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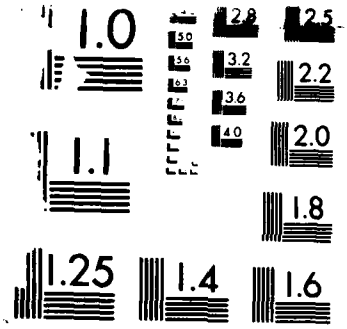
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
Interpenetrating polymer networks (IPNs) elastomers and foams composed of polyurethanes and epoxies were prepared by the simultaneous technique. Fillers and plasticizers were incorporated by random batch mixing. The PU/epoxy ratio was varied. Enhanced energy absorbing abilities were demonstrated by the dynamic mechanical spectroscopy results (broad and high tan behavior as a function of temperature). This was reflected in the mechanical and acoustical energy absorption of the foams. The effects of fillers and plasticizers were mixed.

20. ABSTRACT CONTINUED

Three component IPNs prepared from polyurethane, epoxy, and unsaturated polyester resulted in even broader tan δ behavior.

FINAL TECHNICAL REPORT

ENERGY ABSORPTION OF POLYURETHANE BASED POLYMER ALLOYS

GRANT NUMBER: DAAG25-85-K-0129

Polymer Institute
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September 27, 1986

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I. INTRODUCTION AND OBJECTIVE

The objective of this study is to develop interpenetrating polymer network (IPNs) elastomers and foams which exhibit good sound attenuation characteristics over a broad frequency and temperature range. Interpenetrating polymer networks (IPNs) are unique blends or alloys of cross-linked polymers in which only minimal amounts of grafting occurs between the components. If "semi-miscible" behavior occurs, a broad glass transition behavior results. This is due to the fact that tan δ (the dynamic mechanical energy dissipation factor) is at maximum during the broad glass transition and stays high over a broad temperature (and therefore frequency) range. In the present study, a series of pure polyurethane and IPN elastomers have been prepared from polyurethane and epoxies also containing various amounts of fillers and plasticizers. The formulations with the highest and broadest tan δ vs T behavior (as determined by dynamic mechanical studies on a Rheovibron) were used as the basis from which to prepare IPN foams. The sound attenuation properties of these foams were measured using an Impedance tube technique. In additon, other mechanical absorption measurements in the foams were made.

IPN elastomers using three components such as polyurethane/epoxy/unsaturated polyester resin, were also made and the results are encouraging, they indicate even higher and broader tan δ behavior.

II. PROBLEM STUDIED

A. The effect of various fillers with platelet geometry such as graphite and mica, various plasticizers and combination of plasticizers and fillers.

B. Effect of higher levels of chain extender Isonol-100 on pure polyurethane and PU/E IPN elastomers.

C. To analyze the effect of plasticizer. On the behavior, the solubility parameter of various components, plasticizers and full polymers have been calculated from their chemical structure.

D. To study the effect of post curing, samples of IPN elastomers were post-cured for different periods of time(e.g., 0, 2, 4, 8, and 16 hours). In addition, they were extracted in THF. The dynamic mechanical properties were measured on a Rheovibron.

E. Effect of varying PU/E ratio.

F. IPN elastomers using three components such as polyurethane/epoxy/unsaturated polyester resin were also made in varying preportions.

G. IPN foams with varying PU/E ratio along with fillers & plasticizers were made and tested.

III. SUMMARY OF THE RESULT

A. Pure Polyurethane System

The pure polyurethane system consists of polyols (Niax 31-28), chain extender (Isonol-100), urethane catalyst (T-12) and isocyanate (143L). Various plasticizers were then incorporated in different amounts and their dynamic mechanical peoperites (tan δ) was studied using the Rheovibron.

Thermo-mechanical analysis was also conducted on the samples using a Perkin-Elmer TMS-2 Thermo-mechanical Analyzer.

Plasticizers such as tricresyl phosphate (TCP) santicizer 160 and benzoflex-988 resulted in high tan δ values and a broadening of the transition range. Further studies show that the above mentioned plasticizers also have high solubility parameters. It has been noted that as the solubility parameter of the plasticizer approaches those of the polyurethane group, the height

of tan δ and the temperature range broadens. Plasticizers such as santicizer 141 and Stan Flun LV, with low solubility parameters, resulted in the least enhancement in the height and broadness of the tan δ peak.

Higher amounts of chain extender were also utilized in elastomers and it was noted that the higher % of chain extender increased the temperature range but led to a decrease in the tan δ height. The Tg was also correspondingly higher.

B. Interpenetrating Polymer Networks (IPNs)

From the study of the dynamic mechanical properties of various IPN elastomers it was found that fillers such as graphite and mica do not help much in increasing tan δ height or breadth, with plasticizers such as Benzoflex 9-88, santicizer-160 and santicizer-148 increased tan δ height was obtained but it was accompained by a narrower temperature range. With StanFlux LV, the lower level of plasticizer resulted in very good tan height and temperature range. Where as santicizer-141 and TCP do not help in either way.

Study of combined lower level of filler & plasticizer resulted in reduction in tan δ height with little broadning of the temperature range.

Increased amount of chain extender yields a broad temperature range with reduction in tanδ height.

Solubility parameter analysis of the various components did not show any definite relationship with the IPN elastomer behavior.

For a given IPN elastomer, lower amounts of post-curing resulted in higher tan δ values & broad temperature range. THF extraction has shown that the epoxy has mostly gelled within the mold during partial cure. PU/E ratio of 40/60 & 50/50 yielded higher tan δ values and broader temperature range with plasticizers Benzoflex 9-88 and Santicizer-160 as compared to PU/E ratio 60/40.

C. IPN Foams

Two-component IPN foams consisting of polyurethane and epoxy were prepared by the one-shot method and the effects of PU/Epoxy Ratio on the sound and mechanical energy attenuation characteristics were determined with varying level of different fillers and plasticizers. Addition of epoxy improved the sound absorption of polyurethane foams.

However, the most dramatic improvement of adding epoxy on the energy absorbing abilities of IPN foams occured in the mechanical energy absorption measurements, i.e., rebound and hysteresis. Introducing graphite at different levels of epoxy did not always result in improving the sound absorption, however, PU/Epoxy ratio of 80/20 showed improvement as the level of graphite increased. The tensile strength properites were reduced by increasing the graphite level. The effects of plasticizers was studied on IPN foams. Each plasticizer was used at 20% by weight. Santicizer 160 and Stan Flux LV improved the sound absorption at both the lower and higher frequencies, however, Santicizer 148 and 160 had a larger impact at the higher frequencies. The frequency range was 0-8000 Hz and a cutoff at 500 Hz was chosen to distinguish lower frequency range from higher frequency range. The hysteresis and tensile strength properties dropped in the presence of plasticizers also lowered the rebound values. The effects of density and cell structure were also studied. Increasing density resulted in increasing sound absorption, especially at the lower frequency range. Coarser cell structure, however, resulted in enhanced sound absorption, especially at the higher frequency range.

IV. FEASIBILITY STUDY OF THREE COMPONENT IPN ELASTOMERS

The following results are new and not yet reported, full descriptions of the experiments and results are given below.

A. Materials

The materials used in this study are summerized in Table 1. The polyols, chain extender, and epoxy resin were degassed under vacuum at 70°C for 24 hours. The other chemicals including unsaturated polyester resin were used as received from manufacturers.

B. Preparation of Samples

1. IPN Elastomers

The IPN elastomers based on polyurethane epoxy and unsaturated polyester resin were prepared by the simultaneous polymerization technique. One component contained the isocyanate (Isonate 143L) epoxy resin (DER 330) and unsaturated polyester resin. The other component contained polyols (Niax 31-28), chain extender (Isonol 100), urethane catalyst (T-12), epoxy catalyst (BF_3-etherate) and unsaturated polyester resin catalyst (TBPB).

The two components were mixed together for one minute at room temperature using a high speed mechanical stirrer. The mixture was then poured into a pre-heated mold and pressed on a laboratory platen press at 100°C. The samples were then removed from the press (after curing for 30 min.) and then post cured in an oven at 100°C for 16 hours. Samples were conditioned at 25°C and 50% relative humidity for at least three days prior to testing.

C. Testing

1. Dynamic Mechanical Spectroscopy

All dynamic mechanical measurements were conducted on a Rheovibron dynamic viscoelastometer, DDV II (Toyo Manufacturing Co.) at a scanning rate of 1 to 2°C per minute in the glass transition region or every 3 to 5°C per minute in the non-transition region. The specimens were in the form of rectangular films with dimensions of 2 cm in length, 0.1 cm in width, and 0.05 cm in thickness. The specimens were inserted into the chamber and cooled to

-50°C where the measurements began. All tests were carried out at a frequency of 110 Hz.

V. RESULTS AND DISCUSSION

Dynamic mechanical testing of samples (formulation # 4, 5) on the Rheovibron has shown a great potential for three component IPNs for the sound absorption application as shown in figure (1 and 2) it is quite clear that height of the tan δ and temperature range increases with addition of even 10% of unsaturated polyester resin as compared to 60/40 PU/E elastomer. Another significant development can be seen from figure 2 that along with increase in tan δ height, the tan δ vs temperature curve stays high over a very broad temperature range (i.e. after the transition is apparently complete, tan δ still remains fairly high which is of enormous importance).

Table I

Materials

MATERIALS	CHEMICAL COMPOSITION	Eq.Wt.	SUPPLIER
Isonate 143L	Carbodiimide modified diphenylmethane diisocynate	143	Dow Chem. Co.
Niax 31-28	grafted copolymer of poly (oxypropylene) (oxyethylene) adduct of glycerol	2004.5	Union Carbide
Isonol-100	N, N^1-Bis (2-Hydroxypropyl) aniline	104.5	Dow Chem. Co.
Der 330	Bisphenol A-Epichlorohydrin epoxy resin	177-178	Dow Chem. Co.
T-12	Dibutyltin dilaurate	-	Dow Chem. Co.
BF_3 $(C_2H_5)_2$	Boron trifluoride ethyl ether	-	Eastman Chem.
Unsaturated polyester resin	-	-	Budd Chem. Co.
TBPB	tert.butyl per benzoate	-	Budd Chem. Co.

Table II

Formulations of Polyurethane/Epoxy/Unsaturated Polyester Resin IPN Elastomers

Sample No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14
POLYURETHANE														
Isonate 143L, g	4.54	4.54	4.54	3.89	3.89	3.89	3.24	3.24	3.24	3.24	3.24	2.60	2.60	2.60
Niax 31-28, g	43.57	43.57	43.57	37.35	37.35	37.35	31.12	31.12	31.12	31.12	31.12	24.90	24.90	24.90
Isonol-100, g	0.89	0.89	0.89	0.76	0.76	0.76	0.63	0.63	0.63	0.63	0.63	0.50	0.50	0.50
T-12, g	0.09	0.09	0.09	0.08	0.08	0.08	0.065	0.065	0.065	0.065	0.065	0.052	0.052	0.052
EPOXY														
DER 330, g	14.00	10.50	7.00	21.00	14.00	7.00	28.00	21.00	17.50	14.00	7.00	21.00	14.00	7.00
BF_3 Etherate, g	0.30	0.30	0.15	0.30	0.30	0.15	0.60	0.45	0.40	0.30	0.15	0.45	0.30	0.15
UNSATURATED POLYESTER RESIN														
Polyester resin	7.00	10.50	14.00	7.00	14.00	21.00	7.00	14.00	17.50	21.00	28.00	21.00	28.00	35.00
TBPB	0.022	0.044	0.044	0.022	0.044	0.066	0.022	0.044	0.055	0.066	0.088	0.066	0.088	0.110
P$_u$/E/UPe Ratio	70/20/10	70/15/15	70/10/20	60/30/10	60/20/20	60/10/30	50/40/10	50/30/20	50/25/25	50/20/30	50/10/40	50/30/20	40/20/40	40/10/50

Figure 1: Dynamic Mechanical Property of 60/30/10 PU/E/UPE IPN Elastomer with 2% Isonol-100 Post-cured 16hrs.

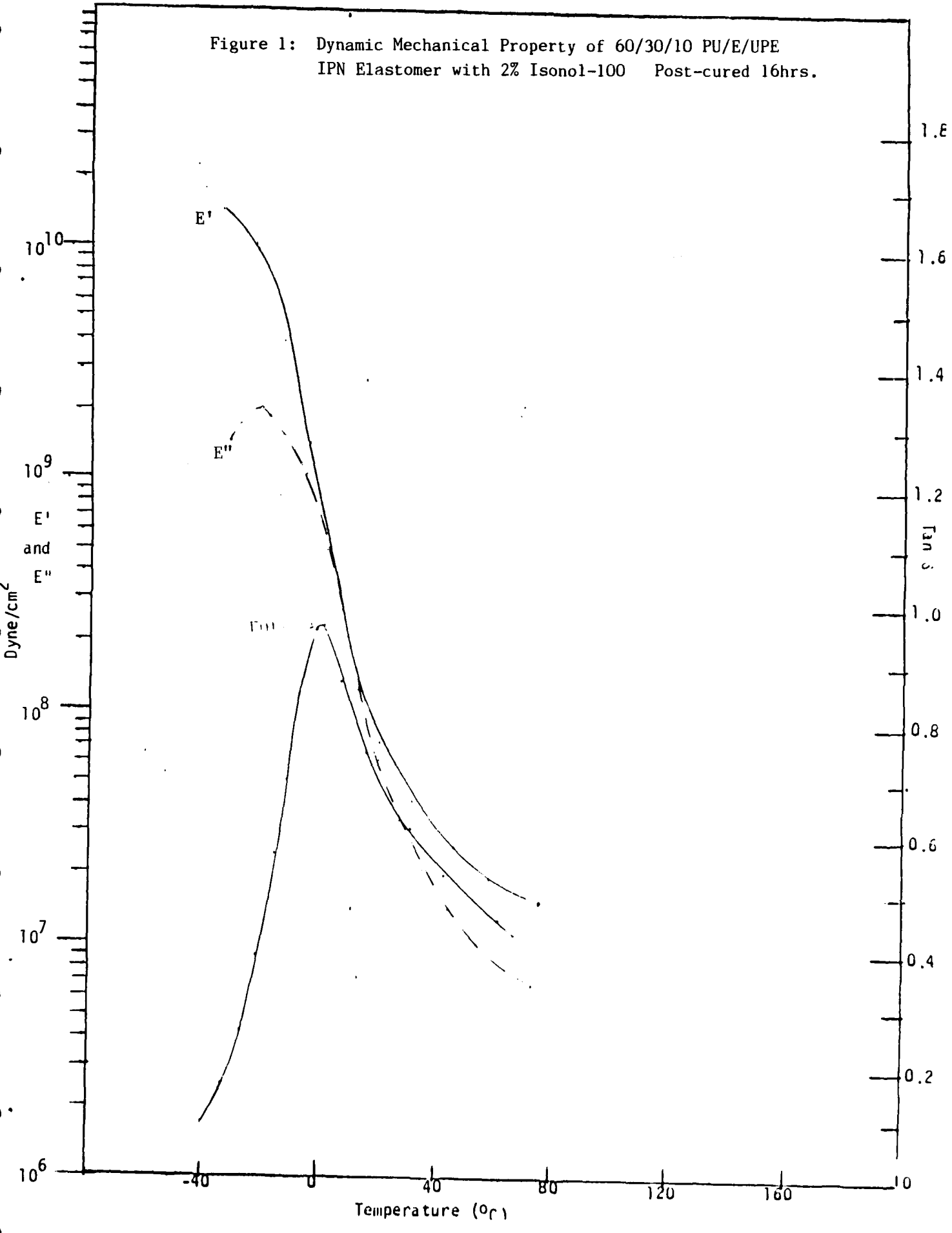
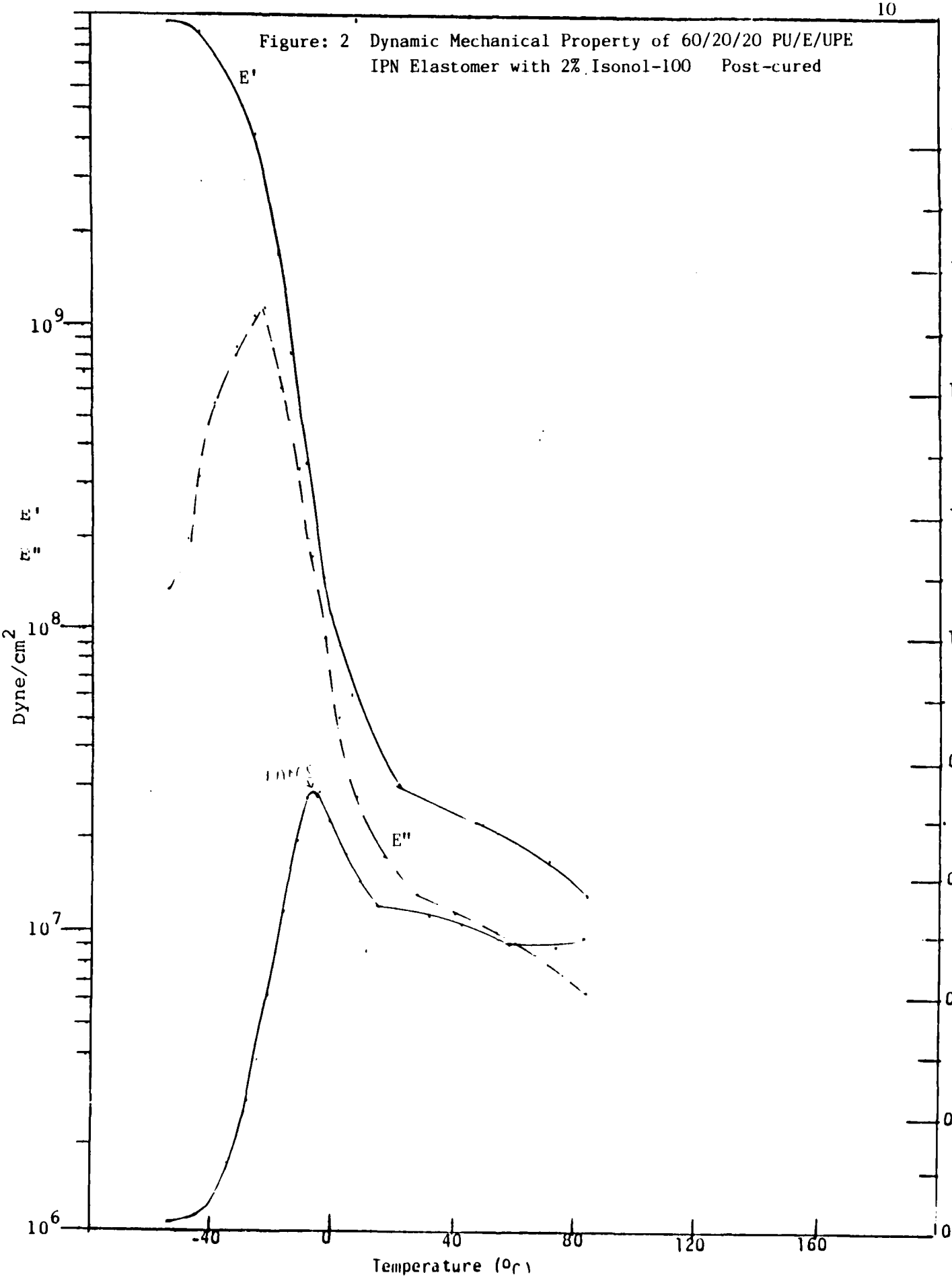


Figure: 2 Dynamic Mechanical Property of 60/20/20 PU/E/UPE IPN Elastomer with 2% Isonol-100 Post-cured



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1. D. Klempner, C.L. Wang, M. Ashtiani, K.C. Frisch, J. Applied Polym. Sci. Vol. 32, 4197-4208 (1986)

2. Interim Technical Report, January 31, 1986.

3. Interim Technical Report, September, 1986.

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