

## **Multiaxial Impact Measurements of Polypropylenes**

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### **Synopsis**

A new puncture tester of the falling weight type for conducting impact tests has been developed. With this tester, impact energy can be measured by means of an accelerometer fixed in the falling weight, and strength by a compression type load cell placed under a pot clamping a sample. Puncture behaviors are traced on an oscilloscope.

Results of puncture measurements of isotactic propylene homopolymers and copolymers with ethylene showed that impact behavior depended noticeably upon temperature. Ethylene concentration, isotacticity and molecular weight of polypropylene resins were not more effective in sustaining impact resistance in the range of temperatures below the brittle point than in bringing down the brittle point itself. It was confirmed by means of tensile impact tests that energy to failure depended not upon yield strength but upon deformation in ductile rupture, whereas in the brittle rupture case energy to failure depended primarily on the strength of the material.

Dynamic mechanical measurement was also carried out to secure the relationship between crystallinity and impact resistance.

### **INTRODUCTION**

It is generally accepted that isotactic polypropylene resins possess better rigidity, creep resistance, shrinkage, and appearance such as transparency and gloss than high density polyethylene resins.<sup>1</sup> Polypropylene has also a higher crystalline melting point which is manifested in a high heat resistance. It is of prime importance that the density of polypropylene is low, and in this respect polypropylene is the most desirable of all plastic materials.

In spite of these various merits, low impact resistance is the most serious defect and it limits the range of application of polypropylene, especially injection molded articles for heavy-duty service such as the large size containers. Propylene copolymers have been developed by incorporating certain proportions of copolymerized ethylene to improve impact resistance. Copolymers bring about lower rigidity than homopolymers but it should be noted that the improvement of impact resistance more than offsets this disadvantage and causes polypropylene resins to be in much greater demand in the injection molding field. Even copolymers containing a considerable amount of ethylene are inferior to high density polyethylene with respect to impact resistance at low temperatures.

Impact behavior can not be discussed without taking into consideration the effects of environmental temperature. Polypropylene resins are brittle at low temperatures, gradually becoming softer, more flexible, and tougher as the temperature increases, and finally reaching a stage where they soften beyond the range of usefulness. With respect to impact strength, both propylene copolymers and homopolymers are very sensitive to temperature changes near the range where their end products are in actual use. It means that their critical points lie not far from room temperature, exhibiting their greatest difference from high density polyethylenes. This is one of the reasons why evaluation of impact strength is difficult.

It is a well known fact that there is a wide variety of methods of measuring impact resistance<sup>2</sup> and several of them have been standardized. It is difficult to decide definitely which one is the most reliable for the appraisal of impact resistance of materials, much less for the correlation between specimen test rating and impact resistance of articles in service. However, the multiaxial puncture test is one approach which most nearly duplicates the way stress is actually produced.

Although knowledge of both impact energy to failure and strength is necessary to investigate the phenomena of rupture, no puncture tester with which both can be simultaneously measured has yet been found. A device must be found to obtain information on both energy and strength in puncture. A detailed description of such a device and the results of sample tests will be reviewed in this paper.

### DESCRIPTION OF THE PUNCTURE TESTER

A puncture tester of the falling weight type developed by the author's laboratory is shown in Figure 1. The height of a falling weight is chosen to obtain the impact velocities required. Three sizes of darts which may be fixed to the weight are available with spherical punch diameters of 15, 20, 25 mm (Fig. 2). Figure 2 also shows an unbonded type linear accelerometer of 100 *g* capacity mounted inside a falling weight by which puncture energy can be precisely measured. Stress is exerted on the wire gauges of the accelerometer, when the punch strikes a clamped specimen.

Because the mechanism of puncture is a multiaxial deformation, the puncture energy can not be calculated either from the area under the puncture load-time curve or the puncture load-displacement curve, the displacement of which is normal to the surface of the test specimen. Puncture energy, therefore, can not be measured by applying only the grip for puncture test to the usual tensile type impact tester because real deformations can not be observed on a recorder. The best way to measure the puncture energy is by calculating it from the change in the velocity of punch occurring when the punch impinges on the test specimen.

A force of 1 *g* is exerted upon the mass inside the accelerometer as the falling weight remains at its initial height, and the mass then becomes gravity free while the weight falls. The change in acceleration produced by

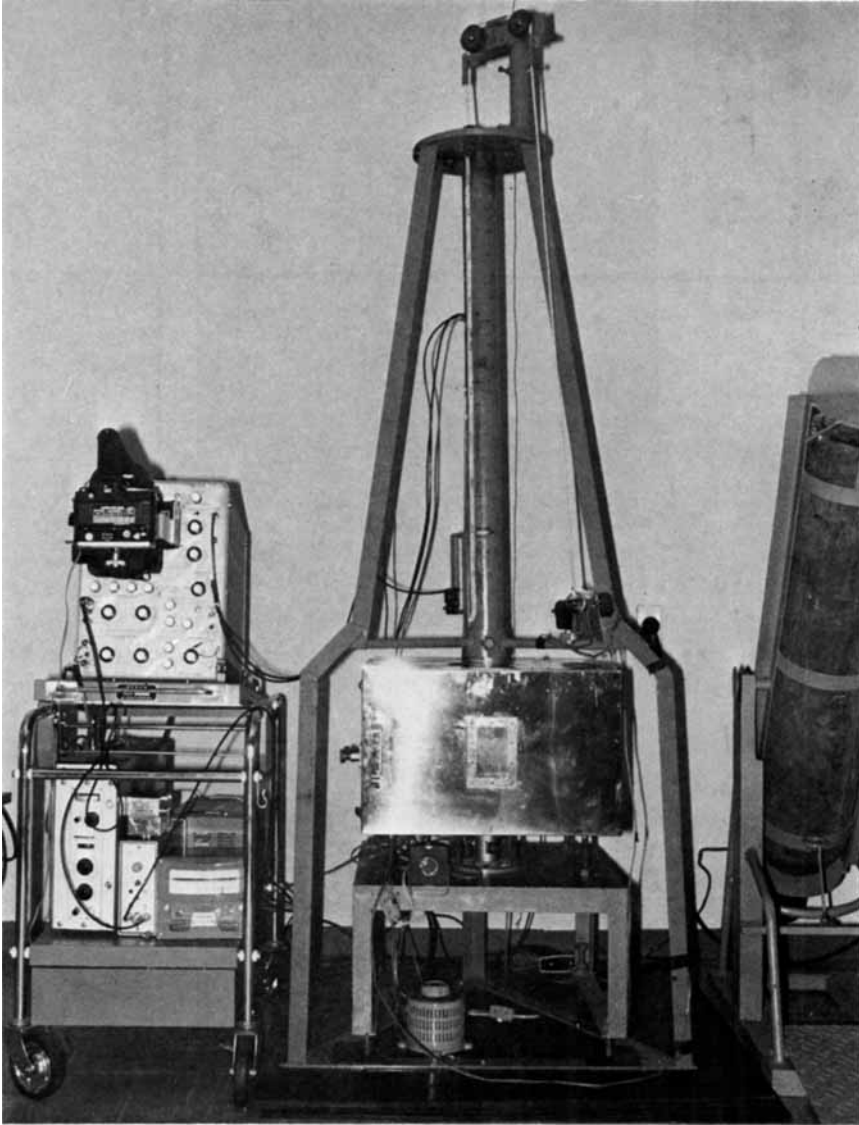


Fig. 1. General view of puncture tester.

a shock given to the punch against a specimen is traced against time on an oscilloscope. Puncture energy, or work-to-break, is calculated in accordance with

$$\text{Puncture energy} = (1/2) M(\Delta v)^2$$

where  $M$  is the total weight acting on a specimen;  $\Delta v$  the change in velocity of the falling weight from just before the punch strikes the specimen to just

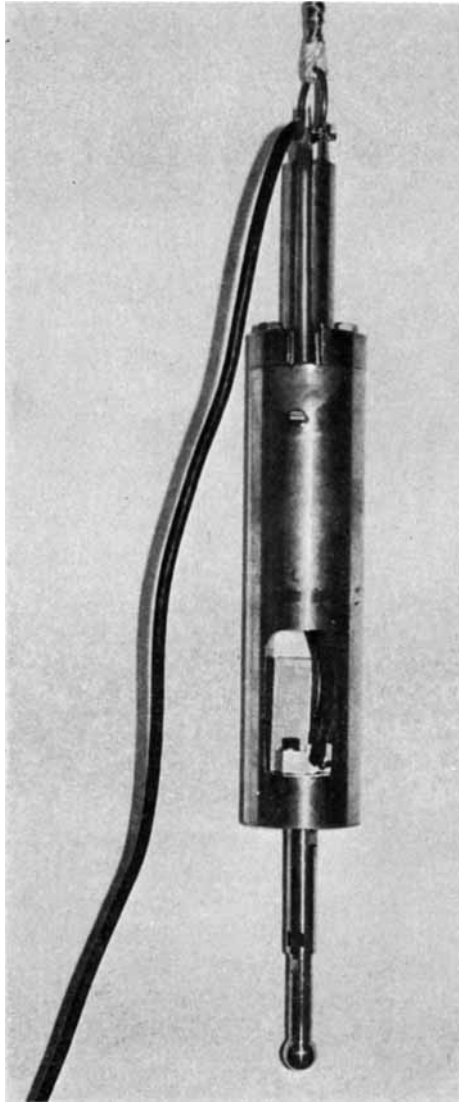


Fig. 2. A dart fixed to a falling weight with an accelerometer inside.

after the punch thrusts through.  $\Delta v$  is determined by measuring the area under the acceleration-time curve with a planimeter, as follows:

$$\Delta v = \int_{t_1}^{t_2} \alpha(t) dt$$

where  $t$  is time,  $\alpha(t)$  acceleration changing with time,  $t_1$  and  $t_2$  are times when the stress begins and when it ends, respectively.

Strength is measured by means of a compression type load cell of 500 kg capacity acting through the fixture clamping the disk specimen, 1 mm thick

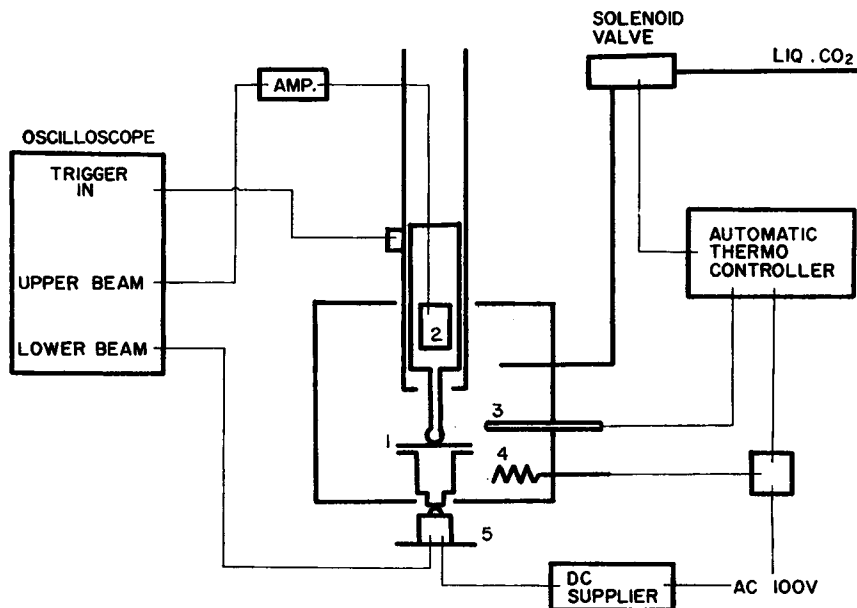


Fig. 3. Schematic diagram of puncture apparatus. (1) specimen, (2) unbonded type linear accelerometer, (3) platinum resistance thermometer, (4) heater, (5) compression type load cell.

and 9 cm in diameter. The two types of transducers, an accelerometer and a load cell, can be replaced with ones of appropriate capacities for test specimens varying in thickness from films to injection molded samples.

Figure 3 is a schematic diagram showing this new multiaxial puncture apparatus. Signals of the accelerometer are traced on the upper beam of an oscilloscope, High Gain Dual Trace, 500 kc (Iwasaki Electronic Measuring Instruments), through an amplifier with a 20 kc carrier, while those of the load cell are traced on the lower beam directly. The oscilloscope sweeps with an external trigger actuated by a switch operated by a side arm on the falling weight just before the punch hits the specimen. The dart runs through the cylindrical guide so that it will hit the center of the specimen tested. The camera shutter is synchronized electrically with the action of the device which holds and then releases the weight, in order to memorize the oscilloscope traces.

Temperature control is rapidly achieved with an accuracy of  $\pm 0.5^\circ\text{C}$  by means of an automatic thermo-controller through a platinum resistance thermometer operating in the range of  $-50$  to  $50^\circ\text{C}$  in an environmental chamber. Temperatures are obtained by liquid  $\text{CO}_2$  for the lower ranges and a heater for the higher ranges (Fig. 4). The disk specimen, with an area 5 cm in diameter exposed, is clamped tightly to the pot, the bottom of which is kept in contact with the head of the load cell, as shown in Fig. 5. The pot is made of titanium in order to prevent it from reducing the natural frequency of the transducer system.

It should be remembered that the natural frequencies of the transducer systems must be high enough to be able to follow the impact behaviors instantaneously without any delay which causes inaccurate measurements. Natural frequencies of each transducer system, including all fixtures and

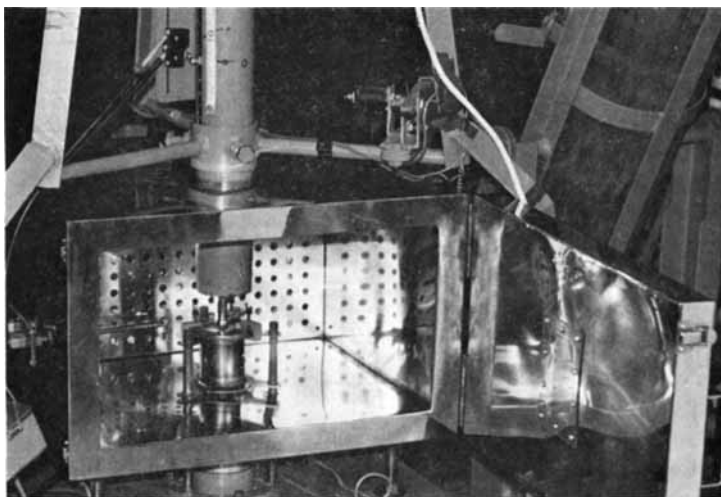


Fig. 4. Inside view of an environmental chamber.

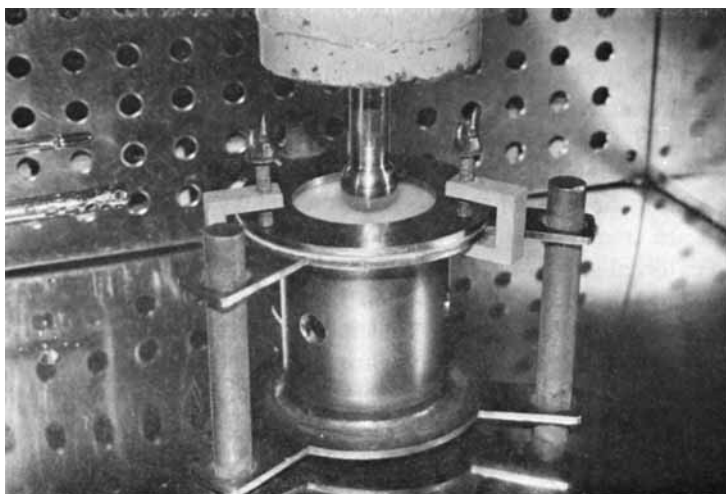


Fig. 5. Close-up of a clamped specimen with a spherical punch.

transmitting media, were approximately 3.3 and 2.0 kc for accelerometer and load cell, respectively. These were adequate for measuring the behaviors of impacts in which the rise time of stress was 3 to 5 msec, so long as polypropylenes were held in the range of temperatures mentioned above.

## EXPERIMENTAL

Propylene homopolymers and copolymers with ethylene available on the market were used. All the test specimens were prepared by compression molding in a laboratory press at 200°C in order that residual molecular orientation might not occur. Samples were quenched rapidly by transferring them to a cold press kept at 25°C. The disk specimens 9 cm in diameter were cut from sheets 1 mm thick. Both work-to-break and yield strength divided by thickness were represented by average values for the 9 samples so that dispersion of measurements would not lead to misleading results.

Tensile impact measurements were carried out at a speed of 3.6 m/sec, using a Plastechon 581.<sup>3</sup> A 1.2 mm thick, 5 mm wide dumbbell specimen was clamped with a space of 20 mm between grips.

The apparatus for dynamic mechanical measurements employs forced nonresonant procedure equipped with stress and strain detectors and a phase difference indicator, Visco-Elastic Spectrometer (Iwamoto Manufactory). The test specimens consisted of 35 × 3 × 0.2 mm rectangular pieces. The distance between clamps was 20 mm and static deformation was 1%. Chamber air temperature was controlled by a heater or by liquid nitrogen.

## RESULTS AND DISCUSSION

The preliminary experiments indicated that the stress-strain behaviors of isotactic propylene homopolymers and copolymers in impact depended noticeably upon the test temperature and very little upon the test speed. From this point of view the effects of temperature on impact resistance were investigated in this study. The heights and the slopes of the curves of energy to failure and yield strength against temperature were influenced appreciably by the diameter of the spherical punch impinging on the test specimen. Of three sizes of punches, a diameter of 20 mm was most suitable for evaluating polypropylene.

A string was provided for positioning the dart at a drop height of up to approximately 1 m from the impinging surface of the dart head to the surface of the test specimen. Dart drop height of up to 1 m provides a speed of up to approximately 4.4 m/sec at impingement. It is impossible to control the speed below 1 m/sec corresponding to a drop height of 5 cm because of the difficulty in securing accurate speed measurements and sufficient potential energy to break the test specimen. The change of speed possible here had no effect on impact behavior. The falling dart, therefore, was fixed at a drop height of 45 cm so that impact velocity would be 3 m/sec, convenient for balancing the speed and the weight. In addition to having a sufficient mass to break the test specimen, the weight must not be so heavy that its impingement against the test specimen will not produce a discernible change in dart speed. Certain experiments confirmed the weight of 6 g as the most suitable for testing both propylene

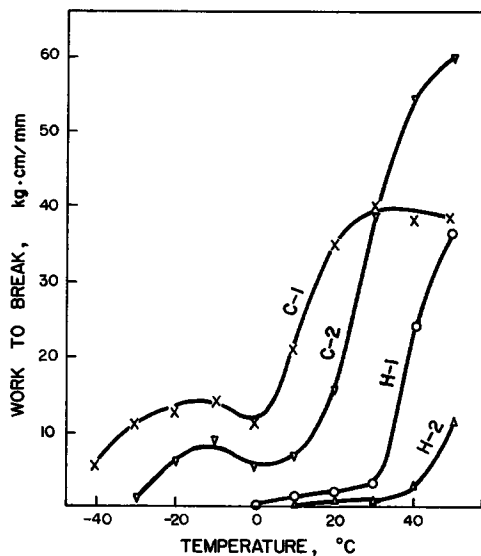


Fig. 6. Variation of puncture energy with temperature for polypropylenes.

homopolymer and copolymer in the temperature range containing the transitional region in which lies the boundary of energy levels.

Work-to-break vs. temperature curve shows that there are both ductile and brittle regions<sup>4</sup> at the temperatures measured (Fig. 6). Puncture energies decrease sharply as the temperature passes from the ductile to the brittle region, and the intermediate region is a so-called transitional region where fluctuation of measurements is great and double peaks sometimes appear in the distribution curve. Typical oscilloscope traces in each

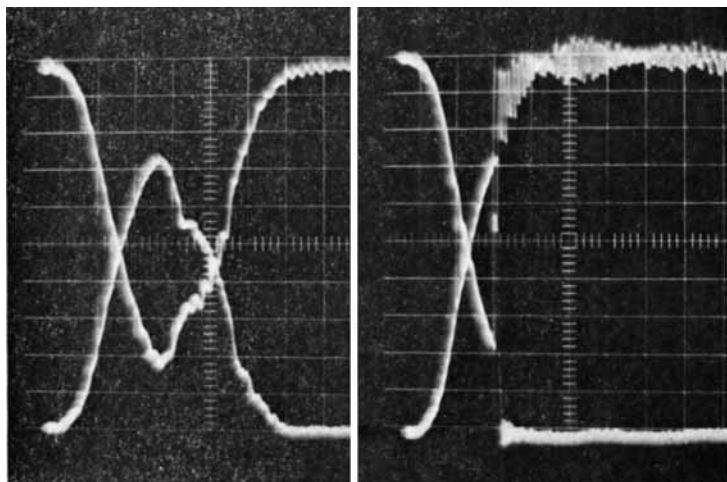


Fig. 7. Typical oscilloscope traces: upper beam showing acceleration-time, lower beam load-time. (a) ductile puncture, (b) brittle one.



ductile and brittle region are shown in Figure 7. Load-time curves were traced on the lower beam and their peaks were considered to be yield strength at impact, while work-to-break values were calculated from the areas bounded by upper beam traces as mentioned previously. Since the abscissa of these traces is time, no deformation of the test specimen can be observed, but it may be assumed that time is roughly proportional to displacement. So, from Figure 7, there is no doubt that high puncture energy in ductile failure is attributed to high deformation rather than to stress.

Some fundamental properties of polypropylenes tested are shown in Table I, where the term C represents propylene copolymers with ethylene, while H represents homopolymers. As shown in Figure 6 where polypropylenes with approximately the same isotactic indexes and densities are compared, copolymers maintain puncture resistance up to a considerably lower temperature, and of the copolymers, C-1 with the higher ethylene concentration maintains a higher energy level at a lower temperature. Although C-2 with a lower ethylene concentration loses its impact resistance at  $-30^{\circ}\text{C}$ , C-1 maintains it even at  $-40^{\circ}\text{C}$ . If the very first temperature where the puncture energy curve dips sharply with decreasing temperature is regarded as its brittle point, increasing ethylene concentration causes the brittle point to shift to a lower temperature, that is, the brittle point of C-2 shifts by approximately  $20^{\circ}\text{C}$  as compared with H-1 homopolymer, and that of C-1 is separated by approximately  $10^{\circ}\text{C}$  from C-2.

The difference in impact resistance between H-1 and H-2 is attributed to the difference in their melt indexes.<sup>5</sup> An increase in molecular weight slightly lowers rigidity, as can be seen from the yield strength in the usual static test represented by YS-static in Table I, but improves inherent impact resistance. Hence the brittle point is reduced by approximately  $10^{\circ}\text{C}$  according as the melt index decreases from 7.9 to 3.1. The rates of slopes from the ductile to the brittle regions are scarcely dependent upon either molecular weight or ethylene concentration.

TABLE I  
Fundamental Properties of Polypropylenes used in tests

	ethylene, <sup>a</sup> mol %	MI, <sup>b</sup> g/10 min	Iso. Ind., <sup>c</sup> %	D <sup>23d</sup>	YS-static <sup>e</sup> , kg/cm <sup>2</sup>
C-1	25	1.5	95.5	0.910	250
C-2	14	1.4	94.4	0.909	260
C-3	14	2.6	79.0	0.897	170
C-4	14	3.4	92.7	0.907	230
H-1	—	3.1	96.4	0.912	280
H-2	—	7.9	95.7	0.912	310

<sup>a</sup> Ethylene concentration: Infra-Red Method.

<sup>b</sup> Melt index: ASTM D-1238-65 T, 2.16 kg,  $230^{\circ}\text{C}$ .

<sup>c</sup> Isotactic index: insoluble matter in boiling n-heptane, based on ISO.

<sup>d</sup> Density: ASTM D-1505-63 T, density gradient technique.

<sup>e</sup> Yield strength: ISO type-I dumbbell, tension speed 50 mm/min.

As contrasted with puncture energy, Figure 8 shows the effect of temperature on the puncture yield strength obtained from the peak of load-time curve. Contrary to the work-to-break, yield strengths of copolymers increase once with falling temperature, which involves the increase of rigidity, and then they decrease sharply through maximum values. Yield strengths of homopolymers tend to decrease gradually from 50°C with falling temperatures and apparently have no peaks. But it can be reasonably expected that their peaks also would be found at the higher temperature if they were examined in a wider range of temperatures. All peaks of yield strengths shown here are found at approximately 20–30°C lower

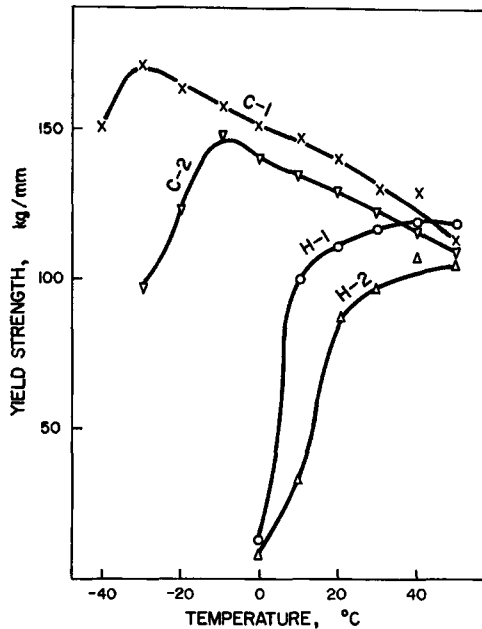


Fig. 8. Variation of puncture yield strength with temperature for polypropylenes.

temperatures than their brittle points determined from their puncture energy curves. From the fact that energy is determined as the product of strength and displacement, this discrepancy is presumed to be attributable to the strength still left and lack of deformation capacity at the temperatures below the brittle point. The reason why the small peak of puncture energy at temperatures below the brittle point occurs only in copolymers can be explained as follows: namely, in that range of temperatures impact failure occurs with a small deformation up to yield point that scarcely varies for the entire range of temperatures, while yield strength still increases with decreasing temperatures. Therefore, the strength level at that very sharp peak must contribute to raising the puncture energy peak slightly.

It was confirmed by another impact test, a tensile type using Plastechon 581, that the level of the deformation was always constant, independent of temperature so far as its failure was due to brittleness. The effect of the deformation-to-failure and yield-strength on the energy-to-failure was investigated on the basis of the results of tensile impact measurements. The correlations between them are illustrated in Figure 9, which shows that the behaviors of tensile impact at 20 and  $-10^{\circ}\text{C}$  are typical of ductile and brittle failures, respectively. Each plot fits the lines well except C-3 which is much different from the others in point of a larger quantity of *n*-heptane soluble matter and hence lowness of static yield strength. It is

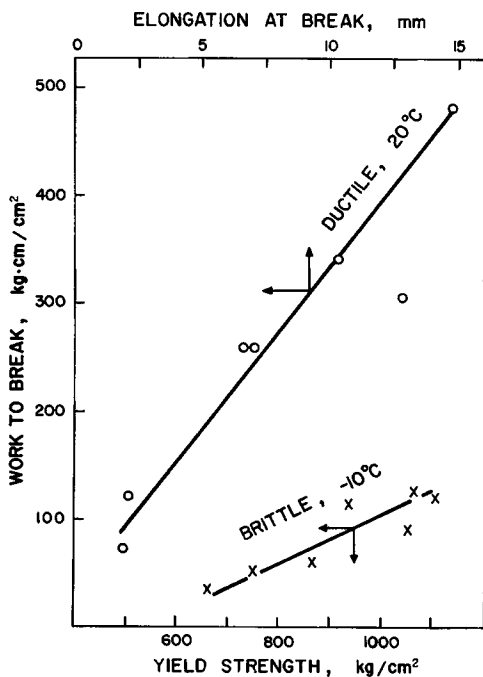
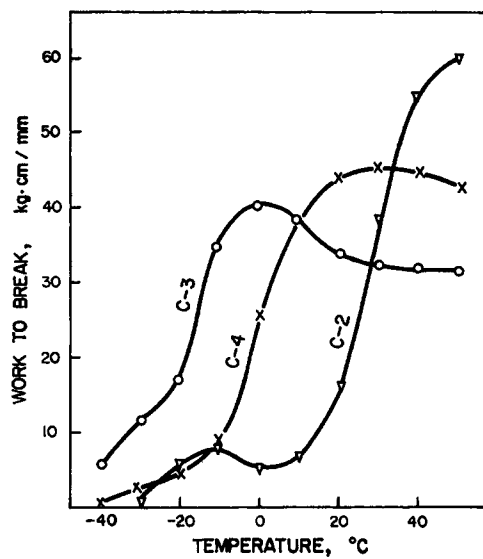


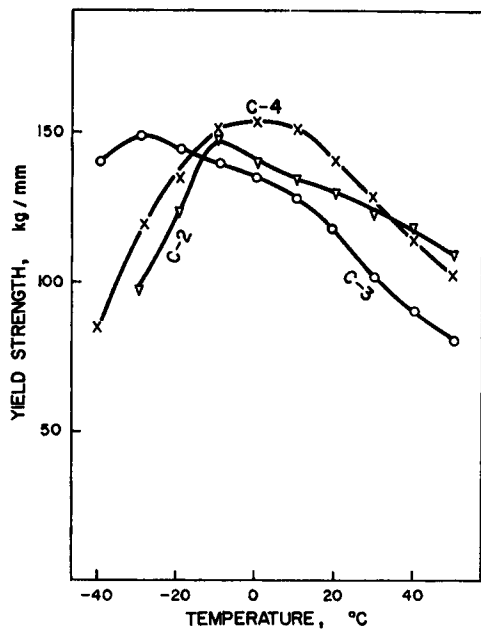
Fig. 9. Correlation of the energy to failure with deformation or yield strength by tensile impact.

understood that the energy to failure depends not upon yield strength but upon deformation to failure in ductile rupture, while, in brittle rupture, it depends not upon deformation but upon strength.

Figure 10 shows the effect of quantity of *n*-heptane soluble matter on puncture impact for propylene copolymers with the same ratio of ethylene concentration. Isotactic index represents the percentage of the resin that is insoluble in boiling *n*-heptane. The percentage of isotactic polymer will be reflected in the degree of crystallinity but this does not mean that there is a simple numerical relationship between them. In copolymers, the quantity of *n*-heptane extractable fraction depends noticeably upon distribution of ethylene units. Crystallinity is also affected by such



(a)



(b)

Fig. 10. Effect of *n*-heptane soluble fraction on puncture resistance for propylene copolymers with same ethylene concentration. (a) puncture energy with temperature, (b) puncture strength with temperature.

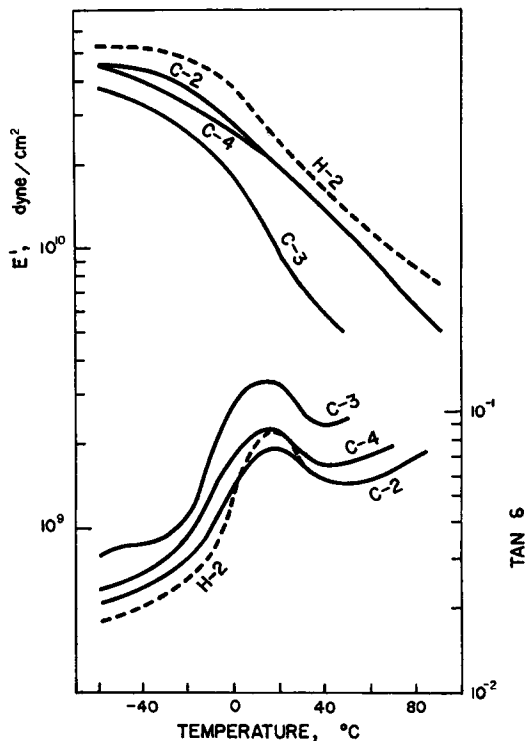


Fig. 11. Temperature dependence of complex dynamic tensile modulus of polypropylenes.

factors, other than the percentage of isotactic material, as heat history and molecular weight. Each isotactic index of three grades illustrated in Figure 10 appreciably corresponds to its density and static yield strength.<sup>6</sup>

Results of measurements proved that isotactic index was as important as ethylene concentration for impact resistance and it was no more effective in sustaining impact resistance at the temperature range below the brittle point than in bringing down the brittle point itself. Another point worth noticing is that C-3 and C-4 having isotactic indexes of 79.0 and 92.7, respectively, have broad yield strength peaks, especially so is C-3. It seems that this is attributed to the larger portion of the noncrystalline fraction, the segmental motion of which is to be frozen at a certain lower temperature. In this case, it is believed that the larger portion of the noncrystalline fraction was caused by copolymerized ethylene units.

For further verification,<sup>7</sup> dynamic mechanical measurement was carried out under a constant deformation of 0.1% at a vibrational frequency of 100 c/s. Complex dynamic tensile modulus  $E^*$  is represented by

$$E^* = E' + iE''$$

where  $E'$  is the component of stress in phase with the strain divided by the strain and is called the real component of the dynamic modulus or the

storage modulus,  $E''$  is the component of stress which is  $90^\circ$  out of phase with the strain divided by the strain and is the imaginary component of the dynamic modulus or the loss modulus. The ratio  $E''/E'$  is the tangent of phase angle  $\delta$  by which the stress leads the strain and is called the loss tangent. Temperature dependence of dynamic storage modulus,  $E'$ , and loss tangent,  $\tan \delta$ , is shown in Figure 11. It is evident that all peaks of loss tangent occur at temperatures from 10 to  $20^\circ\text{C}$  and, the greater the noncrystalline portion, the broader and the higher the peaks become. These peaks correspond to Glass I or  $\beta$ -peak which occurs in amorphous regions and is due to segmental motion of the chain backbone involving approximately 30 monomer units.<sup>8,9</sup> The results of dynamic mechanical measurements also proved that the amorphous portion, and hence impact resistance, increased as isotactic index decreased. Storage modulus of homopolymer H-2 is the highest over the temperature range investigated and those of copolymers are ranked in accordance with their levels of isotactic index. Although, in rigidity, homopolymers gain an advantage over copolymers, the converse is true in impact resistance.

The interactions of many factors influencing crystallinity and conformation of spherulites, and hence impact resistance,<sup>10</sup> are also found in processing and finishing conditions. These processing and finishing conditions which complicate the evaluation of impact resistance of polypropylene resins should be further investigated in detail.

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