

Properties of Blends Containing Petroleum Jelly and 4-Methyl-pentene-1 (TPX-RT-D30)

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Synopsis

The properties of 4-methyl-pentene-1 polymer (TPX-RT-D30) were altered by blending petroleum jelly (P. J.) with the polymer. The polymer was blended with up to 40% by weight P. J. The plasticization of the polymer by the P. J. apparently allows high molecular weight fractions of the polymer to crystallize and influences the crystalline size and perfection. Tensile properties of the blends showed both a break and yield value in all ratios as compared to only a break value for the pure polymer. Breaking strength ranged from 4000 psi for the polymer to 1000 psi at 40% P. J. Yield strength decreased to a 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 the pure polymer to 325% at 30% P. J. Modulus decreased from 1.8×10^4 (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 ranged from 181°C for the polymer to 87°C at 40% P. J. Differential thermal analysis (Stone) showed a melting point depression from 235°C to 218°C at 40% P. J.

INTRODUCTION

The changes in physical properties produced by blending petroleum jelly (P. J.) with TPX-RT-D30 polymer are reported. Blends of up to 40% by weight P. J. were prepared and characterized.

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."¹ 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-D30 is described in the literature as "a new family of stereoregular polyolefins based on 4-methyl-pentene-1."² The polymer is described^{3,4,5} as isotactic, with a crystallinity of 65% for oriented samples and 40% for normal fabricated samples. The TPX-RT-D30 material has

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interesting physical, electrical, and thermal properties. 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(methyl methacrylate). The high melting point of 240°C is much higher than that of 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 ultraviolet 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.

EXPERIMENTAL PROCEDURE

Materials and Equipment

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

Petroleum Jelly (white) was obtained from Pureline Oils Inc., Paterson, New Jersey.

Sample Preparation and Apparatus

The TPX Grade RT-D30 and Petroleum Jelly (white) (P. J.) were blended on a Brabender Plasticorder using an electrically heated mixing head. The Brabender was heated to 275°C and the speed adjusted to 30 rpm. The TPX-RT-D30 was added first and mixed for 3 min; then the P. J. was added and the material blended for 7 min for a total blending time of 10 min. Forty-two grams of material were added in one batch. In order to 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 3 min the platen pressure was raised to 40,000 psi and heating was continued for 7 min. The package was quenched in tap water to room temperature; the appropriate samples were die cut from the material.

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 I). All the samples were kept at 23°C, 50% relative humidity, for at least 24 hr 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 1 in. 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 II), and an initial modulus of 1.77×10^5 psi. 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, Table I). The breaking strength from 10 to 25% P. J. remained fairly constant at 1900 psi to 1700 psi; at this point, it dropped steeply to 1000 psi for 40% P. J. (Fig. 1).

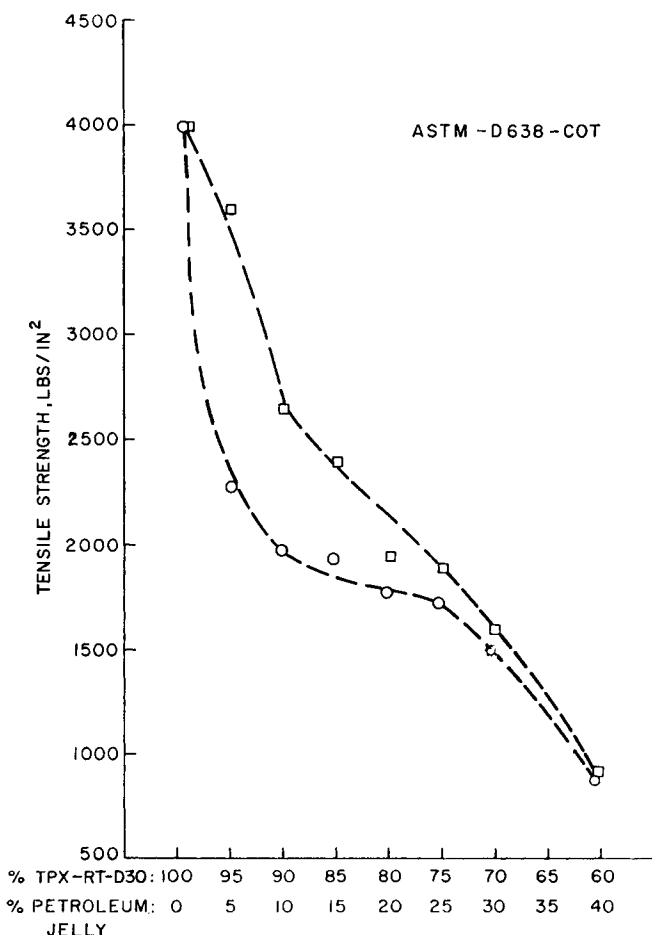


Fig. 1. Tensile strength vs. per cent petroleum jelly/TPX-RT-D30 composition: (○) breaking strength; (□) yield strength.

TABLE I
Properties of TPX-RT-D30/P.J. Blends

Sample TPX- RT-D30, %	P. J., %	Tensile strength ASTM-638-64T		ASTM 638 64T Elonga- tion, %	ASTM D746-57T Brittleness, °C	ASTM 638 64T Tensile modulus, psi	ASTM 1525 Vicat softening point, procedure A, °C	Electrical properties ^b		
		yield, psi	break, psi					ϵ'	$\tan \delta$ $\times 10^5$	Resistivity, ^c ohms
100	0	None	3960	19	38	171,000	180	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			

^a Penetration 1 mm.

^b Determined at 23°C, 15 Rh, and 10⁶ Hz.

^c At 100 V 2 min after current.

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 (Fig. 1).

Tensile Modulus ASTM 638-64T

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

$$E = \frac{\text{stress}}{\text{strain}}$$

The modulus was $1.71 \times 10^{+5}$ psi for TPX-RT-D30 (2.1×10^5 psi literature at 50% straining rate). With the addition of 5% P. J., modulus

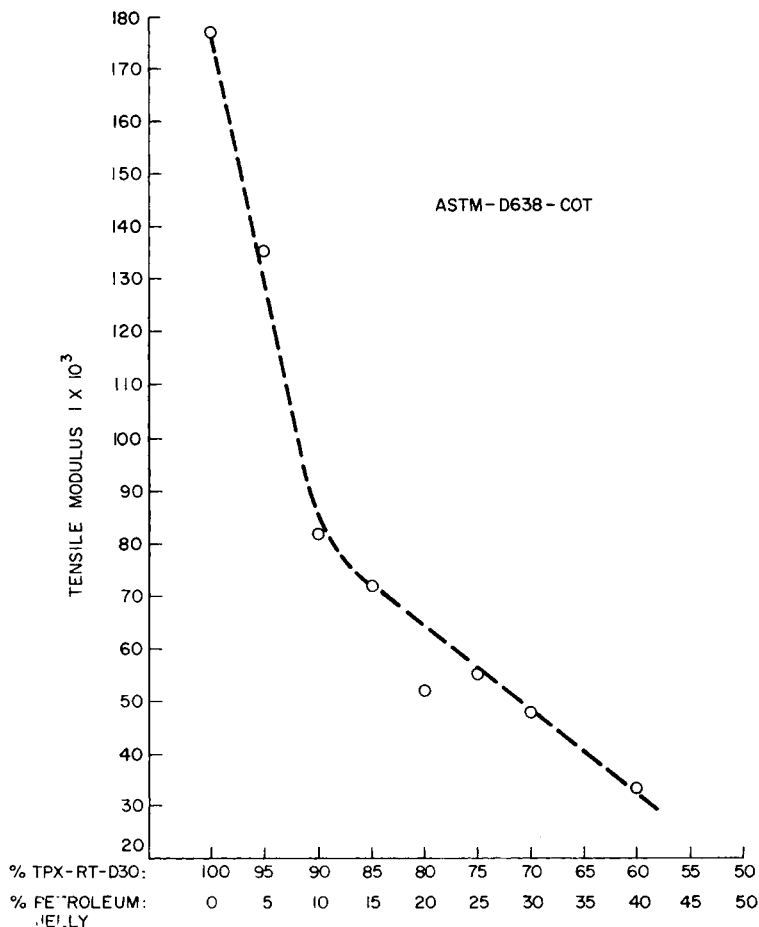


Fig. 2. Tensile modulus vs. per cent petroleum jelly/TPX-RT-D30 composition.

dropped to 1.2×10^5 psi, essentially equivalent to the per cent decrease in breaking strength. The curve abruptly changes at 10% P. J. with a modulus of 0.8×10^5 psi and becomes essentially linear to 40% P. J. at 0.35×10^5 psi (Table I and Fig. 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%

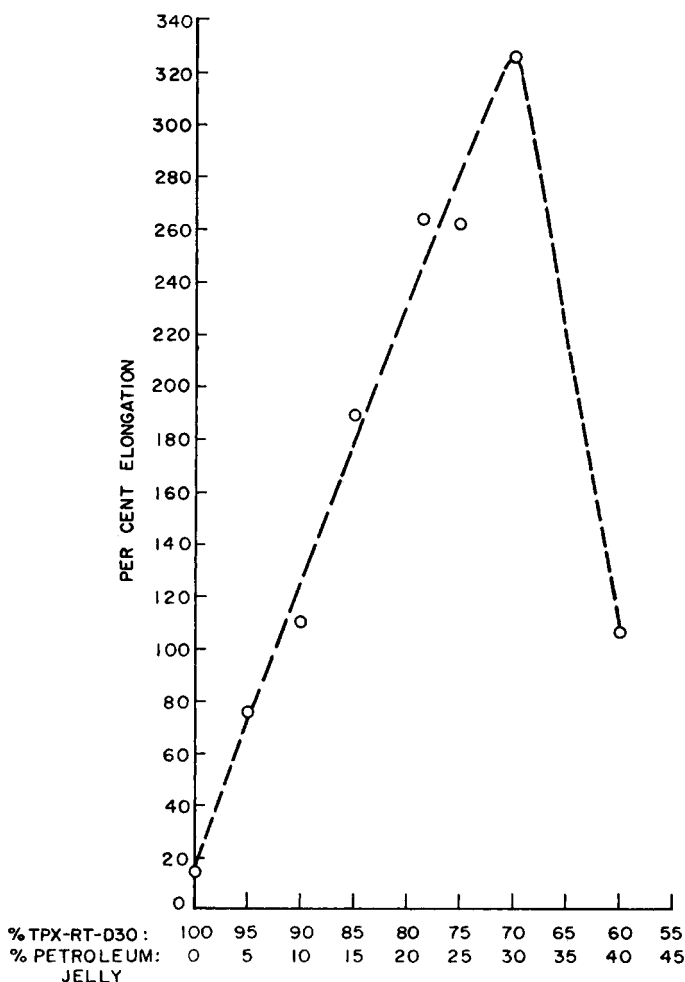


Fig. 3. Per cent elongation vs. per cent TPX-RT-D30/petroleum jelly composition.

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 (Table I, Fig. 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. The 100% TPX-RT-D30 polymer gave the same temperature

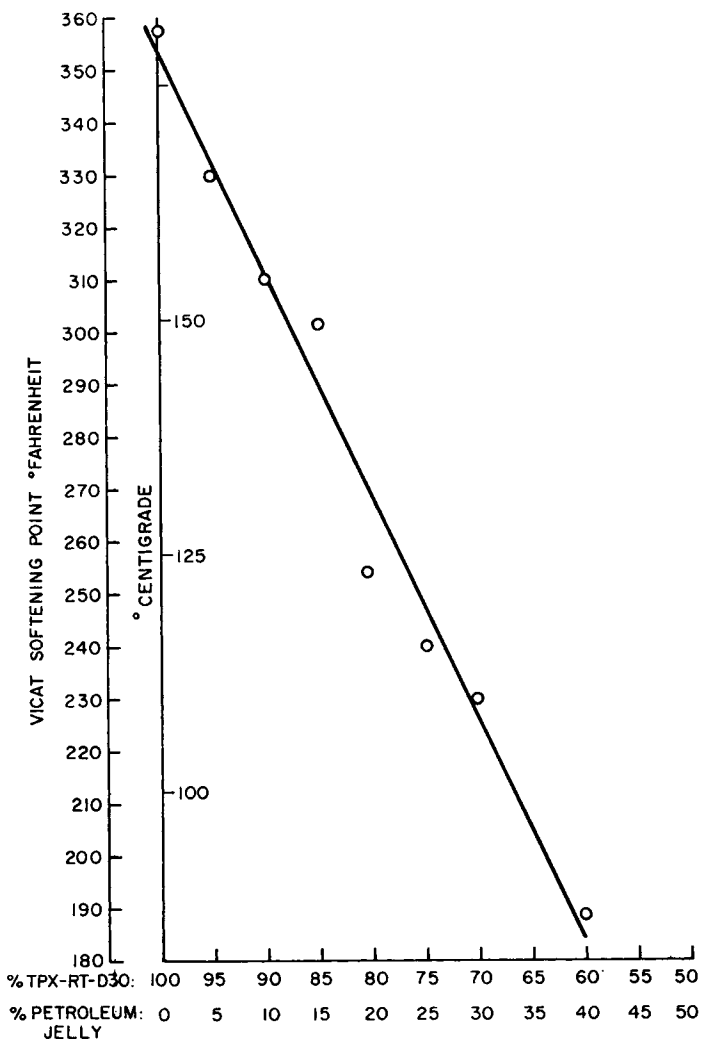


Fig. 4. Vicat softening point vs. per cent petroleum jelly/TPX-RT-D30 composition: 1 mm penetration; heating rate 50°C/hr.

(179°C) as literature values. Subsequent addition of 5% and 10% P. J. gave a decrease to 166°C and 154°C, respectively. 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 (Table I, Fig. 4).

Brittleness ASTM D746-57T

The brittleness temperature was determined on replicates of ten samples at the temperature where 50% broke on impact. The brittleness temperature of pure TPX-RT-D30 was higher than 100°F. Additions of 5% P. J. lowered the brittleness point to 19.4°C. At the 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. (Table I, Fig. 5).

Differential Thermal Analysis

The differential thermal analysis (DTA, Stone) was run at 1 in. Hg pressure with nitrogen at a heating rate of 5°C/min. The sample size averaged

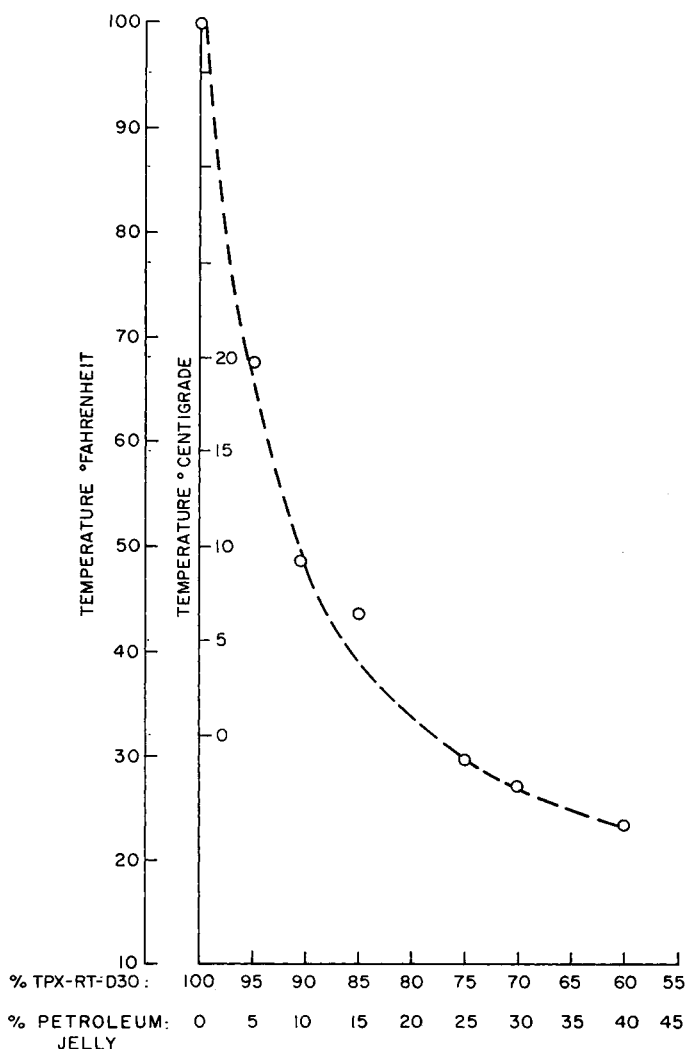


Fig. 5. Brittleness temperature vs. per cent petroleum jelly/TPX-RT-D30 composition.

TABLE II
Differential Thermal Analysis^a

TPX-RT-D30 %	P. J., %	Melting point, °C.	Melt Index ASTM D1238-62T 5 kg. at 260°C g/10 min.	Relative heat of fusion (ΔH_f)			
				Total	Corrected to 100% TPX- RT-D30	Area under curve, in. ²	Ratio, in. ² /mg
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

^a Heating rate 5°C/min, with nitrogen, at 1 in. Hg pressure.

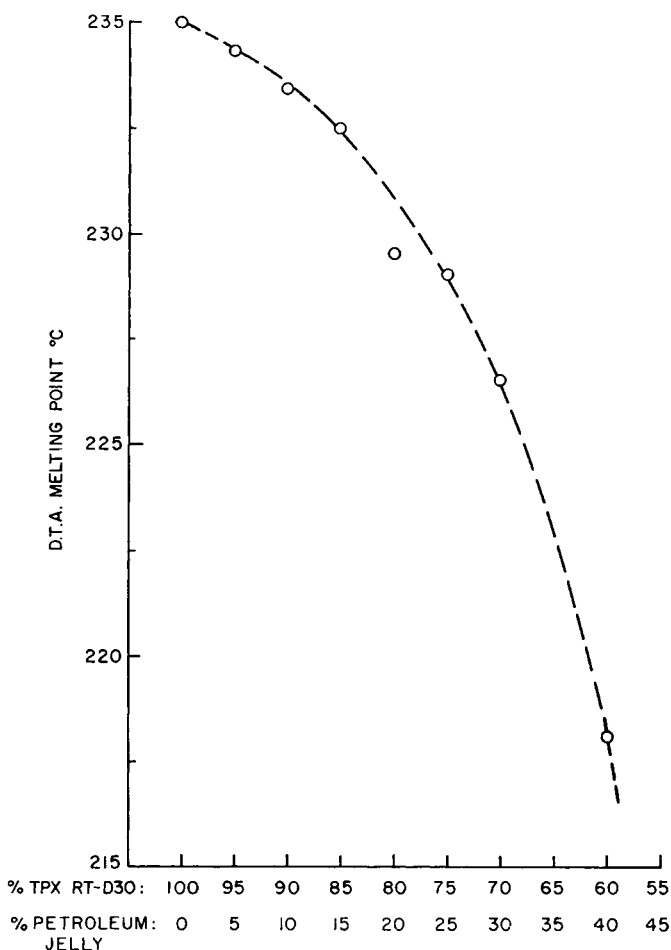


Fig. 6. DTA melting point vs. per cent petroleum jelly/TPX-RT-D30 composition.

3–4 mg (Table II). The material was run from room temperature to 250°C. No noticeable exotherms or endotherms were noticed until the melting point was reached. P. J. tested separately on a differential scanning calorimeter showed an endotherm from -5°C to $+50^{\circ}\text{C}$. The melting points of the blends ranged from 235°C to 218°C (see Fig. 6, Table II). The 100% TPX-RT-D30 polymer melted at 235°C with a single peak. Both the 5% and 10% P. J. samples had single peaks at 234° and 232.5°C, respectively. At the 15% P. J. level, a plateau region developed with a peak at 232°C. The 25% P. J. sample had a similar plateau region and a peak at 229°C. The 30% P. J. sample had only one peak region at 227°C and no plateau. The 40% P. J. had only a slight endotherm at 218°C. 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.

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 (Table II). These data are scattered and show a rise in ΔH_f up to the 30% level, with the exception of 10% and 20% P. J., which dropped below the general rise level.

Electrical Properties

Electrical measurements were made on 50-mil plaques of the blends. The samples were run at 23°C, 15 Rh, and 10⁶ Hz. The dielectric constant, ϵ' , of the blends varied from 2.13 to 2.15. The $\tan \delta$ (loss factor) $\times 10^5$ increased from 4 at 0% P. J. to 58 at 25% P. J. The resistivity of the

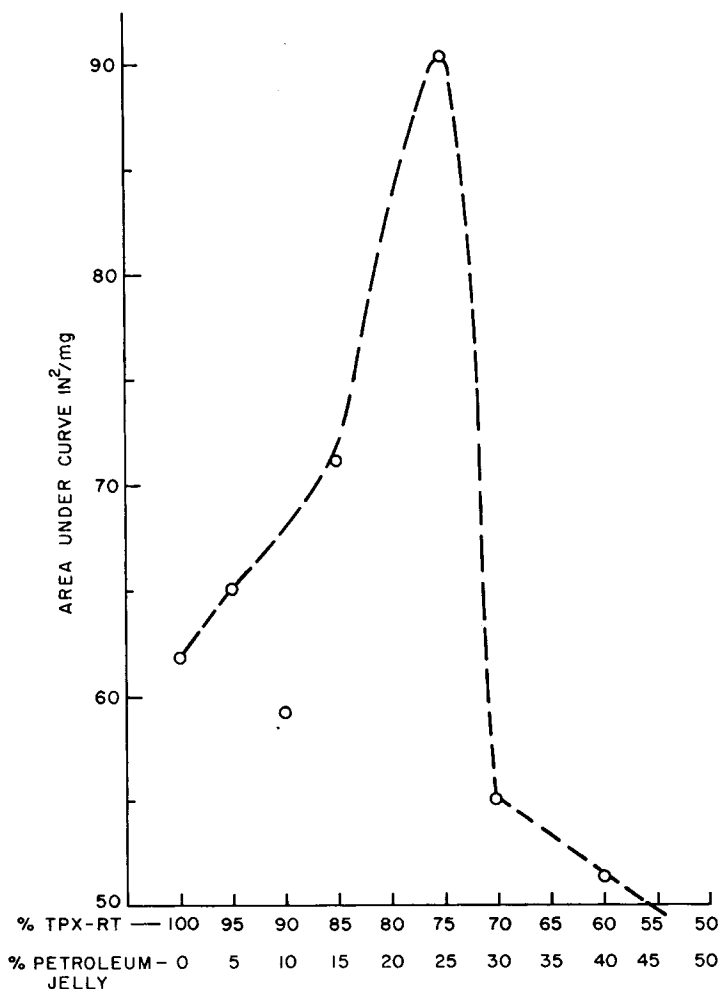


Fig. 7. Relative heat capacity (area under curve, in.²/mg) vs. per cent TPX-RT-D30/-petroleum jelly composition: heating rate 5°C/min.

blends at 100 volts, 2 min. after current was larger than 10^{16} ohms for all of the blends (Table I).

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. P. J. acts as a plasticizer. The DTA curves used by several investigators^{7,8,9} to relate the compatibility of blends of materials show that the depression of the 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. Melting point depressions are a probable indication of 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. Melting of these imperfect and smaller crystals is the probable cause of the observed 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-D30 prepared in various solvents. Frank et al.¹⁰ 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-methylpentene-1 chain in the crystal.¹¹ Crystallinity was not calculated as Ke⁸ did, using the formula $X = (H_a - H_c)/\Delta H_f \times 100$, where H_a and H_c are the enthalpies of polymer in amorphous and crystalline state, respectively, since the heat of fusion of a perfectly crystalline TPX-RT-D30 was not available. Mikhailov⁷ used the density of polyethylene/polypropylene blends as well as heat capacity change to show compatibility. Density of poly-4-methylpentene-1 with its inverted density behavior would not represent per cent 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 crystalline regions of 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 in 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 owing 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 a 4-methyl-pentene-1 polymer 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% 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 polyethylene. 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.

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Received December 23, 1968

Revised July 1, 1969