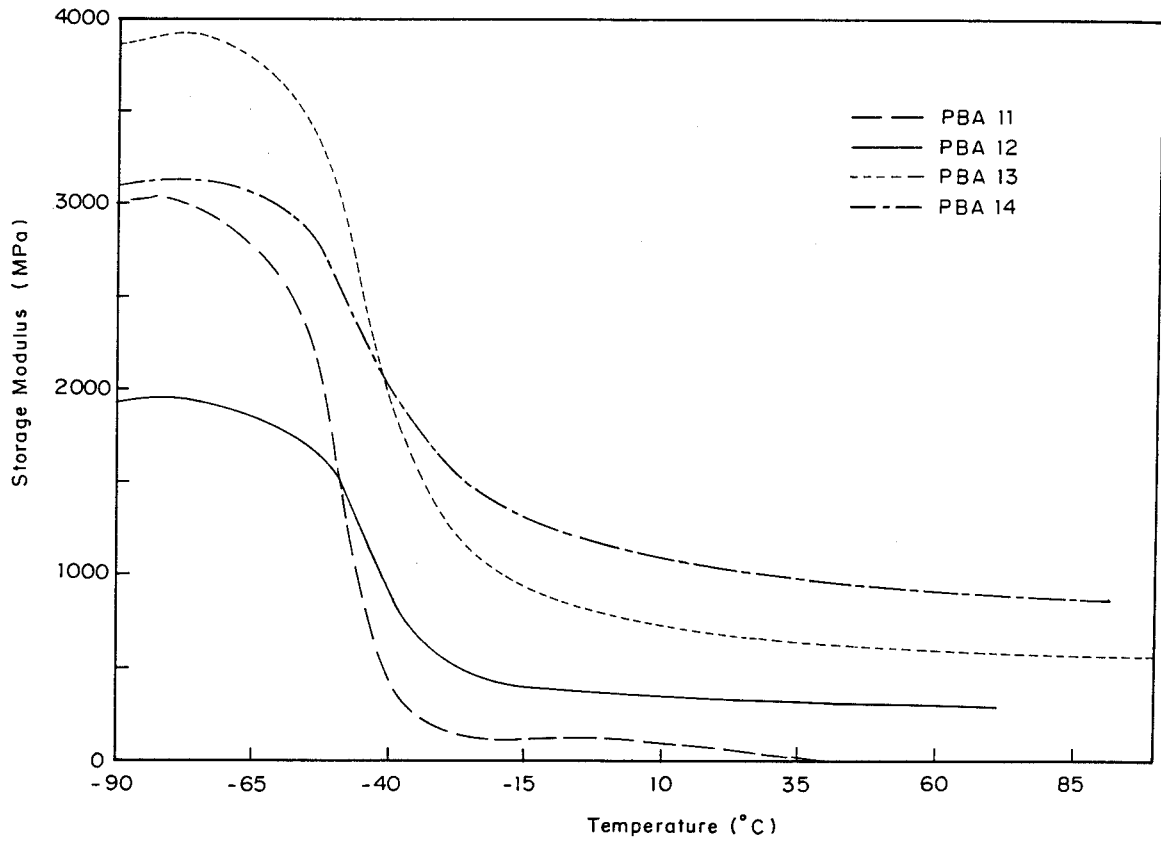


Figure 6 Dependence of the storage modulus on temperature for poly(urethane semicarbazide)s.

A. Palanisamy thanks the Council of Scientific and Industrial Research (India) for a fellowship.

REFERENCES

1. Estes, G. H.; Cooper, S. C.; Tobolsky, A. V. *J Macromol Sci Rev Macromol Chem* 1970, 4, 167.
2. Cooper, S. C.; Tobolsky, A. V. *J Appl Polym Sci* 1966, 10, 1837.
3. Li, Y.; Gao, T.; Chu, B. *Macromolecules* 1992, 25, 1737.
4. Chu, B.; Gao, T.; Li, Y.; Wang, J.; Desper, C. R.; Byrne, C. A. *Macromolecules* 1992, 25, 5724.
5. Li, Y.; Ben, Z.; Zhao, M.; Yang, H.; Chu, B. *Macromolecules* 1993, 26, 612.
6. Campbell, T. W.; Foldi, V. S.; Farago, J. *J Appl Polym Sci* 1959, 2, 155.
7. Sorenson, W. R.; Campbell, T. W. *Preparative Methods of Polymer Chemistry*, 2nd ed.; Wiley Interscience: New York, 1968.
8. Vogel's *Textbook of Practical Organic Chemistry*, 5th ed.; ELBS: Essex, 1996; p 1079.
9. Sorenson, W. R.; Campbell, T. W. *Preparative Methods of Polymer Chemistry*; Wiley Interscience: New York, 1961.
10. Zuo, M.; Takeichi, T. *Polymer* 1999, 40, 5153.
11. Van Bogart, J. W. C.; Gibson, P. E.; Cooper, S. L. *J Polym Sci Polym Phys Ed* 1983, 21, 65.
12. Nielsen, L. E. *Mechanical Properties of Polymers and Composites*; Marcel Dekker: New York, 1974.