THE PLASTICIZATION OF 4-METHYL-PENTENE-1 (TPX-RT-D30) POLYMER WITH PETROLEUM JELLY

BY

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THE PLASTICIZATION OF 4-METHYL-PENTENE-1 (TPX-RT-D30) POLYMER WITH PETROLEUM JELLY

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NEWARK COLLEGE OF ENGINEERING

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APPROVED:

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TABLE OF CONTENTS

LIST OF TABLES

TABLE

LIST OF FIGURES

ABSTRACT

The properties of TPX-RT-D30 (4-methyl-pentene-1 polymer) have been changed by blending petroleum jelly with the polymer. The polymer was blended in a Brabender apparatus with up to 40% by weight petroleum jelly (P.J.) at 270°C, pressed and quenched in water. Samples were die cut for the various tests. The polymer tensile properties (ASTM-638-64T) showed both a break and yield value in all ratios as compared to only a break value for the TPX-RT polymer. Breaking strength ranged from 4000 psi for pure TPX-RT down to 1000 psi at 40% P.J., with a leveling point of 2000 psi at 15% P.J. Yield strength formed a more uniform decrease to a low value of 1000 psi at 40% P.J. The samples had a "necking down" effect at 10% P.J. and elongation ranged from 19% for TPX-RT-D30 to 325% at 30% P.J. Modulus decreased from 1.8×10^5 (literature value 2.1×10^5) to 2.3×10^4 at 40% P.J. Brittle point values varied from above room temperature to 5°C at 40% P.J. The Vicat softening point (ASTM 1525 Procedure A) ranged from 181°C (TPX-RT-D30) to 87°C at 40% P.J. with a break in the curve at 154°C for 15% P.J. Differential thermal analysis (Stone) showed a melting point depression from 235°C to 218°C at 40% P.J. The electrical properties remained excellent. The material was clear up to 30% and opaque at higher ratios.

The plasticization of TPX-RT-D30 by the petroleum jelly apparently allows the high molecular weight polymer to crystallize and must influence the polymer crystalline size and perfection. Lamellar thickness may also be changed. The petroleum jelly lowers the intermolecular forces in the polymer and enables the molecules to rearrange under stress. The ability of the crystalline material within the polymer to rearrange is demonstrated in the blends by the occurrence of a yield point with its subsequent increase in elongation.

INTRODUCTION

4-Methyl-Pentene-1

The chain structure of the 4-methyl-pentene-1 polymer in the solid state is given in the literature as a helix with seven units per two turns.[1] The melting point as reported by Natta et al.[2] is 205°C. Various other melting points have been recorded. B. G. Ranby[3] gives a melting point of 250°C for samples with 70% crystallinity and Reding[4,5] has a melting point of 238°C for 100% crystalline material. The melting point of 238°C appears to be the accepted value in more recent literature on the material. The polymer density was measured at 0.831 g/cc. The polymer has a unique density behavior since the density of the amorphous phase exceeds that of the crystalline phase at room temperature.[6] The curves exhibit a crossover point at 60°C and at this point all of the 4-methyl-pentene-1 polymer samples of varying crystallinity should have the same volume. Thus, the density calculated for the crystalline phase by J. H. Griffith and Ranby[6] at 20°C is 0.828 g/cc while the density derived by Frank et al.[1] from unit cell dimensions is 0.813 g/cc. The heat distortion temperature is listed as 58°C with the polymer melting point at 240°C.[7] The heat distortion temperature of the 4-methyl-pentene-1 polymer is low in relation to the melting point (m.p. 238°C).

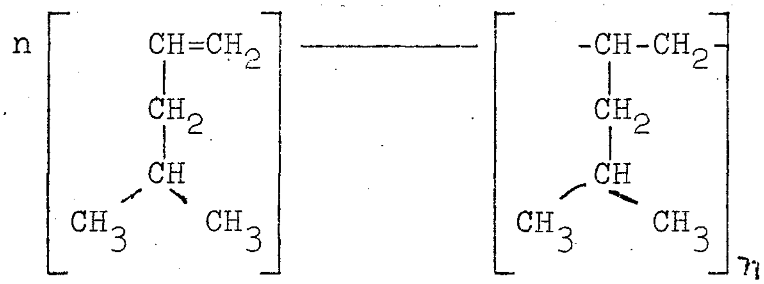
Polypropylene and nylon have distortion temperatures of 110° (m.p. 170°C) and 185°C (m.p. 260°C), respectively. At 50-60°C the polymer possesses only 20% of its tensile strength at break.[7] A review of the literature shows that many researchers who have worked with 4-methyl-pentene-1 polymer have discovered similar ambiguities.

Petroleum Jelly

Petroleum jelly (petrolatum) is described in the literature "as a colloidal system or gel compound of high molecular weight hydrocarbon oils, dispersed in microcrystalline or amorphous waxes."[8] The composition of the material contains both liquid and solid hydrocarbons ranging from 16 to 60 carbon atoms. Approximately 50% of the constituents are isomeric paraffins with naphthenes making up the remainder. The density of the material is 0.868 g/cc at 15.6°C with a melting point range on the differential scanning calorimeter of -5°C to +50°C.

TPX-RT Polymer

TPX-RT is described in the literature as "a new family of stereo-regular polyolefins based on 4-methyl-pentene-1."[9] The TPX-RT-D30 (I.C.I.) is the transparent grade in pellet form. The polymer is described[10,11,12] as isotactic with a repeating structure of



with a crystallinity of 65% for oriented samples and 40% for normal fabricated samples. The TPX-RT-D30 material has interesting physical, electrical, and thermal properties (see Table I). Of special interest is its low density, 0.83 g/cc, which is the lowest of all known polyolefins available. The polymer's transparency is comparable to that of polystyrene and poly(methylmethacrylate). The high melting point of 240°C is much higher than polyethylene or polypropylene. The polymer has excellent electrical properties with a high insulation resistance and low dielectric constant. The mechanical strength of TPX-RT-D30 is 4000 psi (room temperature).

The polymer is lacking in several areas. It is not recommended for continuous outdoor exposure since it is subject to oxidation and degradation by U.V. and other radiation environments. It has a high brittleness temperature (40°C), low elongation (15%) and high modulus which prevent its use in wire and cable jacketing, etc. The heat distortion temperature of 45-50°C at 264 psi is low. The high coefficient of thermal expansion and high mold shrinkage are undesirable.

In order to improve one or several of these deficiencies, work was initiated to modify the material by blending. The original investigation of TPX-RT-D30 began by blending polypropylene, Profax 6323 (M.I. 14.2), Profax 6723 (M.I. 0.8), and polybutene-1. The blends were unsatisfactory as first examined. Finally, TPX-RT-D30 was blended with petroleum jelly and these blends showed sufficient promise to warrant further investigation. Blends of 5, 10, 15, 20, 25, 30, 40% by weight petroleum jelly were prepared using a Brabender. The subsequent blends were characterized to determine any property changes. The purpose of this paper is to report the change in physical properties produced by blending petroleum jelly with TPX-RT-D30 polymer.

TABLE I

Typical Values of TPX-RT-D30 Resin

Properties	ASTM Test Method	Typical Values
Specific gravity	D1505-63T	0.83
Transparency (grade RT), %	D1746-62T	90
Tensile strength at yield, psi	D638-60T	4,000
Elongation at break, %	--	15
Tensile modulus at ambient temp., psi	D638-60T	210,000
Dielectric constant over frequency range 10^2-10^6 c,p.s., 20°C	D150-64T	2.12
Dielectric strength, 1/8-in. molded sheets, 2-in.-dia. electrodes in oil, v./mil	D149-61	700
Crystalline melting point, °C	D2117-64	240
Heat distortion temp., 66 psi, °C	D648-56	116°C
Melt flow index (5 kg. at 260°C), g/10 min.	D1238-62T	13-20
Mold shrinkage, mils/in.	D955-51	15-20
Coefficient of linear expansion, in/in °C×10^5	D696-44	11.7
Specific heat, cal/°Cg	C351-61	0.52
Flammability, in/min	D635-63	1.0
Izod impact strength, notched, ft-lb/in	D256-56T	0.8
Surface hardness, Rockwell	D785-62	L67-74
Vicat softening point, full °C	D1525-58T	179
Water absorption, %	D570-63	0.01

PLASTICIZATION

Plasticization is a mechanism by which pliability and distensibility are introduced into a plastic material.[12] At present, there are two groups of theories, each applying very well to a specific type of material. The first group includes the plasticizer lubrication and the thermodynamic approach. In this group the plasticizer is considered to act as a lubricant to facilitate the ability of the macromolecules to move over each other by increasing free volume and reducing the internal resistance of the polymer.[13] Thus, the internal forces acting between the macromolecular chains must act through a greater distance with a resulting decrease in interchain bonding forces and a subsequent decrease in physical properties. Another approach to explain the loss of strength is given by the "gel" theory. The "gel" theory describes "the rigidity of the unplasticized resinous mass caused by an internal three-dimensional honeycomb structure or gel formed by loose attachments between the resin macromolecules which occur at intervals along the molecular chains."[14] The "gel" theories take into consideration the formation of complex chemical formations or plasticizer dipolar action as discussed below in the mechanistic theory by Doolittle.

The selection of a plasticizer for a specific material leads many authors to believe that both of these mechanisms are probably in operation to a greater or lesser degree, depending upon the specific material combinations. Most would agree that the intermolecular forces between polymer molecules are reduced by the introduction of a plasticizer.

Thermodynamics offers two criteria for solvent effectiveness: Hildebrand solubility parameter γ and the Flory interaction parameter χ. Hildebrand describes the "internal pressure" of a polymer which leads to the cohesive energy density or solubility parameter.

$$\gamma = \left(\frac{\Delta E}{V}\right)^{1/2}$$

ΔE = energy of vaporization

V = molecular volume

$\frac{\Delta E}{V}$ = cohesive energy density

γ = solubility parameter

The interaction parameter (χ) of Flory is expressed in the general formula

$$\Delta F = RT\ (n_1 \ln \varphi_1 + n_2 \ln \varphi_2) + \chi n_1 \varphi_2$$

$$\chi = \beta + \frac{\omega}{RT}$$

ΔF = Free energy of mixing

R = gas constant

T = temperature

n = mole fraction

φ = volume fraction

χ = interaction parameter

β = entropy correction factor

ω = heat of mixing coefficient

The mechanistic theory (gel theory) proposed by Doolittle[15,17] states that cohesive forces (active sites) exist on the polymer and the solvent molecules which attract the molecules to each other. The solvent molecules mask these active centers and render them inoperative (termed solvation). The unmasking of these active sites by the solvent molecules is termed desolvation. The cohesive forces uniting the polymer molecules with one another is called aggregation. The solvation of the polymer causes disgregation. The two processes of solvation-desolvation and aggregation-disgregation are in a dynamic equilibrium and in competition with each other. If the strength of the cohesive forces uniting the macromolecules of the polymer and the solvent is greater than the polymer-polymer bonds, then the solvent can be considered a plasticizer. Thus, the solvent molecules and polymer molecules are forming continuous fleeting unions which depend upon temperature, concentration molecular weight, etc. Doolittle uses the dilution-ratio technique in his experiments.

$$n_{DR} = \frac{1/V}{DR+1}$$

n_{DR} = threshold conc. of solvent in moles/liter

V = molar volume of solvent in moles/liter

$DR = \frac{\text{Volume of diluent at end point}}{\text{Volume of solvent at end point}}$

By plotting the ln n_{DR} versus molecular weight for various molecular weights of a polymer for a homologous series of solvents in various solvents, curves can be constructed to give phase separation of the solvent-polymer system.

Glass Transition Temperature (T_g)

The glass transition temperature is the temperature at which the rate of contraction on cooling changes and the material becomes brittle. A completely miscible plasticizer or solvent will change the T_g from the T_g of the plasticizer at 100% to the T_g of the polymer at 100%.

Viscoelastic Properties

A periodic vibration of controlled frequency is applied to the polymer and the response is measured.[16] An inphase component G′ (energy stored) and out of phase component G″ (energy loss) is analyzed, and the ratio of G″ (energy loss to heat)/G′ energy stored and returned, is an index of the rubberlike character of the material.

Melting Point Depression

The lowering of the melting range for two incompatible polymer mixtures is very small[18,19] (not more than 1°C). However, blends which are compatible exhibit a melting point range similar to copolymers. The use of the DTA to determine the melting range, as well as the heats of fusion (ΔH_f) and finally the entropy of fusion (ΔS_f) can be used to evaluate the plasticization effect of an additive.

$$\Delta S_f = \frac{\Delta H_f}{T_m \text{(melting point)}}$$

EXPERIMENTAL PROCEDURE

Materials and Equipment

TPX Grade RT-D30 Lot No. 84209 METHYLPENTENE POLYMER from I.C.I./Organics/Inc., Providence, Rhode Island.

Petroleum Jelly (white) (Pureline Oils Inc., Paterson, New Jersey) (See Equipment Table IV)

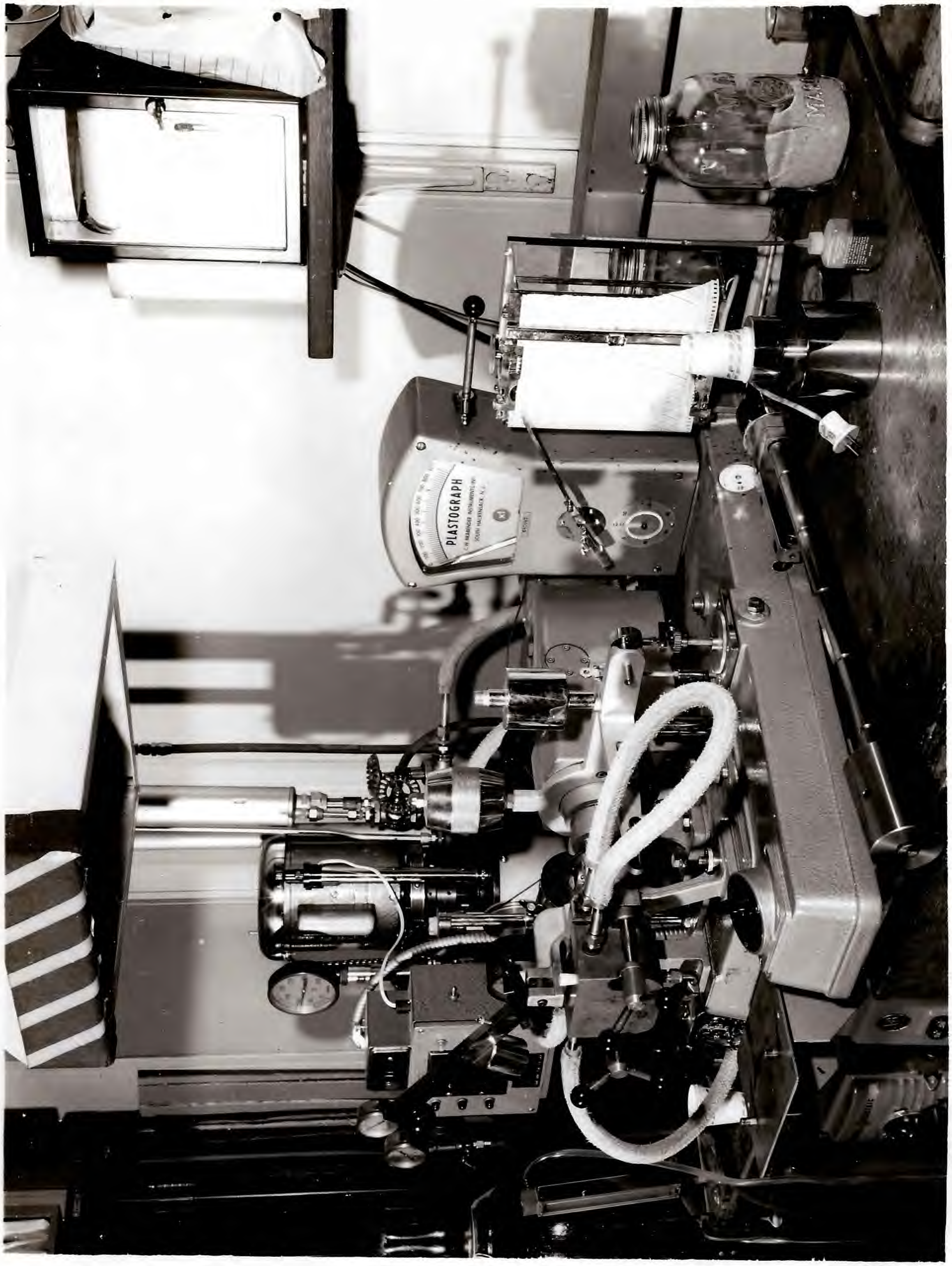
Sample Preparation and Apparatus

The TPX Grade RT-D30 and Petroleum Jelly (white) were blended on a Brabender Plasticorder using an electrically heated mixing head rather than the oil heated mixing head shown in Fig. 1. The Brabender was heated to 275°C and the speed adjusted to 30 rpm. The TPX-RT-D30 was added first and mixed for three minutes, then, the petroleum jelly was added and the material blended for seven minutes for a total blending time of ten minutes. Forty-two grams of material were added in one batch. In order to eliminate oxygen and prevent oxidation of the material, nitrogen was blown over the mixture prior to mixing and during mixing.

The blended material was then pressed in a sandwich consisting of metal plate, aluminum foil, sample with metal shim, aluminum foil, metal plate.

The press was heated to 280°C and the material package placed between the platens at zero pressure. After three minutes the platen pressure was raised to 40,000 psi and heating was continued for seven minutes. The package was quenched in tap water to room temperature; the appropriate samples were die cut from the material.

FIGURE 1



BRABENDER PLASTOGRAPH

EXPERIMENTAL TESTING AND RESULTS

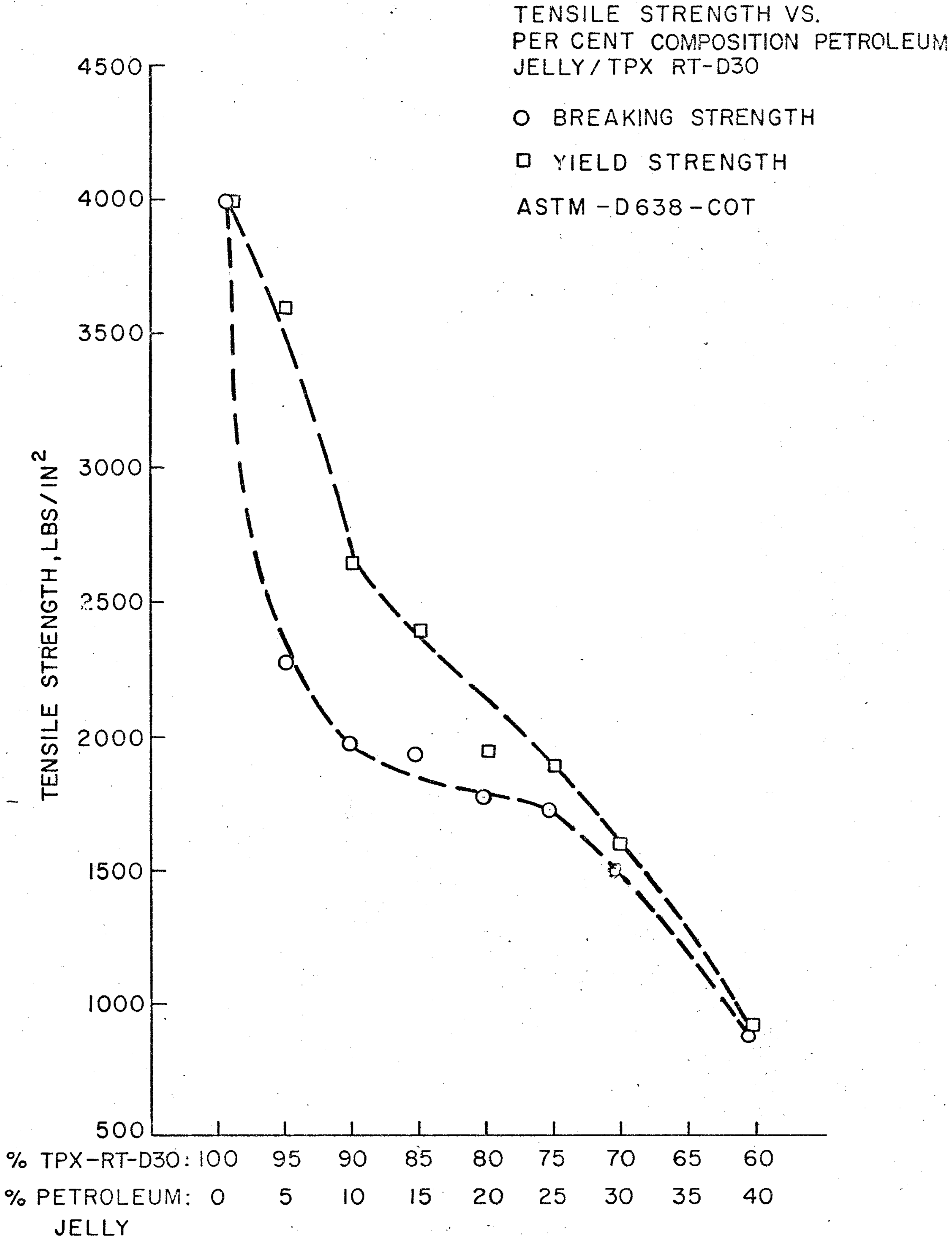
The die cut samples of the various blends of TPX-RT-D30/P.J. were tested to determine the change in properties of the blend (see Table II). All the samples were kept at 23°C, 50% Rh for at least 24 hours before testing. The tensile, elongation, and modulus measurements were made on replicates of five microtensile samples approximately 50 mils thick at a gauge length of one inch and a crosshead speed of 2 in/min. The TPX-RT-D30 polymer showed only a breaking point with 19% elongation at break, a melt index of 14.2 (see Table III), and an initial modulus of 1.77×10^5 psi. These values are in good agreement with the published literature (see Table I). All of the blends of TPX-RT-D30/P.J. had both a yield and a breaking point.

Tensile Strength ASTM 638-64T

The breaking strength dropped approximately 50% with the addition of 5% P.J. from 4000 psi to 2300 psi (see Table II). The breaking strength remained fairly constant from 10% to 25% P.J. at 1900 psi to 1700 psi, at this point, it dropped steeply to 1000 psi for 40% P.J. (see Graph 1).

The 100% TPX-RT-D30 had no yield point. The yield strength curve of the blends had no sharp breaks. At the

5% P.J. level, the yield strength value was 3600 psi. At 10% to 15% P.J., the curve leveled off slightly to 2600 and 2400 psi, respectively. At 40% P.J., the yield value was 1000 psi (see Graph 1).


TENSILE STRENGTH VS.
PER CENT COMPOSITION PETROLEUM JELLY / TPX RT-D30
○ BREAKING STRENGTH
□ YIELD STRENGTH
ASTM - D638 - COT
TENSILE STRENGTH, LBS/IN^2
4500
4000
3500
3000
2500
2000
1500
1000
500
% TPX-RT-D30: 100 95 90 85 80 75 70 65 60
% PETROLEUM JELLY: 0 5 10 15 20 25 30 35 40

GRAPH I

Tensile Modulus ASTM 638-64T

The initial modulus of the curve was calculated according to the formula

$$E = \frac{2}{\text{Width} \times \text{Thickness}} \left(\frac{\text{Stress}}{\text{Strain}}\right)$$

E = Tensile Modulus

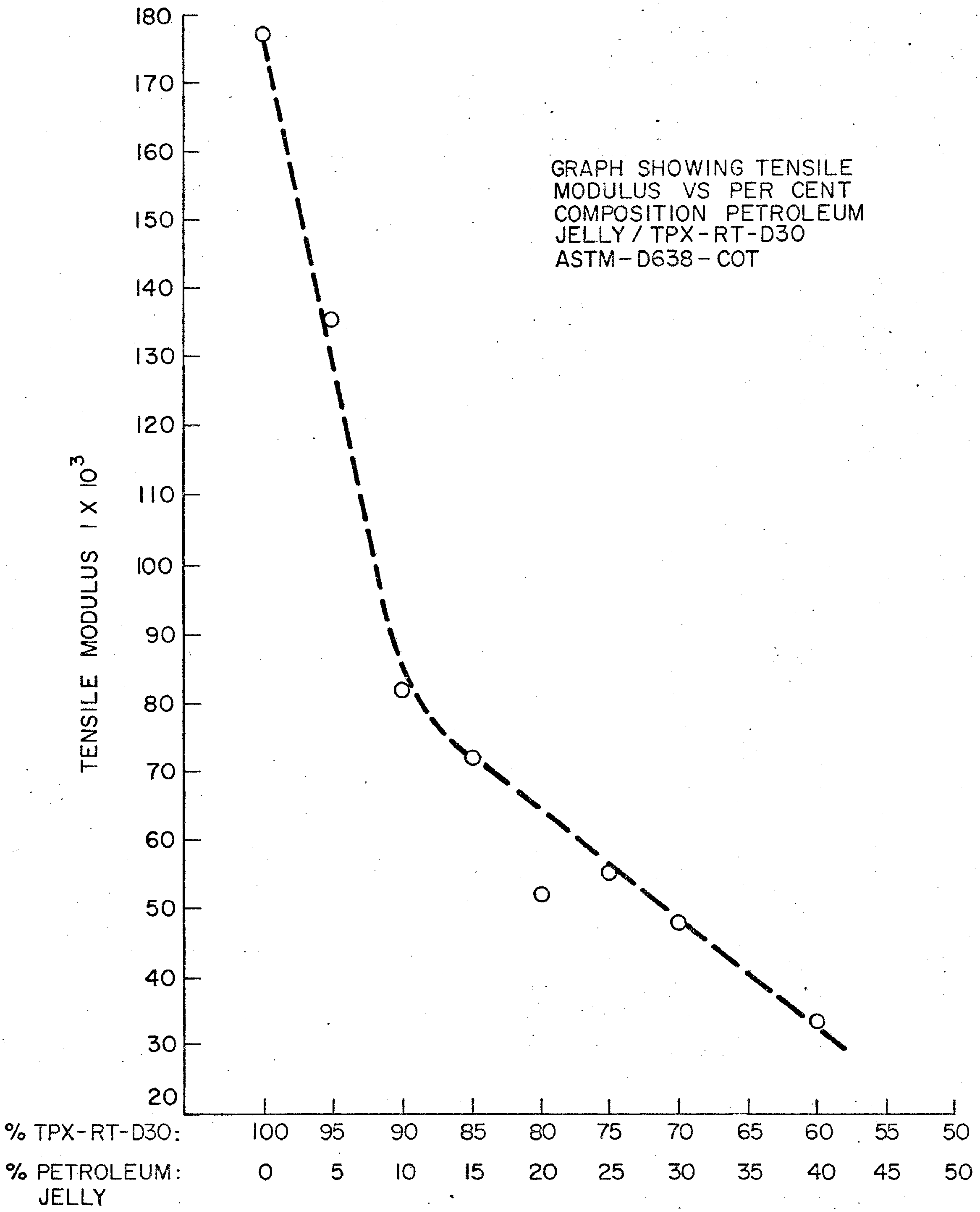
The modulus was $1.71\text{x}10^{+5}$ psi for TPX-RT-D30 ($2.1\text{x}10^{5}$ psi literature at 50% straining rate). With the addition of 5% P.J. modulus dropped to $1.2\text{x}10^{5}$ psi essentially equivalent to the percent decrease in breaking strength. The curve abruptly changes at 10% P.J. with a modulus of $0.8\text{x}10^{+5}$ psi and becomes essentially linear to 40% P.J. at $0.35\text{x}10^{+5}$ psi (see Table II, Graph 2).

Elongation ASTM 638-64T

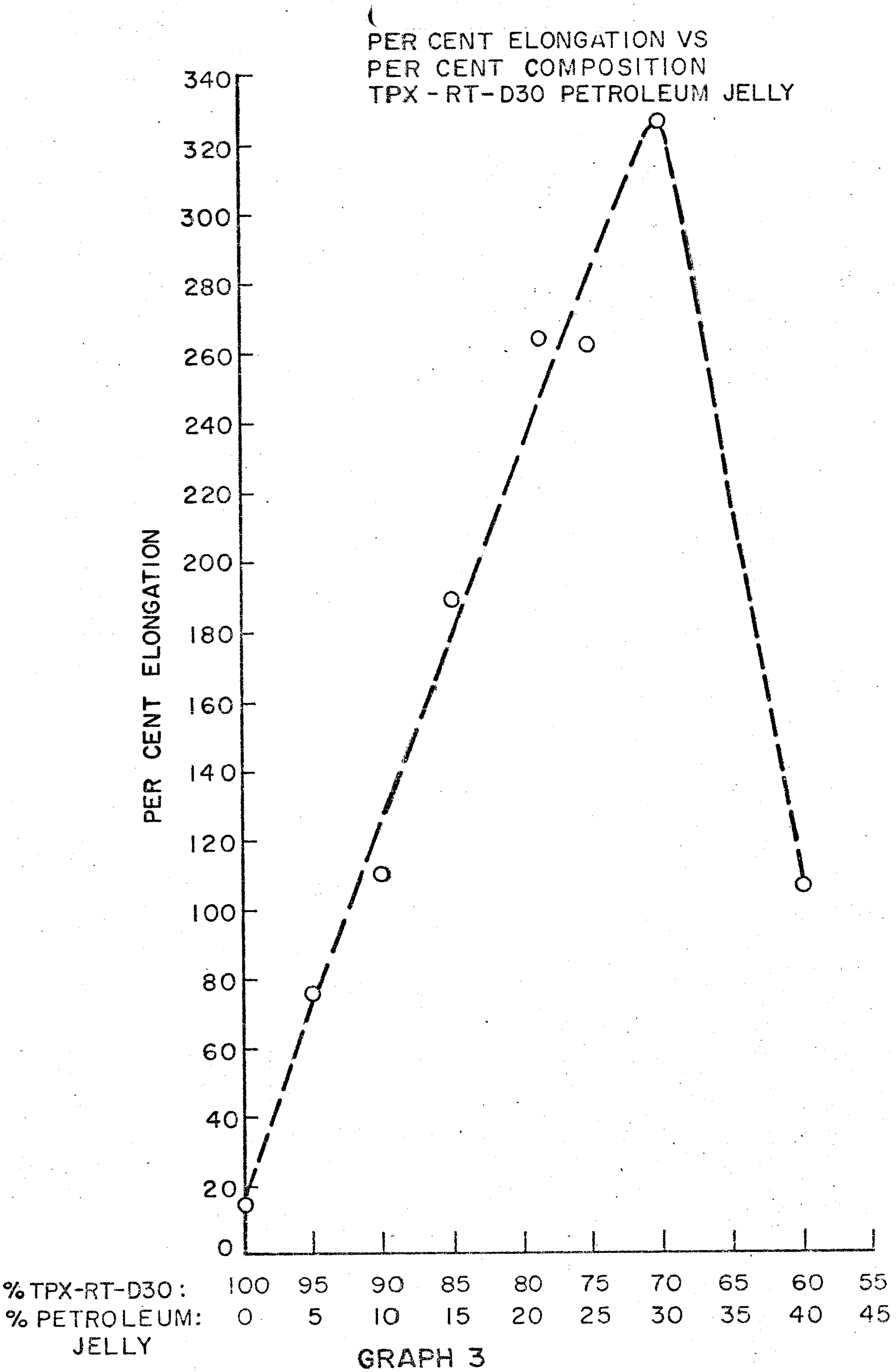
At 100% TPX-RT-D30, the elongation was 19%. With the addition of 5% P.J., the elongation values increased to 75%. At the 15%, 20%, and 25% P.J. level, the samples began to neck down and the elongation reached 190% and 260%, finally reaching a peak of 320% at 30% P.J. The elongation values then dropped to 209% at the 40% P.J. level (see Table II, Graph 3).

Vicat Softening Point ASTM 1525, Procedure A

This test used to determine the maximum service temperatures at which a material loses its rigidity was run on duplicate samples, at a heating rate of 1°C/min.


GRAPH SHOWING TENSILE MODULUS VS PER CENT COMPOSITION PETROLEUM JELLY / TPX-RT-D30 ASTM-D638-COT
TENSILE MODULUS I X 10^3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
% TPX-RT-D30:
100
95
90
85
80
75
70
65
60
55
50
% PETROLEUM: JELLY
0
5
10
15
20
25
30
35
40
45
50

GRAPH 2



PER CENT ELONGATION VS
PER CENT COMPOSITION
TPX-RT-D30 PETROLEUM JELLY

GRAPH 3

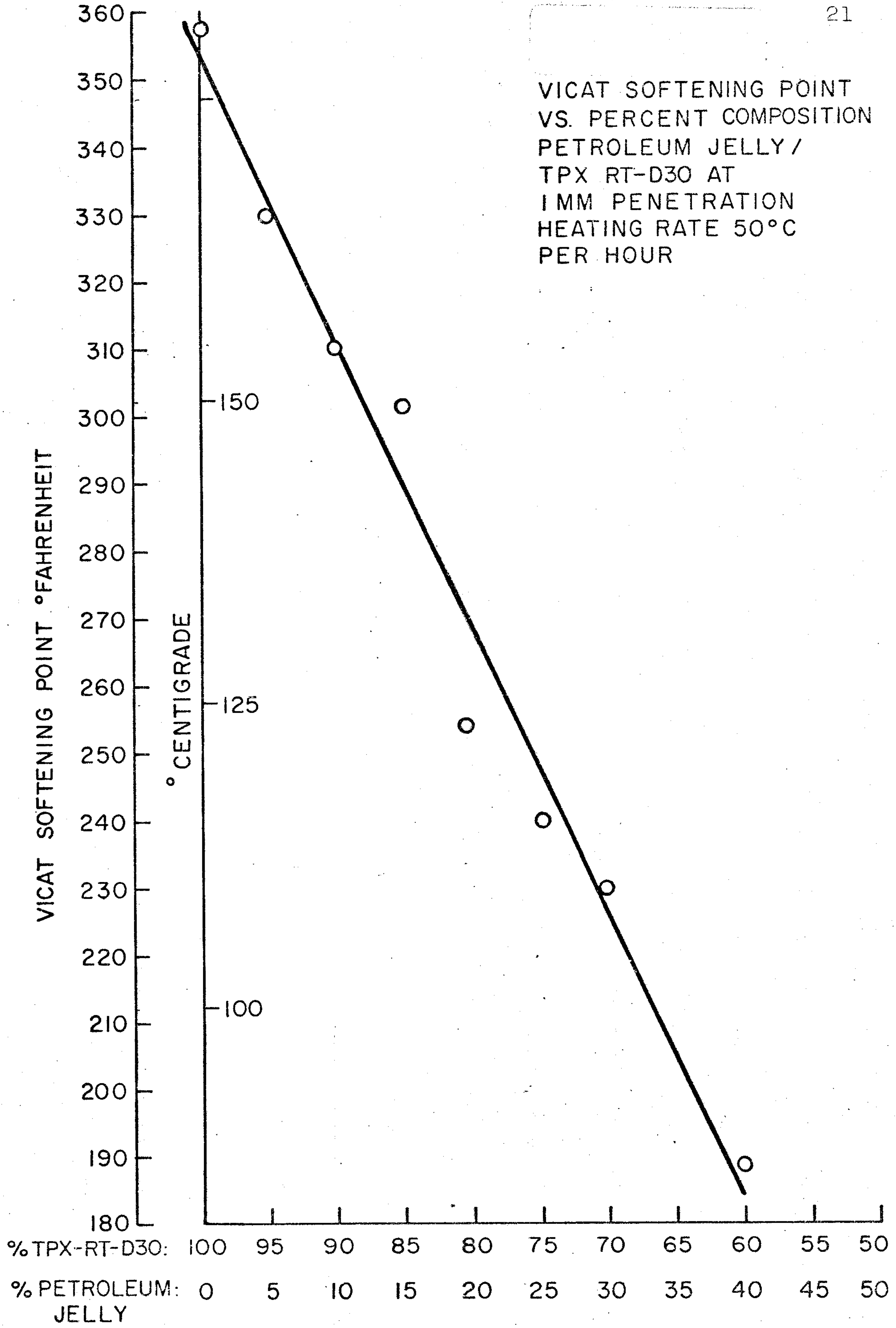
The 100% TPX-RT-D30 polymer gave the same temperature 179°C as literature values. Subsequent addition of 5%, and 10% P.J. gave a decrease 166°C and 154°C. At the 25% P.J. level the value was 116°C and the 40% P.J. level had a Vicat softening point of 88°C (see Table II, Graph 4).

Brittleness ASTM D746-57T

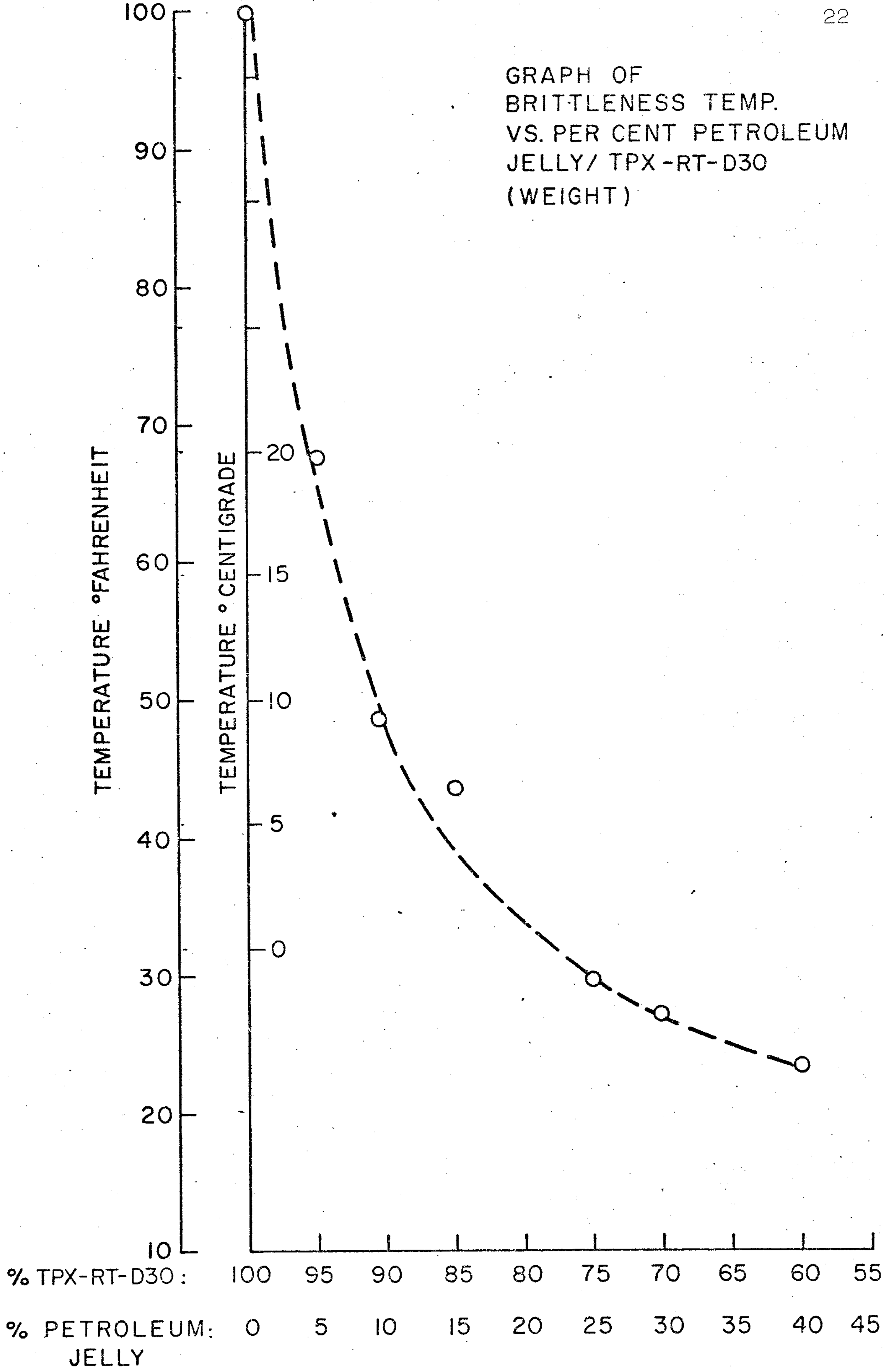
The brittleness temperature was determined on replicates of ten samples at the temperature where 50% broke on impact. TPX-RT-D30 was higher than 100°F. Additions of 5% P.J. lowered the brittleness point to 19.4°C. At the 10, 15% P.J. level, the curve began to level off at 7°C, and then dropped to -1.5°C at the 25% level. Finally, it dropped to -5°C at 40% P.J. (see Table II, Graph 5).

Differential Thermal Analysis

The differential thermal analysis (D.T.A., Stone) was run at one inch Hg pressure with nitrogen at a heating rate of 5°C/min. The sample size averaged 3-4 mg (see Table III, Fig. 2). The material was run from room temperature to 250°C. No noticeable exotherms or endotherms were noticed until the melting point was reached. Later, the P.J. was tested on a Differential Scanning Calorimeter below room temperature showed an endotherm at

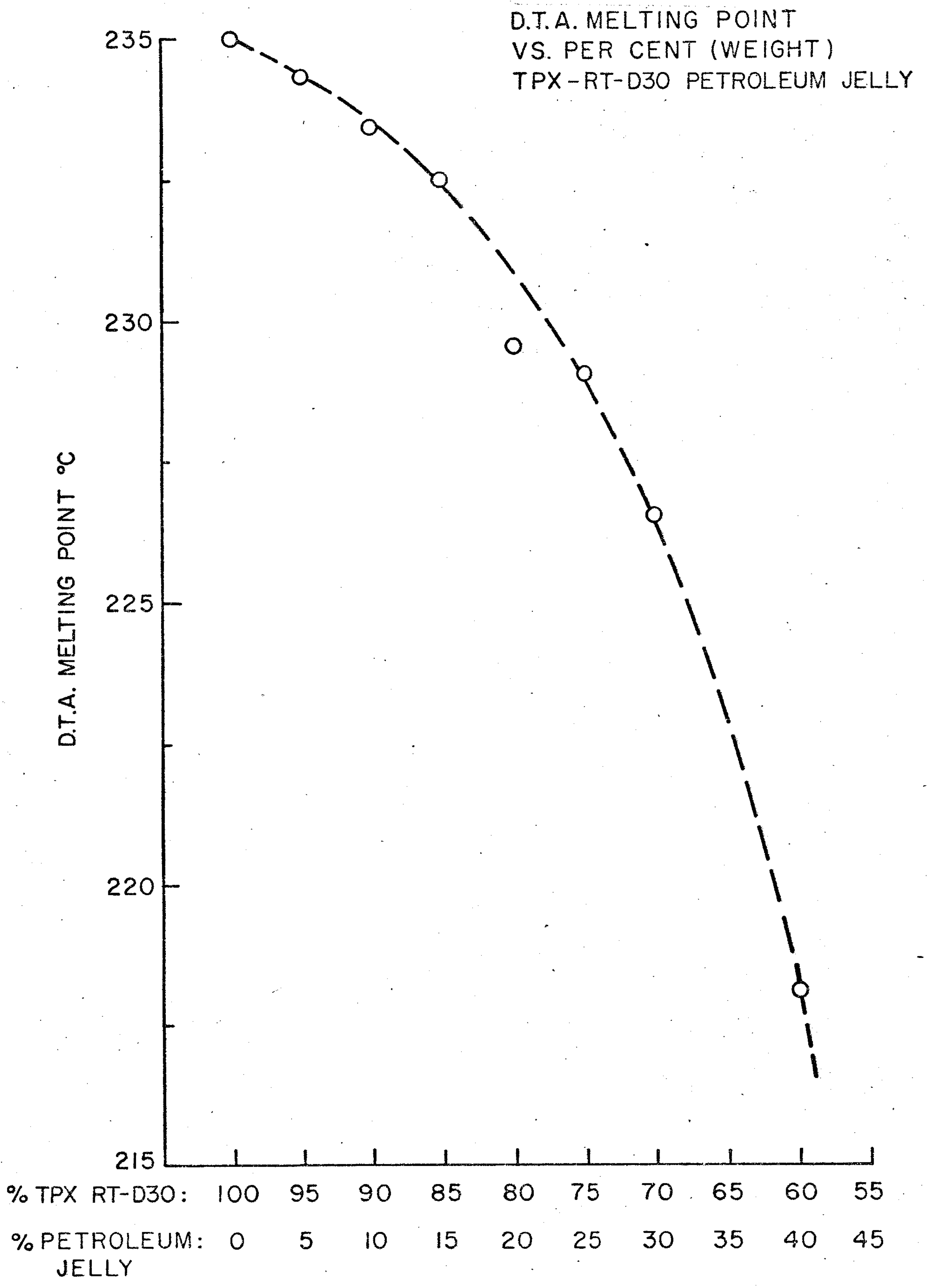

VICAT SOFTENING POINT
VS. PERCENT COMPOSITION
PETROLEUM JELLY/
TPX RT-D30 AT
1MM PENETRATION
HEATING RATE 50°C
PER HOUR
VICAT SOFTENING POINT °FAHRENHEIT
360
350
340
330
320
310
300
290
280
270
260
250
240
230
220
210
200
190
180
°CENTIGRADE
150
125
100
%TPX-RT-D30:
100
95
90
85
80
75
70
65
60
55
50
% PETROLEUM: JELLY
0
5
10
15
20
25
30
35
40
45
50

GRAPH 4



GRAPH OF
BRITTLENESS TEMP.
VS. PER CENT PETROLEUM
JELLY/ TPX-RT-D30
(WEIGHT)

GRAPH 5


D.T.A. MELTING POINT
VS. PER CENT (WEIGHT)
TPX-RT-D30 PETROLEUM JELLY
D.T.A. MELTING POINT °C
235
230
225
220
215
% TPX RT-D30: 100 95 90 85 80 75 70 65 60 55
% PETROLEUM JELLY: 0 5 10 15 20 25 30 35 40 45

GRAPH 6

-5°C to +50°C. The melting points of the blends ranged from 235°C to 218°C (see Graphs 6-13, Table III). The 100% TPX-RT-D30 polymer melted at 235°C with a single peak (Graph 7). Both the 5 and 10% P.J. samples had single peaks at 234 and 232.5°C, respectively (Graphs 8 and 9). At the 15% P.J. level a plateau region developed with a peak at 232°C (Graph 10). The 25% P.J. sample had a similar plateau region and a peak at 229°C (Graph 11). The 30% P.J. sample had only one peak region at 227°C and no plateau (Graph 12). The 40% P.J. had only a slight endotherm at 218°C (Graph 13). The control of 100% P.J. gave only a straight line on heating from room temperature to 250°C. The tensile strength curve bears out the plateau region at the 10 to 25% P.J. area (see Graphs 6-12).

The relative heat of fusion (ΔH_f) curve was calculated by dividing the area under the curve by the sample weight based on 100% TPX-RT-D30 polymer (see Table III). This data is scattered and shows a rise in relative (ΔH_f) up to the 30% level with the exception of 10 and 20% P.J. which dropped below the general rise level (see Graph 14).

Electrical Properties

Electrical measurements were made on 50-mil plaques of the blends. The samples were run at 23°C, 15 Rh, and 10^6 Hz. The dielectric content (ε') of the blends varied from 2.13 to 2.15. The tan δ (loss factor) $\times 10^5$ increased from 4 at 0% P.J. to 58 at 25% P.J. The resistivity of the blends at 100 volts, 2 min. after current was $> 10^{16}$ ohms for all of the blends (see Table II).

DTA FURNACE ASSEMBLY

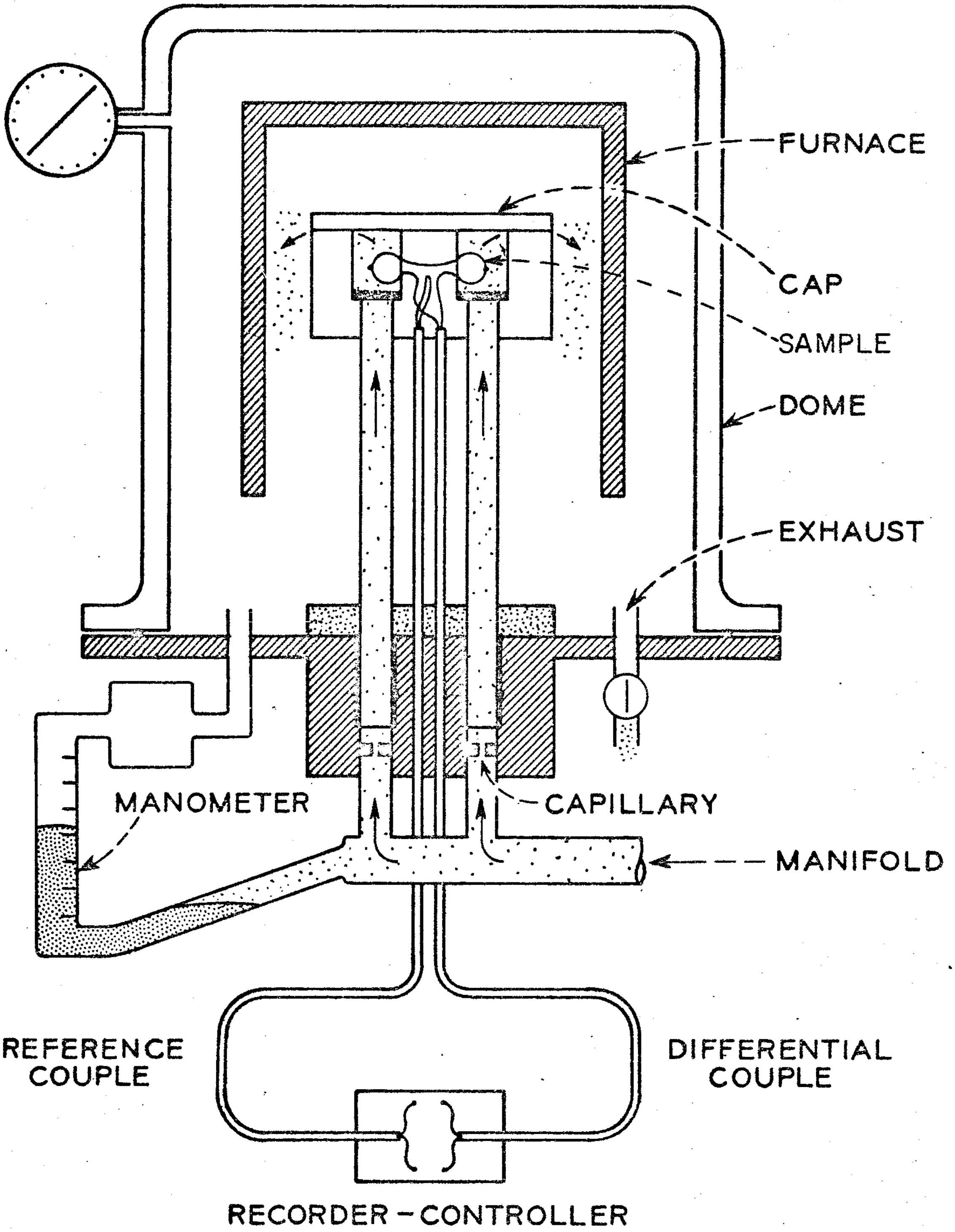
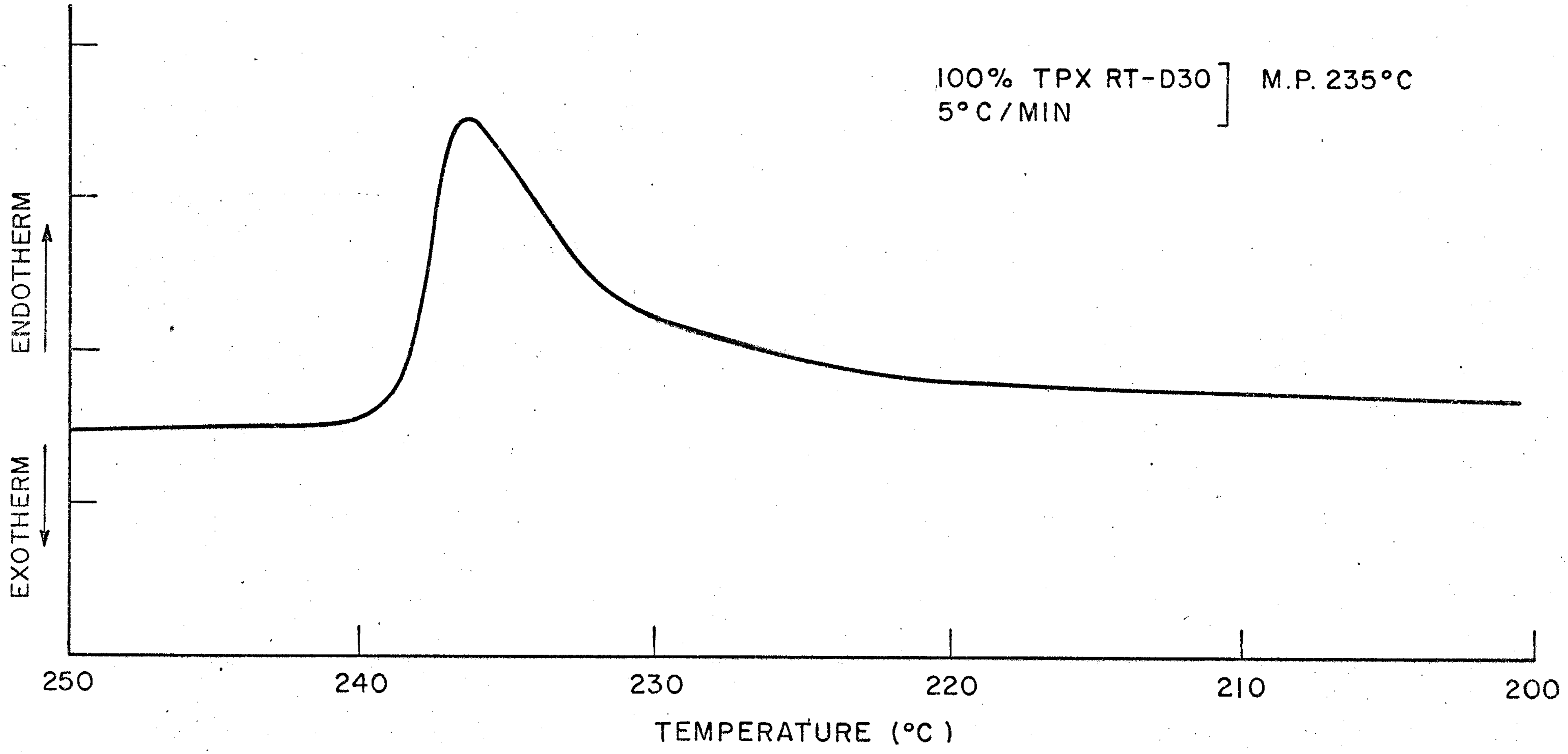
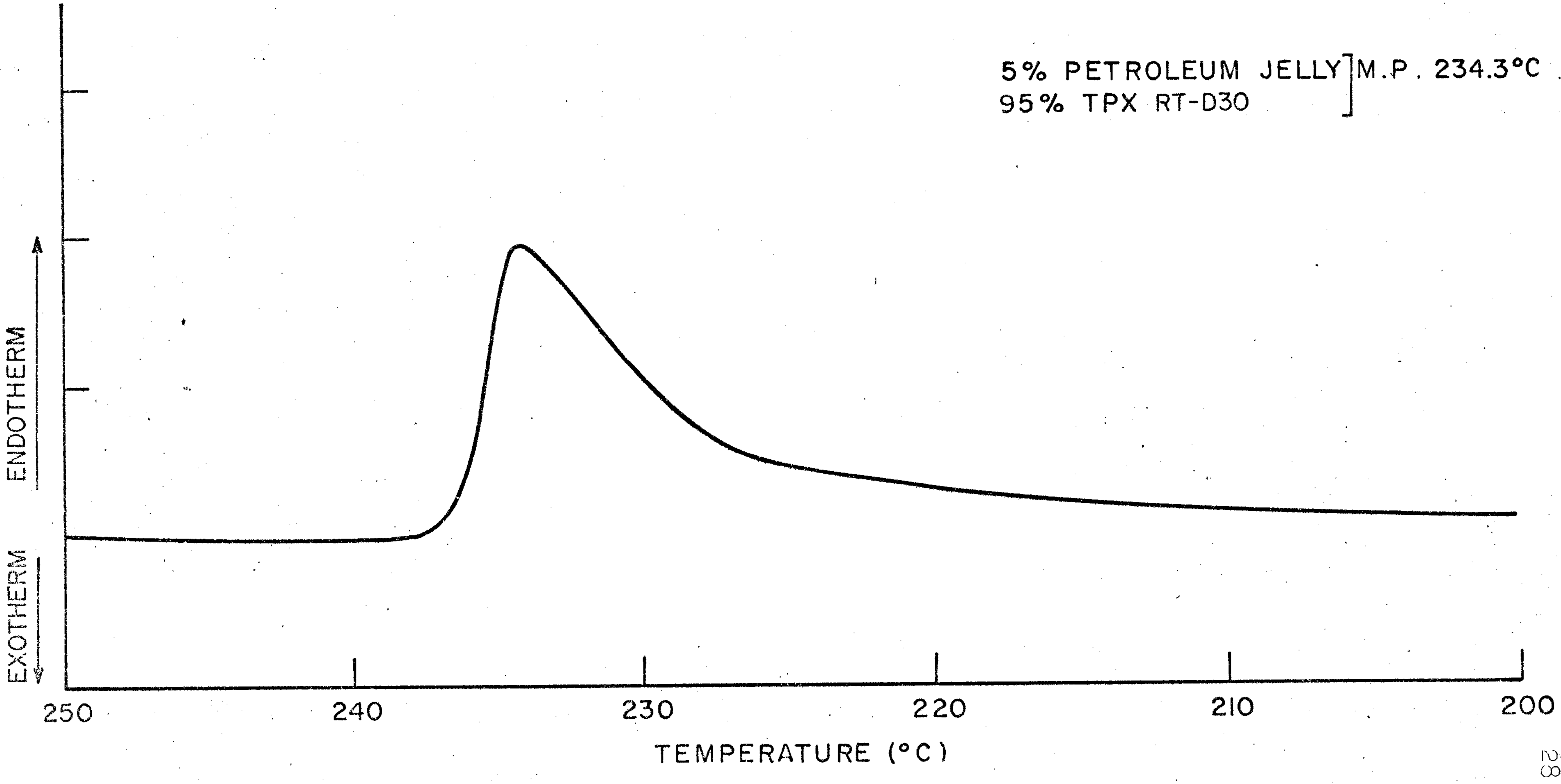


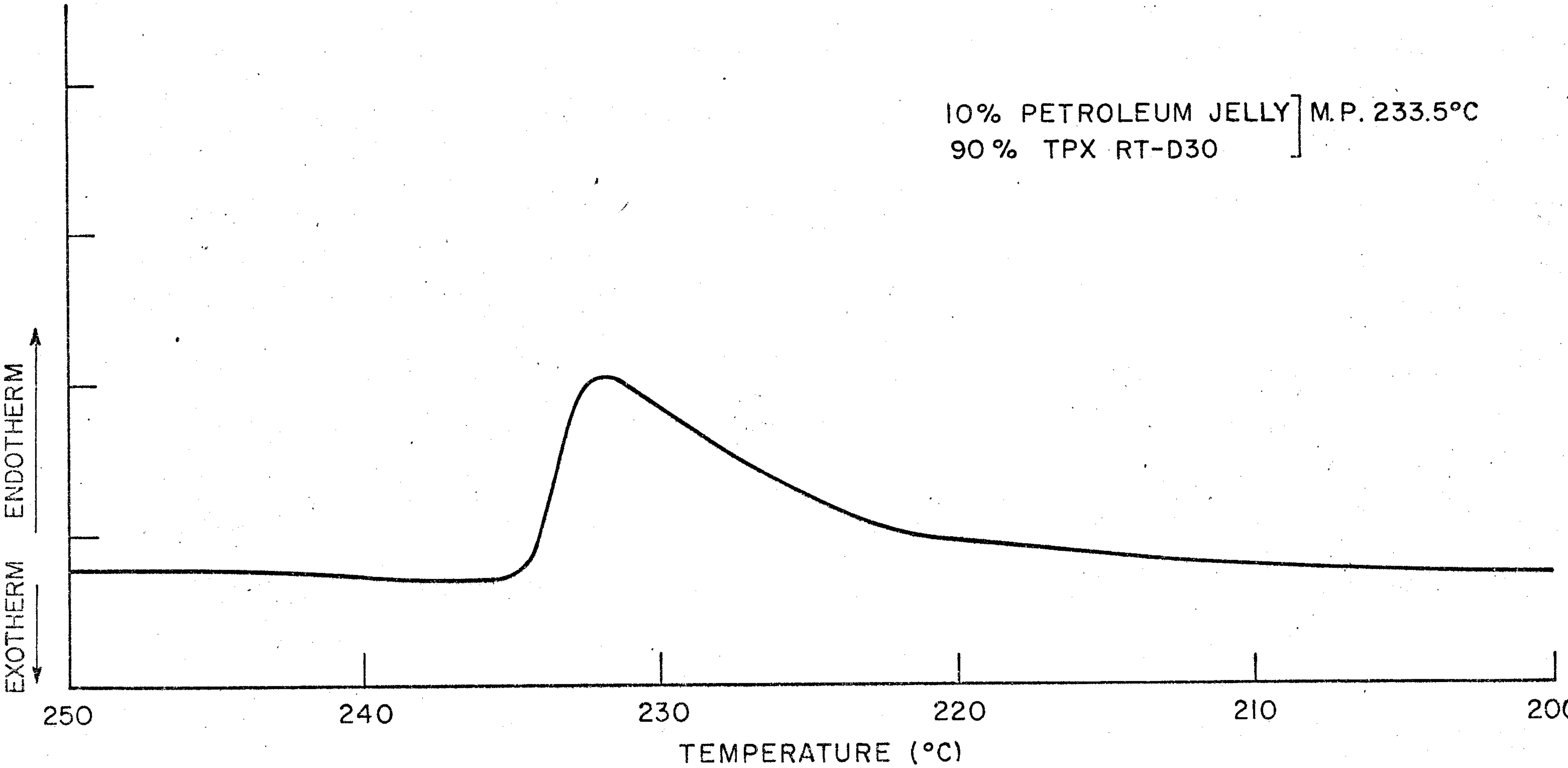
Fig. 2


100% TPX RT-D30
5°C/MIN
M.P. 235°C
ENDOTHERM
EXOTHERM
250
240
230
220
210
200
TEMPERATURE (°C)

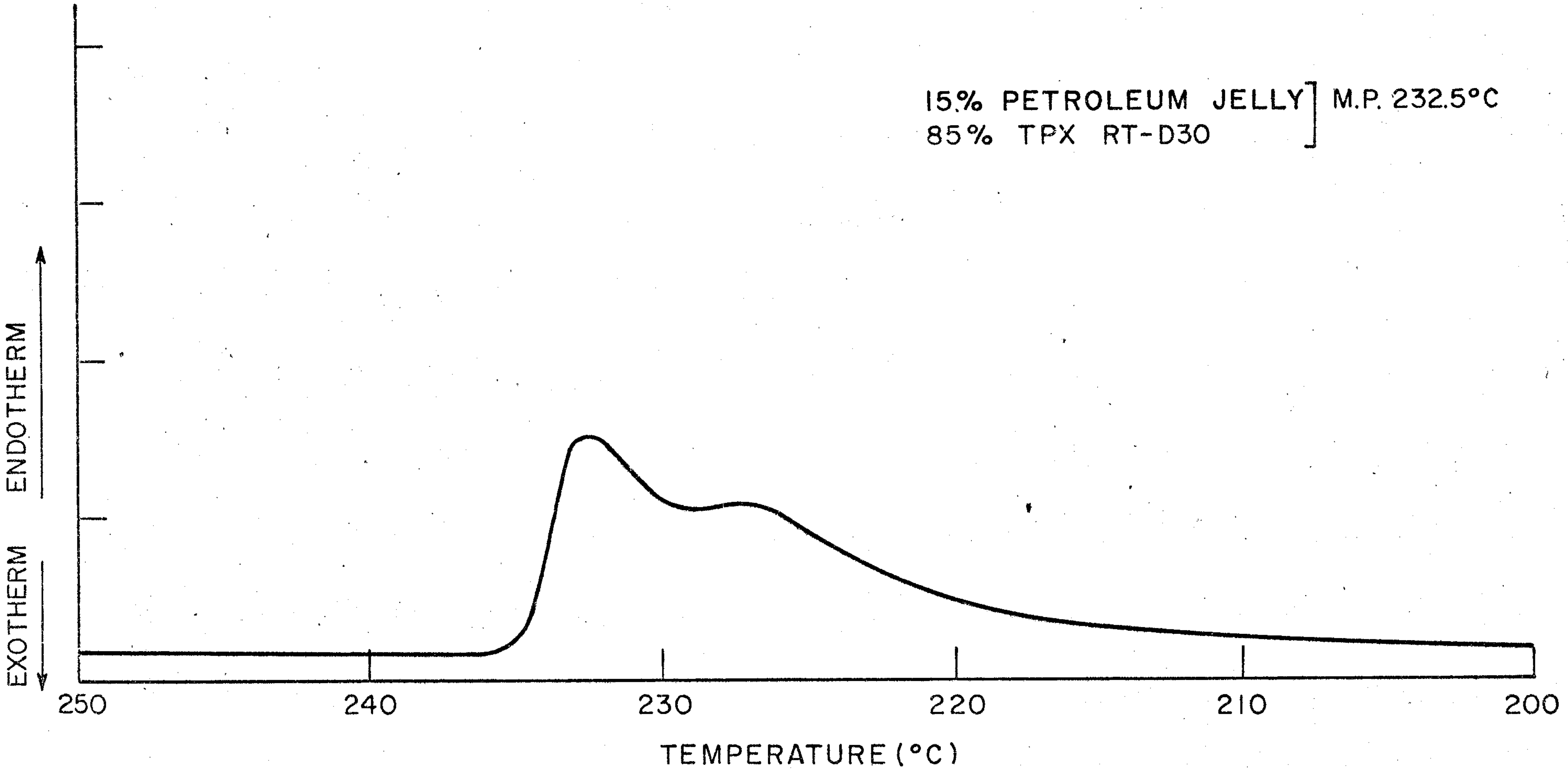
GRAPH 7


5% PETROLEUM JELLY
95% TPX RT-D30
M.P. 234.3°C
ENDOTHERM
EXOTHERM
250
240
230
220
210
200
TEMPERATURE (°C)

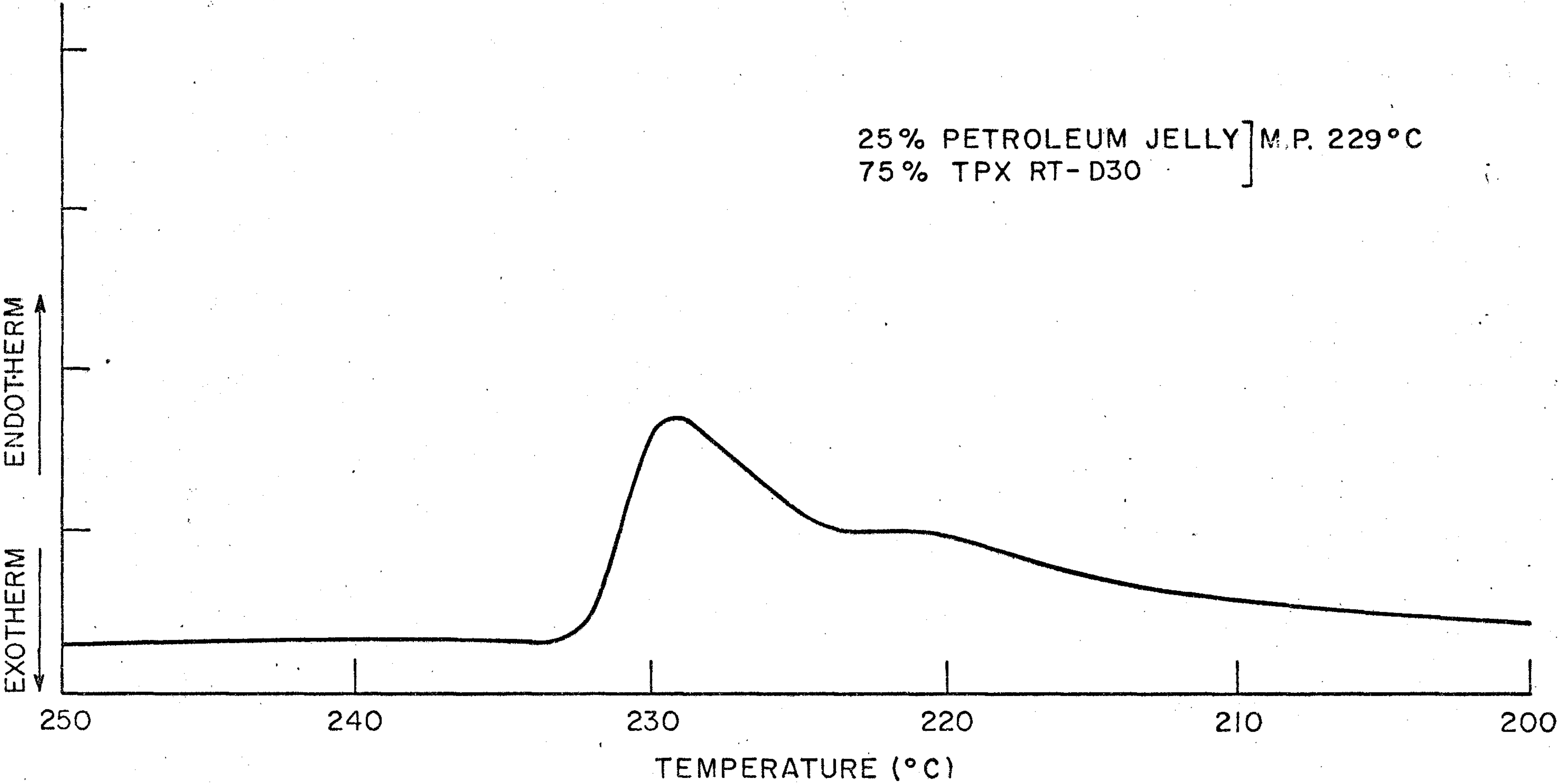
GRAPH 8


10% PETROLEUM JELLY
90% TPX RT-D30
M.P. 233.5°C
ENDOTHERM
EXOTHERM
250
240
230
220
210
200
TEMPERATURE (°C)

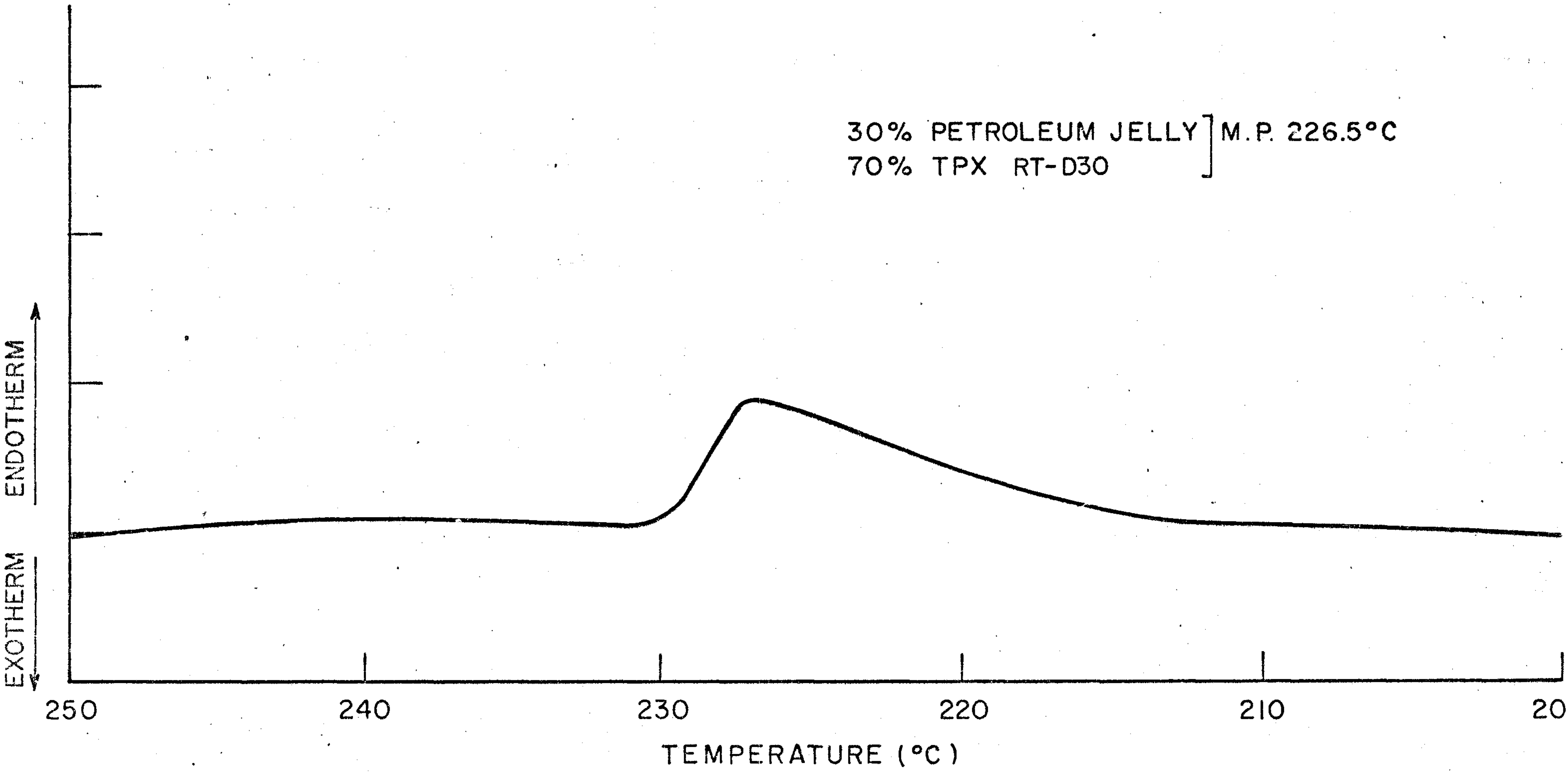
GRAPH 9


15% PETROLEUM JELLY
85% TPX RT-D30
M.P. 232.5°C
ENDOTHERM
EXOTHERM
250
240
230
220
210
200
TEMPERATURE (°C)

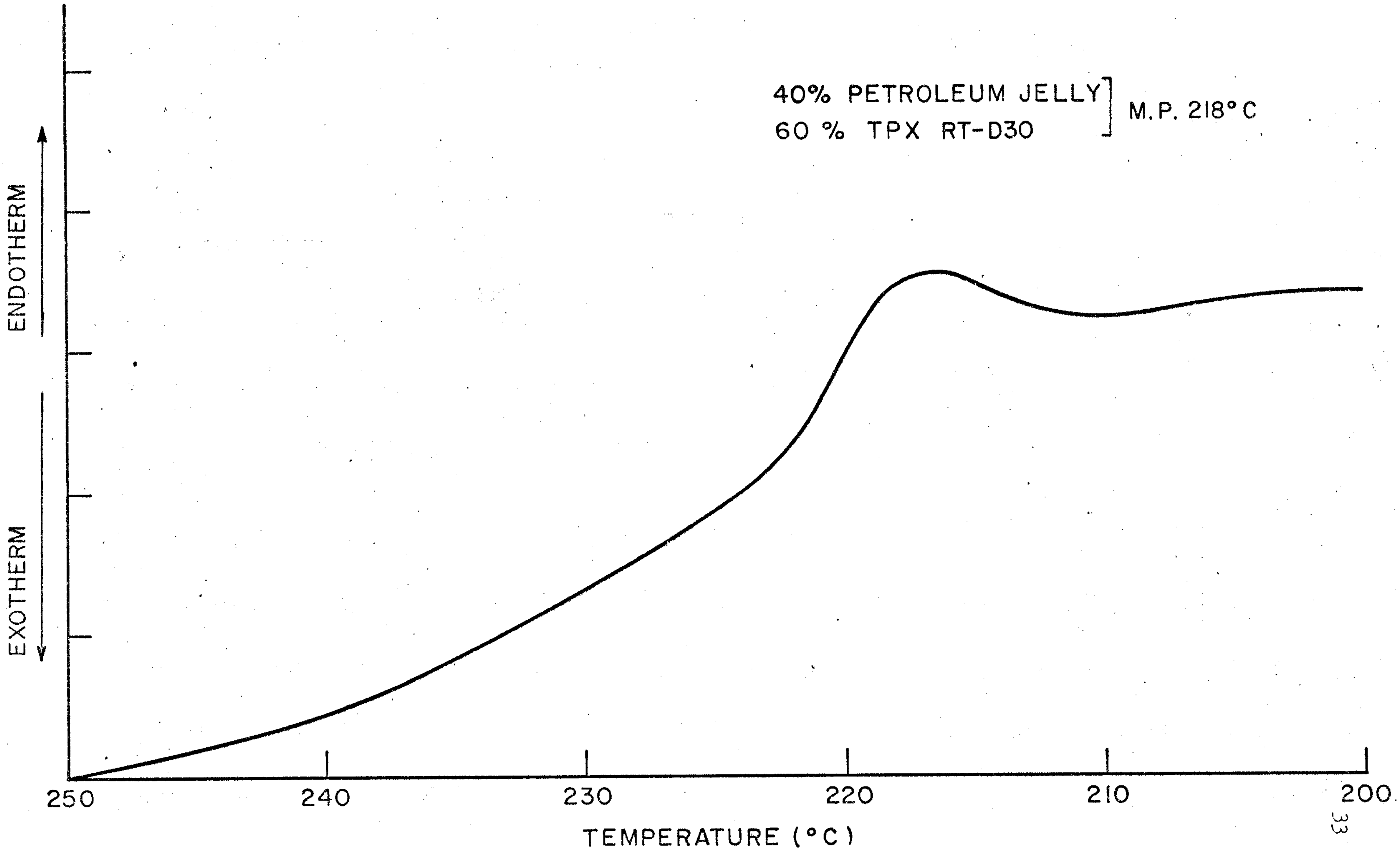
GRAPH 10


25% PETROLEUM JELLY
75% TPX RT-D30
M.P. 229°C
ENDOTHERM
EXOTHERM
250
240
230
220
210
200
TEMPERATURE (°C)

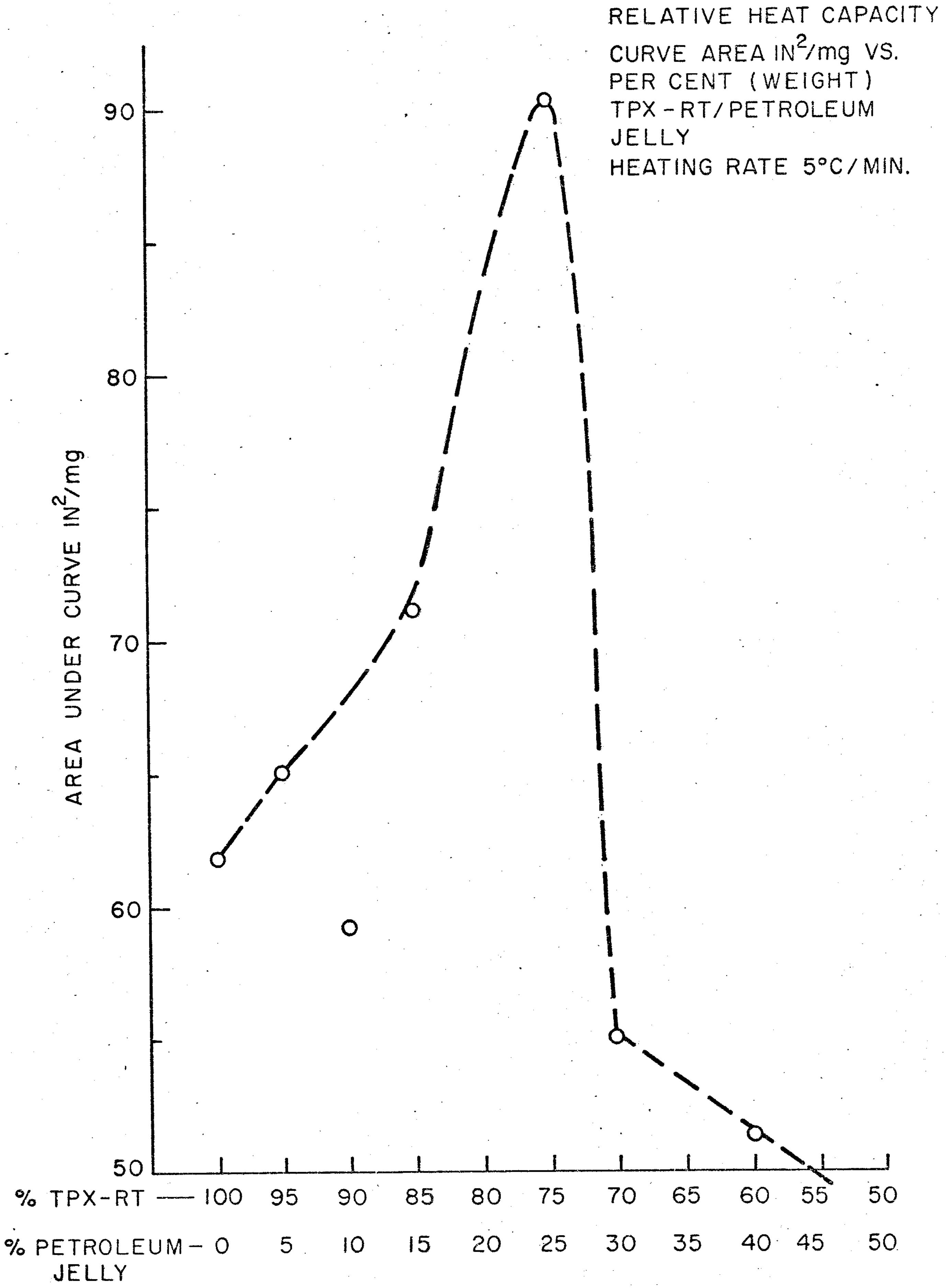
GRAPH II


30% PETROLEUM JELLY
70% TPX RT-D30
M.P. 226.5°C
ENDOTHERM
EXOTHERM
250
240
230
220
210
20
TEMPERATURE (°C)

GRAPH 12


40% PETROLEUM JELLY
60 % TPX RT-D30
M.P. 218° C
ENDOTHERM
EXOTHERM
250
240
230
220
210
200
TEMPERATURE (° C)

GRAPH 13


RELATIVE HEAT CAPACITY
CURVE AREA IN²/mg VS.
PER CENT (WEIGHT)
TPX-RT/PETROLEUM
JELLY
HEATING RATE 5°C/MIN.
AREA UNDER CURVE IN²/mg
90
80
70
60
50
% TPX-RT — 100 95 90 85 80 75 70 65 60 55 50
% PETROLEUM JELLY – 0 5 10 15 20 25 30 35 40 45 50

GRAPH 14

DISCUSSION OF EXPERIMENTAL RESULTS

Petroleum jelly (P.J.) blended with the TPX-RT-D30 polymer in various percentages, produces definite changes in the polymer's properties. The petroleum jelly acts as a plasticizer for the polymer. The DTA curves used by several investigators[18,19,20] for relating the compatibility of blends of material show that the depression of TPX-RT-D30 melting point by several degrees (9°C for 30% P.J.) is an indication of change in crystalline morphology, and a sign of intimate mixing of the materials. This is also revealed in the tensile strength and elongation of the polymer. The causes for this decrease in melting point could be the formation of imperfect crystals due to the inclusion of P.J. in the crystals. The DTA curves show the development of a plateau at the 15 and 25% P.J. level. The plateau could be caused by the formation of smaller crystals which would have more chain ends, row vacancies and voids. Thinner lamella thickness would also affect the observed melting point change because of specific heat capacity differences in thick and thin lamellae. The P.J. could also allow the higher molecular weight polymer to crystallize and form less perfect crystals. The melting of these crystals could give rise to the plateau region. Some authors have suggested that the decrease in melting point of TPX-RT-D30 could be due to the establishment of domains of right-handed and left-handed helical spirals for the crystalline TPX-RT prepared in various solvents. Frank et al.[1] favored this alternating molecular packing which would require a regular alternation from a right- to left-handed helix after each fold in the poly-4-methyl-pentene-1 chain in the crystal.[21] Crystallinity was not calculated as Ke[18] did using the formula $X = ([H_a-H_c]/\Delta H_f)100$ (H_a,H_c - enthalpies of polymer in amorphous and crystalline state) since the heat of fusion of a perfectly crystalline TPX-RT-D30 was not available. Mikhailov[17] used the density of polyethylene/polypropylene blends as well as heat capacity change to show compatibility. Density of poly-4-methyl-pentene-1 with its inverted density behavior would not represent percent crystallinity.

The mechanical and thermal properties are significantly changed as shown in the results. Yield values are obtained at all levels of P.J. addition. The "necking down" effect, as seen in polyethylene, etc. shows that the crystallites in the polymer have been plasticized sufficiently to allow them to rearrange, with the chain molecules lining up parallel to the stretching force. This process can result in the crystals being broken up into smaller units, or recrystallization taking place in an oriented condition.

The leveling off of the breaking strength of the polymer between 10-25% P.J. is interesting since it reflects the plateau area which developed in the DTA curves and indicates very slight changes in the polymer structure. It is in this area that the elongation begins to show the "necking down" effect exhibited in polyethylene. The elongation shows that internal friction of the molecule has decreased due to the formation of uniform crystallites, or small domain areas. The drop in brittleness temperature (related to impact strength) gives a good indication that the amount of energy which can be absorbed by the system has been changed to allow its use at lower temperatures. The Vicat softening point (related to heat distortion temperature) shows that the softening point has been lowered, but not to the extent that the polymer is no longer usable at higher temperatures. Electrical properties are still excellent as would be expected for each material has good electrical characteristics.

CONCLUSIONS

The addition of P.J. to TPX-RT-D30 has plasticized the polymer to the extent that it has lowered the melting point, decreased the tensile strength, modulus, brittleness point, and Vicat softening point of the polymer. The TPX-RT-D30 polymer has only 15 percent elongation with no yield value or necking down. The plasticized polymer has up to 300% elongation yield values, and the necking down effect prevalent in polyethylenes. The P.J. enables the higher molecular weight polymer to crystallize, giving rise to a plateau region at the 15 to 25% P.J. level.

RECOMMENDATIONS

A great deal of work still remains to determine the effect of P.J. on the outdoor aging of the TPX-RT-D30 polymer as well as the rate of exudation of the P.J. from the polymer. The exact determination of crystallinity using X-ray, etc., and the effect on T_g using dilatometry, or a "Vibron" to measure loss modulus would be of great interest.

TABLE II

PROPERTY TABLE OF BLENDS

Sample		Tensile Strength ASTM-638-64T			ASTM D746-57T		ASTM 1525 VICAT Softening Point, °F ←	Electrical Properties 10^6 Hz, 23°C, 15% RH		
		Yield	Break	Elongation	Brittleness	Tensile Modulus	Procedure A	ε'	Tan $\delta \times 10^5$	Resistivity*
% TPX	% P.J.	psi	psi	%	°C	psi	1.0 mm	10^6 Hz		ohms
100	0	None	3960	19	38°	171,000	180°C	2.13	4	$> 10^{16}$
95	5	3600	2270	76	19.4°	124,000	166	2.13	14	$> 10^{16}$
90	10	2630	1937	81	9.0°	81,960	154			
85	15	2400	1940	188	7.0°	71,800	150	2.14	35	$> 10^{16}$
80	20	1820	1680	260		52,000		2.14	45	$> 10^{16}$
75	25	1832	1730	260	-1.5°	54,600	116	2.15	58	$> 10^{16}$
70	30	1580	1440	330	-2.8°	48,720	110			
60	40	980	960	210	-5°	35,220	87			

* at 100 V 2 min. after current

TABLE III

DIFFERENTIAL THERMAL ANALYSIS

TPX-RT 30	Petroleum Jelly White	Melting Point Heating Rate 5°C/min Nitrogen, 1 inch Hg.	Melt Index ASTM D1238-62T 5 kg at 260°C g/10 min.	Relative Heat of Fusion (ΔH_f)			
				Weight			
				Total mg	Corrected to 100% TPX-RT-D30	Area under Curve in^2	Ratio in^2/mg
%	%	°C					
100	0	235	14.2	3.5	3.5	2.16	61.7
95	5	234.2		4.0	3.8	2.47	65.0
90	10	233.5		3.7	3.33	1.97	59.2
85	15	232.5		3.5	2.98	2.22	71.0
80	20	229.5		3.2	2.56	1.44	56.5
75	25	229		3.7	2.78	2.51	90.3
70	30	226.5		3.3	2.31	1.27	55.3
60	40	218		3.5	2.10	1.08	51.4
0	100	-5 to +50°C					

EQUIPMENT TABLE IV

Supplier	Machine Make and Model
TINIUS OLSEN Testing Machine Co., Inc. Willow Grove, Pa.	U-CELTRONIC (Tensile Tester)
	BRITTLENESS IMPACT
	THERMODYNE
C. W. BRABENDER INC. South Hackensack, N. J.	PLASTI-CORDER Measuring Head No. 211-63 Type. E. H. Roller-5
BAR WORTH, INC. Springfield, N. J.	DIE CUTTER
PASADENA HYDRAULICS INC. Pasadena, 4, Calif.	PRESS, Steam, electrically heated, 12x12" plates 40,000 psi SPWR-220
R. L. STONE CO. Austin, Texas	DIFFERENTIAL THERMAL ANALYZER Model KA-W

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