

Study of Mechanical Properties of Urethane-Chlorinated Rubber Graft Copolymer System. I

K. ANBAZHAGAN, C. RAMI REDDY, and K. THOMAS JOSEPH,
*Polymer Division, Central Leather Research Institute,
Adyar, Madras 600 020, India*

Synopsis

The isocyanate-terminated urethane prepolymer was prepared from toluene diisocyanate and a mixture of castor oil-polypropylene glycol (PPG) (MW 2000). The chlorinated rubber (CR) graft copolymers (A and B) containing small percentage of hydroxyl groups were mixed with the urethane prepolymer in different proportions (1:1, 2:3, and 1:2), and the films were cast using these systems. Tensile strength and percent elongation were evaluated for A and B series with and without triethanolamine (TEA). Morphological characteristics of the films were also studied by using a scanning electron microscope (SEM). Deviations noticed in tensile strength values at yield as well as at break for A and B series and for the samples cured with additional TEA have been discussed.

INTRODUCTION

Work on polyurethane coatings has been carried out by several workers.¹⁻⁴ The synthesis of prepolymers using various types of diisocyanates and polyols which can be cured subsequently is an important step to achieve the desired properties of the end products. The mechanical properties such as tensile strength, modulus of elasticity, abrasive resistance, etc., determine the nature and strength of the resultant material. The variation in the mechanical properties depends to some extent on the type of polyols used in the formation of polyurethane products.^{5,6}

Castor-oil-based polyurethanes are widely used for coating formulations.⁷⁻¹¹ However, the drying time is too long unless slight modification is effected on the polyurethane structure.¹² In order to impart sufficient abrasive resistance, a new approach was resorted to in the present study. A mixture of castor oil and poly(propylene glycol) (PPG) in the weight ratio of 3:2 was reacted with diisocyanate to form a prepolymer. This was then allowed to react with a chlorinated rubber-acrylate graft copolymer system containing small percentage of hydroxyl groups. The mechanical properties of the films obtained from this product and the morphological change observed when the system was cured in the presence of TEA are reported in this communication.

EXPERIMENTAL

Materials

Castor oil (Swastik Brand-Commercial IP Grade), toluene diisocyanate (Fluka), polypropylene glycol (MW 2000) (Fluka), chlorinated Rubber (CR) (Chlorub-40, 65% chlorine, M/s Rishiroop Private Ltd., Bombay).

Ethyl acrylate (Mitsubishi Chemical, Japan), *n*-butyl methacrylate (Riedel, LR), 2-hydroxyethyl methacrylate (Eastman), and triethanolamine (BDH, LR) were all used as such without further purification.

Toluene (BDH, LR) and xylene (BDH, LR) were used after distillation at constant boiling point. Benzoyl peroxide (BDH, LR) recrystallized from the chloroform-methanol system was used for grafting reactions.

Preparation of Polyurethane Prepolymer

The isocyanate-terminated prepolymer was prepared from castor oil-PPG (MW 2000) and excess of toluene diisocyanate (TDI) in xylene medium at 60°C for about 4 h under nitrogen atmosphere. The reaction mixture was cooled and stored in an air-tight bottle after flushing with dry nitrogen. Castor oil-PPG (MW 2000) mixture (weight ratio 3:2) and TDI were taken in such a proportion so that the NCO/OH ratio is about 2 in the resultant mixture. The percent free NCO was determined by the dibutylamine method.¹³

Preparation of Graft Copolymer

The CR graft copolymer was prepared in toluene medium using ethyl acrylate (EA), *n*-butyl methacrylate (nBMA), and 2-hydroxyethyl methacrylate (HEMA) in the presence of benzoyl peroxide (0.5 g) as initiator. The backbone and the monomers (1:1 weight ratio) were charged in a three-necked flask fitted with a stirrer, condenser, and a nitrogen inlet. The reaction was allowed to proceed at 80°C until conversion to polymer was complete. The completion of the reaction was found out by estimating the solid content of the system.

Two graft copolymers (A and B) were prepared with different amounts of HEMA without changing the weight ratio of the backbone polymer and the grafting monomers.

The prepolymer and the graft copolymers were mixed thoroughly in the weight ratio of 1:1, 2:3, and 1:2, and the films were cast on a mercury pool. Films were also made in the presence of additional curing agent, triethanolamine (TEA).

The systems cured without TEA are named as A1, A2, A3, B1, and B3 whereas those cured in the presence of TEA are named as AT1, AT2, AT3, BT1, and BT3. The resultant films were removed and dried in a vacuum oven for sufficient time to get rid of the traces of solvent. The films were conditioned in a desiccator at a temperature of $25 \pm 2^\circ\text{C}$ and $65 \pm 2\%$ relative humidity, for a period of 4 h to ensure full equilibrium before carrying out the tensile strength measurements.

Measurement of Tensile Properties

Using a die, test specimens of the films were cut out according to the ASTM procedure.¹⁴ Test samples of even thickness were selected by measuring the thickness of the films using a thickness gauge having a sensitivity of the order of 0.0001 in. Films were suitably mounted on a cardboard and conditioned again as described above. Individual test films were removed from the desiccator and immediately tested using an Instron Universal

Testing Machine (Model No. 1112). About five samples for each film were tested. The tensile strength and the percent elongation were calculated by using the following expressions:

$$\begin{aligned} \text{tensile strength} &= \frac{\text{breaking load (kg)}}{\text{cross-sectional area (cm}^2\text{)}} \\ \text{magnification ratio} &= \frac{\text{chart speed (0.5 cm/min)}}{\text{crosshead speed (5 or 50 cm/min)}} \\ \text{percent elongation} &= \frac{\text{increase in length}}{\text{original length}} \times 100 \\ &= \frac{\text{length in the chart/magnification ratio}}{\text{original length}} \times 100 \end{aligned}$$

The films (B1 and BT1) were stretched up to 7% strain level and were allowed to stress-relax as a function of time (Fig. 1).

Scanning Electron Microscopy

The dry samples (B1 and BT1) were mounted on aluminium stubs. They were given a thin coating of gold in Edwards coating unit and scanned in a S-150 Stereoscan Scanning Electron Microscope. The samples which were allowed to stress relax at 7% strain for a minimum period of 24 h were also viewed in the SEM to study the morphological characteristics of the

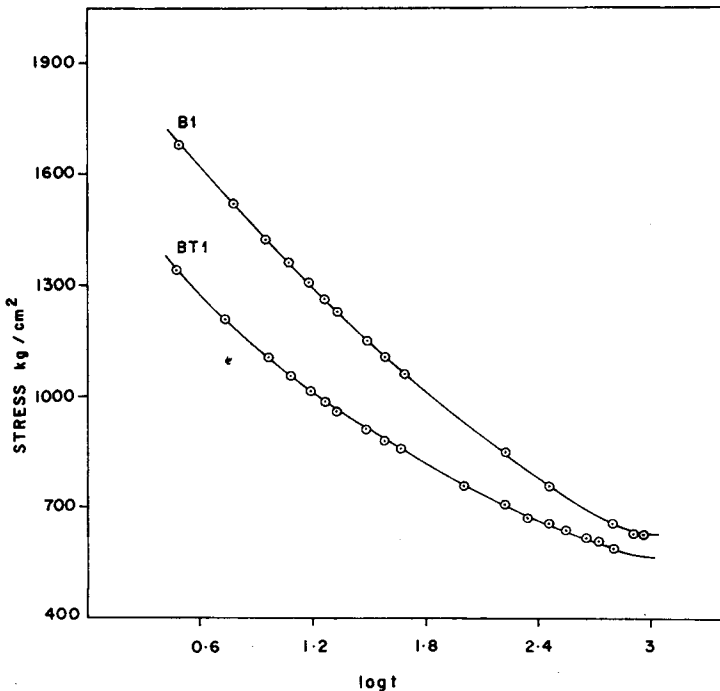


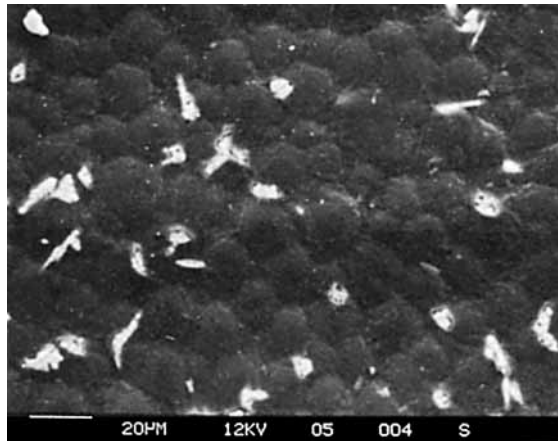
Fig. 1. Stress-relaxation of films B1 and BT1 as a function of time.

stretched films (Figs. 2 and 3). The strain level has been chosen as 7% since beyond this level there is a plastic flow in the films as is observed from the stress-strain behavior shown in Figure 4.

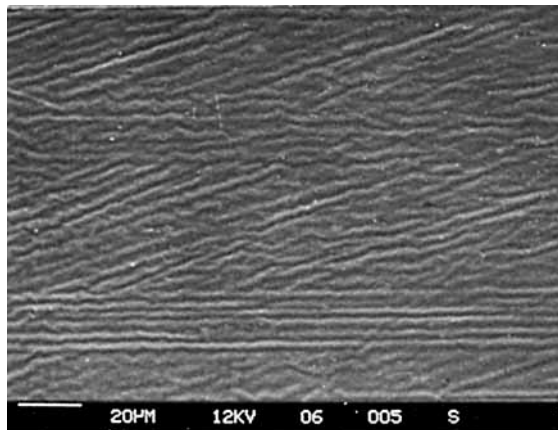
RESULTS AND DISCUSSION

The determination of the mechanical properties like tensile strength and percent elongation at yield as well as at break enables one to assess the relative strength of different film forming materials in general. In the present study, the polyurethane prepolymer based on castor oil was cured with chlorinated rubber-acrylate graft copolymers containing hydroxyl groups.

From the data in Tables I and II, it is observed that the tensile strength values of the films prepared from the constant composition of polyurethane

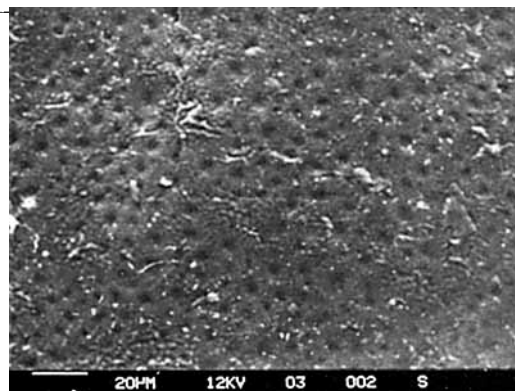


(a)

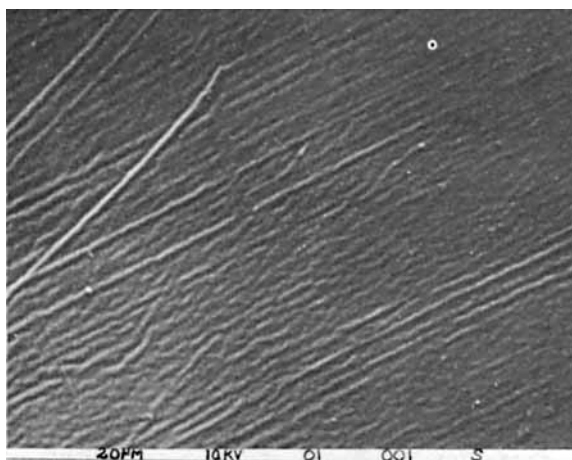


(b)

Fig. 2. Scanning electron micrographs (BT1); (a) Control (regular orientation); (b) sample stretched up to 7% strain. The morphological feature is similar to B1. However, the crimps are more prominent than those in B1.



(a)



(b)

Fig. 3. Scanning electron micrographs (B1); (a) Control (regular orientation); (b) sample stretched up to 7% strain. The morphological feature exhibited in (a) is indicative of the crimp formation.

prepolymer and CR graft copolymer of B series are greater than those prepared from A series.

Further it is found that the tensile strength of the films at yield is increased with increasing amount of CR graft copolymers in a given series (i.e., TS of A1 < A2 < A3 or AT1 < AT2 < AT3 or B1 < B3 or BT1 < BT3). However, the tensile strength values at break are increased with increasing amount of CR graft copolymers for A and B series but decreased for AT and BT series (i.e., TS at break A1 < A2 < A3 or B1 < B3. But AT1 > AT2 > AT3 or BT1 > BT3). Also substantial reduction in tensile strength values of the films containing TEA is found in all compositions at yield and at break (i.e., AT1 < A1 AT2 < A2, BT1 < B1 and so on)

The percent elongation at yield as well as at break is decreased for all the series with increasing amount of CR graft copolymer.

During the experimentation, it is noticed that the films of A series as

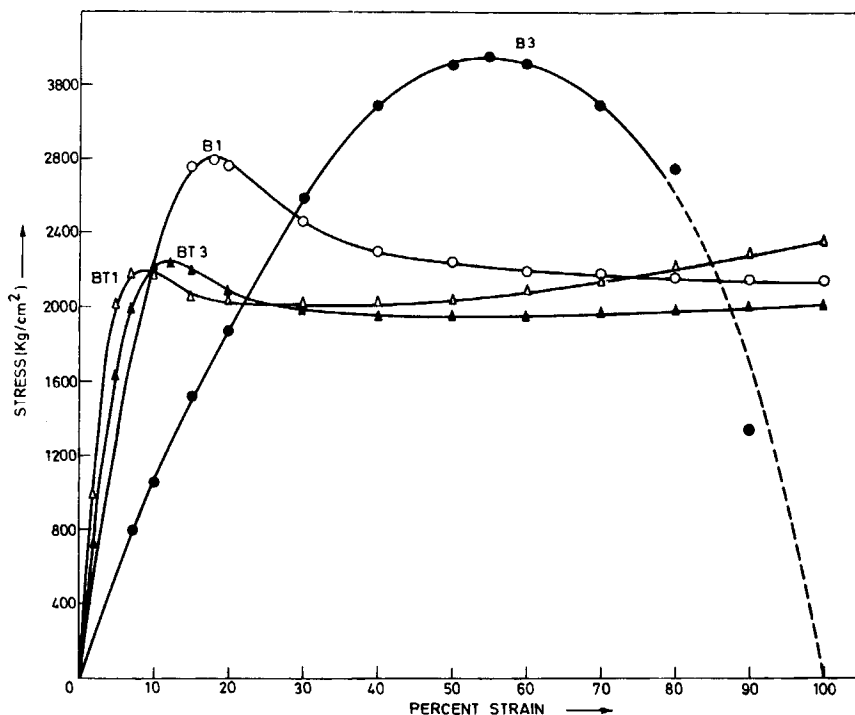


Fig. 4. Stress-strain curves of cured polyurethane films.

well as B series were broken except B3, which was torn off at the corresponding stress.

Films obtained with 1:2 weight ratio of urethane prepolymer and chlorinated rubber graft copolymer gave maximum value of tensile strength at yield as well as at break.

From the plots (Fig. 5) of applied stress (kg/cm^2) vs. percent strain, it is observed that A3 attained maximum value and gradually reduced until break whereas A1 and AT3 attained their respective maximum values and maintained the same values until the break with a slight reduction in the middle. The stress-strain curve of AT1 after attaining maximum gradually increased until 100% strain.

The stress-strain curves (Fig. 4) of B1, BT1, and BT3 are of the same type

TABLE I

Code no.	Urethane prepolymer/ graft copolymer (A) (weight ratio)	Tensile strength (kg/cm^2)		Percent elongation	
		At yield	At break	At yield	At break
A1	1.00	1836.09	1960.35	13.50	111.70
A2	0.67	2463.63	2041.32	11.00	63.38
A3	0.50	3157.99	2254.64	9.50	40.30
AT1	1.00	1234.56	1934.76	13.58	182.66
AT2	0.67	1627.98	1803.77	12.00	151.68
AT3	0.50	1664.27	1739.27	11.00	162.60

TABLE II

Code no.	Urethane prepolymer/ graft copolymer (B) (weight ratio)	Tensile strength (kg/cm ²)		Percent elongation	
		At yield	At break	At yield	At break
B1	1.00	2755.90	2236.94	10.50	106.50
B3	0.50	3340.50	—	9.00	—
BT1	1.00	2164.00	2312.00	13.40	149.20
BT3	0.50	2272.20	1967.40	12.20	100.80

as of A series. But, the stress-strain curve of B3 is a parabolic type exhibiting maximum at 55% strain. At 80% strain the curve has come down to very low value, and the film was suddenly torn off. Similar to AT1, the curve of BT1 also gradually increased after the maximum. BT3, on the other hand, reduced to minimum value at 100% strain. Films containing TEA attained maxima in stress-strain relation below 10% strain whereas the films without TEA reached the maxima after 10% strain.

The amount of HEMA in the graft copolymer B is more than that of A, which is randomly distributed in the entire grafted chain. Therefore, the crosslinking density is more in films of B series than those of A series. Hence, the tensile strength exhibited by the films of B series is high in all proportions correspondingly.

Hydroxy functionality is increased with increasing the amount of CR

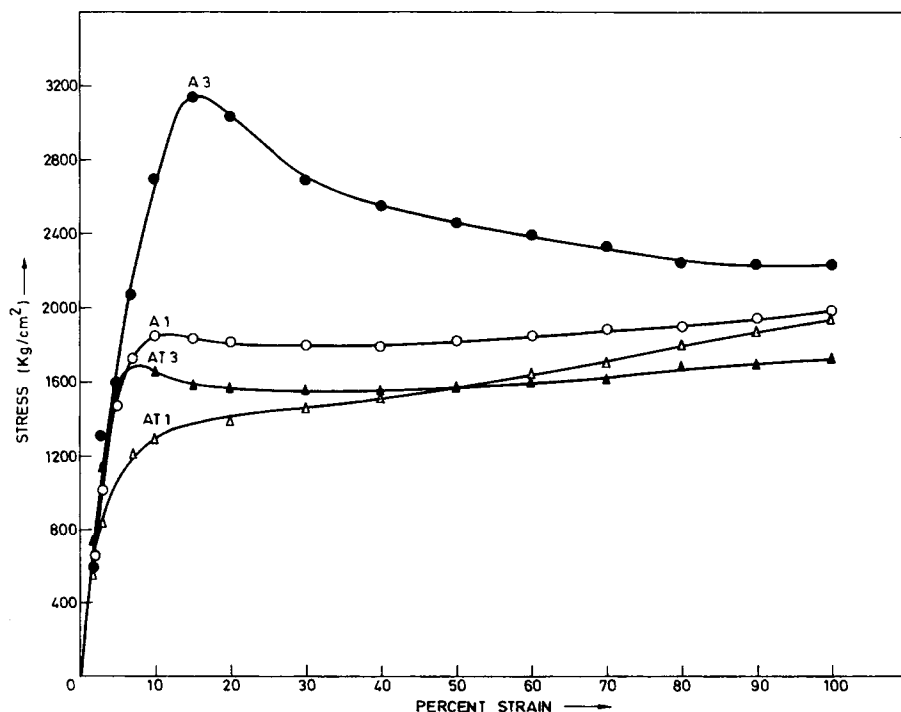


Fig. 5. Stress-strain curves of cured polyurethane films.

graft copolymer in a given set of films, i.e., A1-A3 or B1-B3, etc. The increased hydroxyl content facilitated increase in the crosslinking density. Hence, gradual increase in tensile value and decrease in percent elongation were resulted in a given series.

In addition to hydroxyl groups present in CR graft copolymers, TEA provides a large number of crosslinking sites, and, hence, it is to be expected that a rise in crosslinking density with a consequent rise in tensile strength may result in this case. On the contrary, tensile strength values of the films containing TEA were found to decrease in both A and B series at yield.

In terms of net work imperfections or defects described by Flory,¹⁵ compounds which exhibit decreased tensile strength with increased polymer net work impart a relatively more number of intrachain (wasted loop) crosslinkages and/or terminal dangling flaws per unit volume of the polymer phase than less crosslinked systems. These intrachain crosslinkages and/or terminal dangling flaws act as softening agents or plasticizers leading to decrease in tensile strength.

It is expected that the presence of TEA provides a number of crosslinking sites which resulted in a larger number of intrachain wasted loop crosslinkages and terminal dangling flaws. These factors may be responsible for the fall in tensile strength values at yield.

Bueche^{16,17} and Bueche¹⁸ put forward evidence by computation that, as the degree of crosslinking increases significantly, a number of highly stressed chains result. Consequently, there is a significant reduction in the ability of the network to release local stresses by rearrangement of the special configurations of the individual chains. Therefore, beyond a certain optimum degree of crosslinking, the chains become susceptible to collapse rapidly, leading to the decrease in the tensile strength at break.

It is assumed that the crosslinking density has reached an optimum value by the addition of TEA to 1:1 weight ratio of urethane prepolymer and CR graft copolymer system. This is obvious from the tensile strength values of A1 and AT1, B1 and BT1 at break, which are of the same order. However, beyond this limit of addition of CR graft copolymer, excess crosslinking density probably resulted as a consequence of which the films showed reduced tensile strength at break.

Though there is a reduction in the tensile strength due to high crosslinking density, the observed increase in percent elongation can be explained by SEM. The regular orientation of the film as is evident from the SEM indicates that the film is initially crimped, and these crimps might play a role in the extension at yield. This may be one of the reasons for the anomaly observed in the percentage elongation at break (Tables I and II). However, it is interesting to note that the stress increases at a steady rate up to yield point despite the presence of crimps.

Tensile values of some of the individual constituents, used in the present system which are noted from the literature, are given in Table III. From Table III, it is clear that tensile strength values of pure graft copolymers are low whereas the tensile strength values of cured castor oil based polyurethane systems are moderate. The series worked out in the present study have shown improved tensile properties and are therefore found to

TABLE III

Sample no.	Constituent polymer system	Weight ratio CR:copolymer	Weight ratio nBMA:EA	TS (kg/cm ²)	Reference
1.	CR-g-nBMA-co-EA	1:1	3:1	128	19
2.	CR-nBMA-co-EA blend	53:47	11:7	150	20
3.	CR-nBMA-co-EA blend	47:53	11:7	128	20
4.	CR-nBMA-co-EA blend	53:47	3:2	195	20
5.	CR-nBMA-co-EA blend	47:53	3:2	165	20
6.	CR-nBMA-co-EA blend	40:60	3:2	145	20
7.	CR-nBMA-co-EA blend	33:67	3:2	130	20
Moisture-cured polyurethane based on:					
8.	Anhydrous castor oil	—	—	266	5
9.	Ethylene glycol monoricinoleate	—	—	401	5
10.	Monoglyceride of castor oil	—	—	625	5
11.	Castor oil/diethanolamine	—	—	684	5
12.	Pentaerythritol monoricinoleate	—	—	184	6
13.	Diisopropanolamine diricinoleate	—	—	241.91	6

be much superior than the other systems mentioned in Table III. It may be concluded that these systems are excellent to use as film forming material.

One of the authors (K. A.) is thankful to the Council of Scientific and Industrial Research, New Delhi, India, for the financial assistance in the form of fellowship. The authors are grateful to Dr. N. Ramanathan, Director, CLRI, for his keen interest in this work. The authors express sincere thanks to Dr. R. Sanjeevi, Chemical Lab, Dr. D. L. V. Rao and Mr. V. A. Arumugam of Biophysics Department, CLRI, Madras, for their help.

References

1. K. J. Kedlaya, S. Rajadurai, and D. Ramaswamy, *Leather Sci.*, **18**, 309 (1971).
2. J. H. Saunders and K. C. Frisch, *Polyurethanes—Chemistry and Technology* in *High Polymers*, Wiley-Interscience, New York, 1964, Part II, Vol. 16.
3. W. Speicher, *J. Soc. Leather Trades Chemists*, **45**, 104 (1961).
4. K. Eitel, *Das Leder*, **4**, 234 (1953).
5. R. N. Mukherjea, K. K. Saha, and S. K. Sanyal, *J. Am. Oil Chem. Soc.*, **55**, 653 (1978).
6. C. K. Lyon and V. H. Garret, *J. Am. Oil Chem. Soc.*, **50**(4), 112 (1973).
7. T. C. Patton, A. Ehrlich, and M. K. Smith, *Rubber Age*, **86**, 639 (1960).
8. T. L. Smith and A. B. Magnusson, *Rubber Chem. Technol.*, **35**, 753 (1962).
9. A. J. Sherburne, *Insulation*, (July 1965).
10. N. D. Ghatge and V. B. Phadke, *J. Appl. Polym. Sci.*, **11**, 629 (1967).
11. L. Montesano, *Ind. Eng. Chem., Prod. Res. Dev.*, **3**, 133 (1964).
12. S. Rajadurai, C. Saikumar, R. Vedarajan, K. J. Kedlaya, and M. Santappa, *Leather Sci.*, **21**(5), 171 (1974).
13. D. J. David and H. B. Staley, *Analytical Chemistry of the Polyurethanes*, Wiley-Interscience, New York, 1969, Part III, Vol. 16.
14. Method of tensile testing D-1708, part 27, *Book of ASTM Standards*, American Society for Testing and Materials, Philadelphia, 1965.

15. P. J. Flory, *Chem. Rev.*, **34**, 51 (1944).
16. A. M. Bueche, *J. Polym. Sci.*, **19**, 275 (1956).
17. A. M. Bueche, *J. Polym. Sci.*, **19**, 297 (1956).
18. F. Bueche, *J. Polym. Sci.*, **24**, 189 (1957).
19. K. Kaleem, C. Rami Reddy, S. Rajadurai, and K. T. Joseph, *Leather Sci.*, **29**, 402 (1982).
20. S. Pitchumani, C. Rami Reddy, S. Rajadurai, and K. T. Joseph, *Eur. Polym. J.*, **18**, 949 (1982).

Received September 16, 1982

Accepted May 18, 1984