JOURNAL OF APPLIED POLYMER SCIENCE VOL. 11, PP. 1931–1940 (1967)

Effect of γ-Radiation on the Thermal Conductivity of Polypropylene

J. N. TOMLINSON* and D. E. KLINE, *Nuclear Engineering Department, The Pennsylvania State University, University Park, Pennsylvania*

Synopsis

The effect of ^{60}Co γ-radiation on the thermal conductivity of polypropylene (PP) has been studied over the temperature range 0–160°C. for radiation doses of 600 and 1800 Mrad. The conductivity of unirradiated specimens rises from 4.5×10^{-4} cgs units (cal./cm.-sec.-°C.) at 0°C. to 4.8×10^{-4} cgs units at 80°C. and subsequently decreases with temperature to a value of about 3.1×10^{-4} cgs units at 160°C. Upon irradiation to 600 Mrad the thermal conductivity is lowered over the 0–150°C. temperature range. Above 90°C. the conductivity decreases with temperature and becomes relatively constant at 3.4×10^{-4} cgs units from 120 to 160°C. Differential scanning calorimeter (DCS) measurements from 30 to 200°C. show that irradiation to 600 Mrad lowers the energy associated with crystalline melting and shifts the endotherm melting peak from about 160 to 105°C. Irradiation to 1800 Mrad results in additional lowering of the thermal conductivity over the 50–160°C. range, a further decrease in area of the endothermic peak and a shift of its maximum peak position to about 75°C. The effects of radiation on the thermal conductivity of polypropylene are compared and correlated with the observed effects of radiation on the dynamic mechanical behavior.

Introduction

Studies have indicated that structural changes initiated by nuclear irradiation can be effective in altering the thermal conductivity of a polymer. An investigation of polyethylene (PE) irradiated to doses ranging from about 100 to 3000 Mrad has shown that prominent changes in the thermal conductivity occur at all temperatures in the range 0–170°C.[1] These changes are postulated to be related to radiation-induced defects in the crystallites and a lower per cent crystallinity and extensive intermolecular crosslinking[1] which occur upon irradiation.

Important physical property changes have been previously noted in the properties and structure of polypropylene (PP) subjected to moderate doses of nuclear radiation.[2] Changes in the dynamic mechanical properties (DMP)[3] further suggest that alterations would occur in the thermal conductivity behavior of PP irradiated to doses up to a few thousand Mrad, as compared to unirradiated PP. It is the purpose of the present paper to report on the effect of irradiation on the thermal conductivity of isotactic polypropylene and to suggest some explanations for the observed behavior.

* Present address: HRB-Singer, Inc., State College, Pennsylvania.

Experimental

The isotactic polypropylene (Profax 6523, Hercules Powder Co.) used for these experiments was received in the form of $^1/_2$-in. diameter extruded rods. Profax Type 6500 resins are defined[4] as having a melt flow rate of 2–4 (ASTM D-1238, measured at 230°C.). The weight-average molecular weight $\bar{M}_w$ of the as-received material was reported[4] to be about 300,000 and the ratio of $\bar{M}_w/\bar{M}_n$ is typically 6 to 7 as determined by gel permeation chromatography. The crystallinity was estimated[4] to be 60%.

Thermal conductivity measurements were carried out by using the radial heat flow method reported earlier by Kline[5] and Tomlinson et al.[1] This method consists of using a cylindrical electric heating element, surrounded by a tubular sample and a coaxial heat sink. Temperatures were stabilized to provide a steady-state measurement of the temperature difference ΔT across the wall of the sample. Using this temperature difference and the power, Q, supplied by the heating element, the conductivity k was calculated by the relationship

$$k = Q \ln (D/d)(2\pi L \Delta T)$$

where L is the sample length, and D and d are the outside and inside sample diameters, respectively.

Test samples 6 in. in length were machined to approximate inside and outside diameters of 0.250 and 0.375 in., the exact dimensions being determined by a close fit on the axial heating element and the coaxial heat sink. The power level was maintained at about 1 w., resulting in a temperature differential of 2–3°K. Each test sample length was composed of three 2-in. sections for ease in machining and loading.

Sample densities reported herein were measured by a displacement method with ethyl alcohol. Calorimetric measurements were made on a Perkin-Elmer differential scanning calorimeter (DSC). The scanning rate was 5°K./min. over the entire temperature range of 310–470°K. After testing the first time, each sample was immediately cooled to 310°K. in a period of about 6 min. It was then rerun over the temperature range 310–470°K. During scanning, a positive pressure of N_2 was maintained in the sample chamber. The calorimeter was not calibrated on an absolute basis, thus areas under the endotherm curves represent relative values. Area estimates obtained by using a planimeter are given in Table I along with other pertinent data.

Irradiations were carried out on the as-received rods in the National Bureau of Standards ^{60}Co radiation source at an approximate average dose rate of 9.4×10^6 r./hr. This is equivalent to 9.2×10^6 rad/hr. in PP. The material was positioned near the center of the source, but some variations in dose rate (several per cent) occurred over the length and breadth of the samples because of axial and radial variations in dose rate within the source volume. On a relative basis, the average doses received are believed to be accurate to within a few per cent. On an absolute

TABLE I
Characteristics of Polypropylene Specimens

Specimen	Radiation dose, Mrad	Density, g./cc.[a] After irradiation	Density, g./cc.[a] After conductivity test	Endotherm area (relative)	Temp. of endotherm peak, °K.[b]
A	0	0.907 (as-received)	0.919	First run 100	434
				Rerun 100	434
B	600	0.896	0.887	First run 73	377
				Rerun 23	366
C	1800	0.889[c]	0.882	First run 15	336
				Rerun 0	No max.

[a] As-received density, 0.907 g./cc.; temp. of density measurements, 27°C.; specimen size, 3/8 in. OD; 1/4 in.; 6 in. long.

[b] Endotherm peak temperature is not usually considered to be the melting point.

[c] An additional sample irradiated to about 1100 Mrad had a density of 0.885 g./cc. after irradiation, indicating that a minimum in the density occurs with increasing dose.

basis the doses received are considered to be accurate to within about ±10%. Total doses received by each specimen are given in Table I.

Results

Data for the thermal conductivity behavior of the as-received polypropylene (sample A) and the two irradiated polypropylene samples (B and C) are presented in Figure 1. Conductivity of the unirradiated PP is characterized by a slight rise from a value of 4.5×10^{-4} cal./(cm.-sec.-°C.) near 275°K. to a high of about 4.8×10^{-4} cal./(cm.-sec.-°C.) at 355–60°K., followed by a decrease to about 4.2×10^{-4} cal./(cm.-sec.-°C.) near 420°K. Beyond this temperature the thermal conductivity drops precipitously to about 3.2×10^{-4} cal./(cm.-sec.-°C.) at 435°K. Slight dips occur in the data near 290, 330, 375, and 395°K.

The thermal conductivity data of polypropylene irradiated to a dose of 600 Mrad are somewhat lower over essentially the whole temperature range than that for unirradiated polypropylene. From 275°K. the conductivity value rises from 4.1×10^{-4} cgs units to a relatively constant value of 4.2×10^{-4} cgs units over the temperature range 280–360°K. Near 325°K. there is a slight dip in the curve, followed by a rise to slightly more than 4.2×10^{-4} cal./(cm.-sec.-°C.) near 360°K. Beyond 360°K. the thermal conductivity drops rather rapidly. Near 390°K. the value abruptly levels off at 3.4×10^{-4} cgs units.

Data for sample C, which was irradiated to a dose of 1800 Mrad are again significantly lower than that of sample A over the entire temperature range. Beginning at 4.0×10^{-4} cgs units at 275°K. the curve rises to almost 4.2×10^{-4} cgs units at 310°K. These values are rather close to

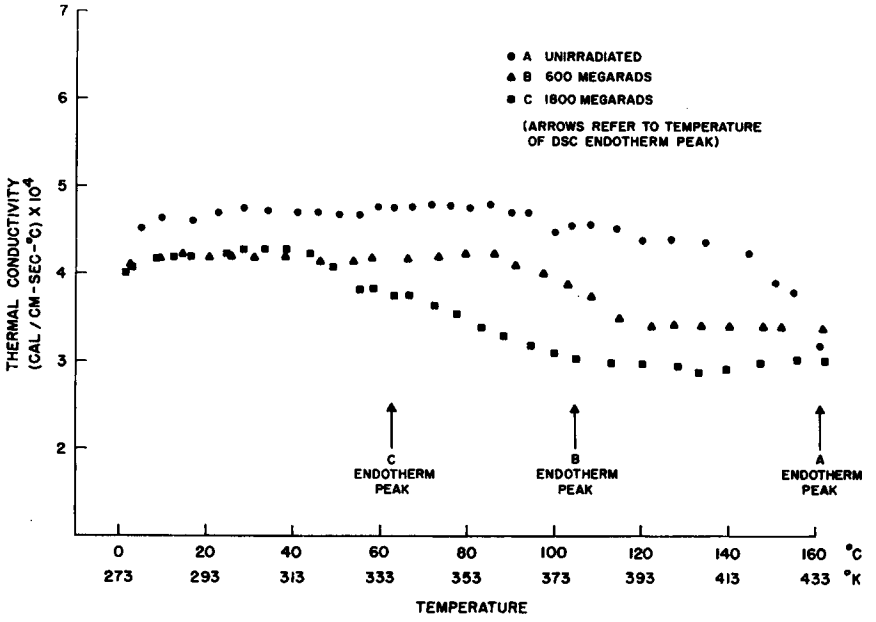

Fig. 1. Thermal conductivity as a function of temperature for unirradiated and for γ-irradiated polypropylene.

those for sample B in this region. Beyond 310°K. the conductivity monotonically decreases with slight modulations to about 2.9×10^{-4} cal./(cm.-sec.-°C.) at 405°K. This is followed by a very slight rise at higher temperatures.

The DSC data for the samples are presented in Figure 2. It is noted that the endotherm peak associated with crystallite melting occurs near 434°K. for sample A and that of the rerun occurs at approximately the same temperature. The endotherm for sample B (irradiation dose of 600 Mrad) occurs near 377°K. and is substantially lower in height. Upon retesting (B rerun) the results indicate that the peak is further reduced in size, broadened, and shifted downward in temperature to about 366°K. Sample C, irradiated to 1800 Mrad, has a small endotherm peak near 336°K. and a small broad endotherm extending to higher temperatures. Sample C rerun showed no evidence of a peak in the temperature range 310–470°K.

Relative areas under the endotherm peaks are presented in Table I. It is noted that the endotherm areas decrease with irradiation and that reruns of the DSC tests of the irradiated samples taken previously to temperatures beyond the crystalline melting temperatures resulted in further reductions of the endotherm areas.

Discussion

It has been observed that partially crystalline polymers tend to have a higher conductivity than amorphous polymers. For instance, it has been

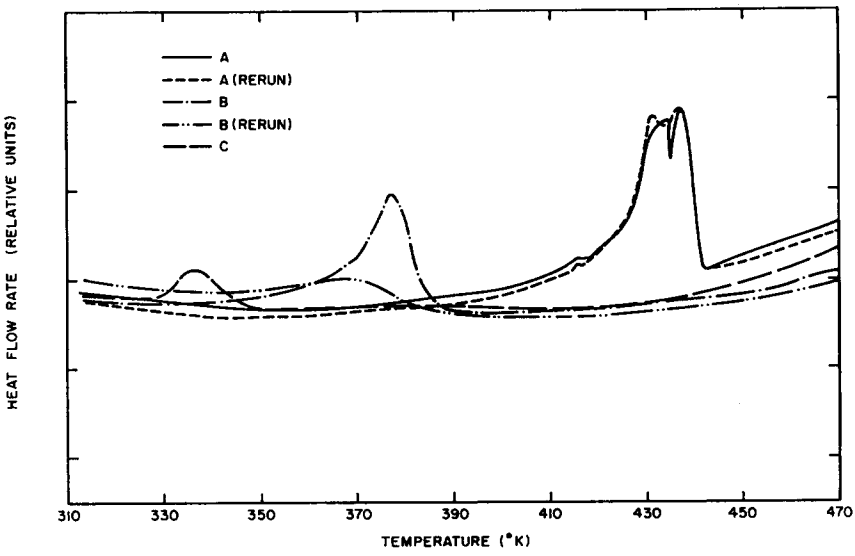

Fig. 2. Differential scanning calorimeter data for unirradiated and for γ-irradiated polypropylene specimens as a function of temperature.

reported that polytetrafluoroethylene (PTFE), poly(hexamethylene adipamide), and polyethylene (PE) have thermoconductivity values of approximately 6×10^{-4} cgs units or higher between room temperature and their crystalline melting points[5,6] while on the other hand amorphous polystyrene has a typical conductivity of slightly more than 3×10^{-4} cgs units[5,7] and polymerized epoxy resins have a thermal conductivity of slightly more than 4×10^{-4} cgs units,[5] even though the latter has considerable crosslinking. The higher conductivity of partially crystalline polymers is usually attributed to the higher conductivity of the crystallites, the combination of crystalline and amorphous regions leading to a higher overall conductivity than would be observed in a purely amorphous arrangement.

The general thermal conductivity behavior of unirradiated polypropylene (sample A, Fig. 1) is consistent with that reported for other partially crystalline polymers and is similar to that of unirradiated polyethylene. From room temperature upward toward the crystalline melting point the overall conductivity level is typically higher than that of principally amorphous polymers, and, as the melting points of the crystalline regions are approached, the conductivity begins to fall from a high of 4.8×10^{-4} cgs units to the conductivity level that unirradiated PP would presumably have in the melt. From DSC measurements (Fig. 2) it is confirmed that the crystallites in the as-received material probably begin to melt near 400°K. and continue to about 440°K. The conductivity curve in Figure 1 suggests that the conductivity is still falling rapidly at 435°K. where the last datum point was recorded.

The conductivity behavior of the unirradiated PP shows some fine struc-

ture between 280 and 400°K. Slight humps occur near 285 and 300°K., or approximately in the same temperature region at which the main amorphous relaxation is noted to occur in studies of the dynamic mechanical properties (DMP) of PP.[3] Since the thermal conductivity test is essentially a static or low frequency test, it would seem logical to associate the large DMP peak at 300°K. (of the order of 1 kc.) with the hump in the thermal conductivity near 285°K. It is noted that the conductivity change is very slight in magnitude, whereas the mechanical relaxation at this temperature region is reported to be very prominent.[3] This type of behavior has also been observed in other polymers where mechanical relaxations are observed in the same temperature region as the thermal conductivity measurements (for instance polytetrafluoroethylene, polyethylene, epoxy systems, polyamides, etc.).[1,5,8]

A noticeable drop in the thermal conductivity behavior of the as-received material also occurs near 375°K. A mechanical relaxation, which appears as a shoulder in the damping curve, occurs near this temperature region in dynamic mechanical studies.[3] It seems reasonable that while transitions in already amorphous or disordered regions might produce a slight rise in conductivity, motion at transitions in crystalline regions ought to produce a drop in k values, since the molecular motions are a disordering influence and tend to hinder the flow of energy in the previously more highly ordered crystallites. As such, the drop in k value near 375°K., which is related to the shoulder in the mechanical damping curve, may itself be an indication that the mechanical transition is one associated with moelcular motion and disordering processes in crystallites.

DMP studies[3] and the work of Chappell et al.[9] indicate that high-energy irradiation of polypropylene produces crosslinking into a three-dimensional network accompanied by the destruction of the crystallites and a loss of rigidity. At lower doses where the crystallites were still present, it was reported that heat treatments at temperatures above the crystalline melting points tended to cause a decrease in density, while at higher doses, where the crosslinking density was higher and very few crystallites existed, a similar heat treatment caused an increase in density. The results reported herein (samples B and C of Table I) show that post-irradiation testing at temperatures beyond the crystalline melting temperature causes the density to decrease. The highest doses, required to simulate the irradiation conditions of the work by Sauer et al.,[3] were not attained. For the present work, it should also be noted that the samples have been subjected to some expansion pressure during testing by confinement within the metal tubes while heating.

Sample B (irradiation dose about 600 Mrad) shows a decidedly lower conductivity as compared to sample A. This is probably a direct result of a reduced degree of crystallinity as indicated by the DSC graph. From a value of about 4.2×10^{-4} cgs units up to 360°K., the conductivity begins to fall rapidly toward a value of about 3.4×10^{-4} cgs units near 390°K. This drop is probably associated with the onset of melting of the remaining crys-

tallites. From Figure 2 one can observe that the melting endotherm peak for sample B occurs in the same region as the drop in the thermal conductivity curve. Beyond 390°K. the conductivity for sample B is nearly independent of temperature. This behavior is similar to that reported for other polymers in the melt.[1,10] It is of interest to note that the conductivity level of sample B in the range 390–430°K. is somewhat lower than that reported for irradiated polyethylene[1] in the temperature region beyond the crystalline melting temperature.

The data for sample C indicate that the conductivity level from about 275°K. to about 325°K. is largely unchanged from that of sample B. Beyond this temperature, however, the conductivity decreases rather rapidly, reaching a level of about 3×10^{-4} cgs units at 375°K. From the DSC data, it is observed that the maximum in the endotherm occurs near 336°K., suggesting that the initial drop in conductivity near 325°K. is associated with the onset of crystallite melting. Closer analysis of the DSC data (Fig. 2) shows that a slight endothermic peak continues up to about 410°K., paralleling the continuing decrease in thermal conductivity. The melting of crystallites over such a wide temperature range may be associated with a much greater heterogeneity of local environments following irradiation to higher dose. It should also be noted that, whereas the DSC data were taken at a relatively rapid rate (scan rate 5°K./min.), the thermal conductivity measurements require rather long time intervals at each temperature to attain equilibrium. Thus some annealing of crystalline defects might be occurring during the conductivity tests which could lead to apparently higher crystallite melting temperatures than the DSC data would indicate.

The slight peak near 310°K. in the thermal conductivity data of sample C may be related to the main amorphous transition in irradiated polypropylene as observed by Sauer et al.[3] Their observations show that this transition in unirradiated PP shifts upward in temperature about 25°K. for a sample irradiated to a dose of about 5.7×10^{18} nvt (about 2000 Mrad). This is about the same magnitude as the shift of the slight thermal conductivity peak (sample A $\sim$ 285°K.; sample C $\sim$ 310°K.).

The increase in conductivity with temperature for all samples near the lowest test temperatures may be related to the onset of increased molecular motion in the amorphous regions, as mentioned earlier. It is also considered possible that errors in the apparatus cause this apparent rise below room temperature. However, a similar rise in the data for polyethylene has also been noted by the present authors[1] and by others.[11]

In the high-temperature region the conductivity of sample C is appreciably lower than that of sample B (Fig. 1). If crosslinking occurred with relatively little scission during irradiation one would anticipate that the conductivity would increase with increasing radiation dose rather than decrease as noted above. This has been observed in PE.[1] However, in PP the rate of scission is believed to be relatively high.[2] The lower thermal conductivity in the melt for the sample (C) irradiated to the higher dose may be an indication that significant scission occurred during the irradia-

tions and that any expected increase in k due to additional crosslinking is more than overcome by a decrease in k due to scission, etc.

Below 315°K. the thermal conductivity values of sample C are comparable to those of sample B, whereas one might expect them to be lower because the DSC results indicate reduced crystallinity. Possibly the additional crosslinking has approximately canceled the effect of the decreased crystallinity. In this temperature range, scission may not be very effective, since the chains are already folded and simple chain scission need not greatly disturb the crystalline structure. However the crystallites apparently do begin to melt at lower temperatures for higher irradiation doses, as the DSC results suggest for the irradiated samples. This would explain why the conductivity for sample C begins to decrease at a lower temperature compared to sample B. After melting, the radiation-induced scission would probably be an important factor in lowering the conductivity.

Several additional observations concerning irradiated polypropylene can be made from examination of the DSC results in Figure 2 and Table I. The endotherm for the unirradiated sample (A) shows that the endotherm maximum occurred at 434°K., about the temperature of maximum slope of the curve for the thermal conductivity measurements. If the relative area under the curve is taken as 100 units, a rerun on the same sample, designated A rerun, shows no change in the area under the curve. Thus, without irradiation, testing to elevated temperatures as described herein has little effect on the magnitude of the endotherm.

Endotherm curve B (600 Mrad) indicates that the temperature of the maximum has shifted to 377°K. from 434°K. for curve A and that the relative endotherm area has dropped from 100 units to 73 units, indicating a substantial decrease in the energy required for melting and/or a decrease in per cent crystallinity. Upon taking sample B to 470°K. and subsequently cooling to about 310°K. and rerunning the test, the endotherm area was further decreased substantially, i.e., from 73 units to about 23 units. Also the temperature of the endotherm maximum decreases from 377°K. to about 366°K. After melting and subsequent cooling it would appear that the crystallites of irradiated PP are somewhat restricted from re-forming as a result of crosslinking and other radiation-induced defects.

Data for sample C indicate that an endotherm is still present, although small (15 units), after irradiation to 1800 Mrad, and the endotherm maximum occurs at about 336°K. At this point, the physical appearance of the sample was rather clear and somewhat rubbery. This change in appearance was also observed by Sauer et al.[3] for samples irradiated to this approximate dose. It should be further noted that upon heating sample C to 470°K. and subsequently cooling to 310°K. and rerunning the test, no endotherm maximum was discernible. From this one concludes that the crystallinity, after irradiation to 1800 Mrad and testing to −170°C., is very nearly zero.

Results from the DSC experiments show that the melting of crystallites in irradiated polypropylene is generally irreversible at dose levels used

in the present work. Consequently, it is probable that the initial properties of the material which depend upon or are related to the crystallinity, including the thermal conductivity, do not recover to their initial values after being cycled through elevated temperatures.

Upon examining the density data of Table I, it is observed that irradiation causes the density to decrease from 0.907 to 0.896 g./cc. after irradiation to about 600 Mrad. Upon irradiation to about 1800 Mrad, the density decreased from about 0.907 to 0.889 g./cc. However, a fourth sample which received about 1000 Mrad (data not presented herein) had a density after irradiation of 0.885 g./cc., which indicates that a minimum in density occurs between 600 and 1800 Mrad. This type behavior was reported earlier.[3]

If one uses a conversion factor of about 35 Mrad/10^{17} nvt,[11] an estimate can be made of the correlation of changes observed by Chappell et al.[9] and work presented herein. On this basis their sample which received a radiation dose of 3.2×10^{18} nvt (reactor radiation) received a radiation dose of about 1100 Mrad. They noted that at this dose the sample had become very rubbery as compared to unirradiated sample and that the modulus had decreased probably as a result of decreased per cent crystallinity. This estimated dose of approximately 1100 Mrad lies between the doses for sample B and sample C as reported here.

The authors are indebted to Drs. Florin and Wall of the National Bureau of Standards, Washington, D. C., for the irradiation of specimens and to Professor D. Hansen of Rensselaer Polytechnic Institute and Professor J. A. Sauer of Rutgers, The State University, for comments on the manuscript. This work was supported in part by the National Aeronautics and Space Administration.

References

1. J. N. Tomlinson, D. E. Kline, and J. A. Sauer, *SPE Trans.*, **5**, 44 (1965).
2. A. Charlesby, *Atomic Radiation and Polymers*, Pergamon, London, 1960.
3. J. A. Sauer, L. J. Merrill, and A. E. Woodward, *J. Polymer Sci.*, **58**, 19 (1962).
4. F. H. McTigue and D. E. Grant, Plastics and Elastomer Division, Hercules Pow der Co., private communication.
5. D. E. Kline, *J. Polymer Sci.*, **50**, 441 (1961).
6. L. N. Cherkasova, *Zh. Fiz. Khim.*, **33**, 1928 (1959).
7. K. Ueberreiter and E. Otto-Laupenmuhlen, *Z. Naturforsch.*, **8a**, 664 (1953).
8. K.-L. Hsu, D. E. Kline, and J. N. Tomlinson, *J. Appl. Polymer Sci.* **9**, 3567 (1965).
9. S. E. Chappell, J. A. Sauer, and A. E. Woodward, *J. Polymer Sci., A*, **1**, 2805 (1963).
10. D. Hansen and C. C. Ho, *J. Polymer Sci. A*, **3**, 659 (1965).
11. D. Hansen, private communication.

Résumé

L'effet de la radiation gamma de cobalt-60 sur la conductivité thermique du polypropylène (PP) a été étudié sur une gamme de température de 0 à 160°C. pour des doses de radiation de 600 et 1800 megarads. La conductivité des échantillons non irradiés augmente de 4.5×10^{-4} unités cgs (cal./cm.-sec.-°C.) à 4.8×10^{-4} unités cgs à 80°C., et décroissait ultérieurement avec la température jusqu'à une valeur d'environ 3.1 ×

10^{-4} unités cgs à 160°C. Par irradiation à 600 megarads, al conductivité thermique est abaissée dans le domaine de 0 à 150°C. Au-dessus de 90°C., la conductivité décroit avec la température et devient relativement constante à 3.4×10^{-4} unités cgs depuis 120 jusqu'à 160°C. Un calorimètre enregistreur différentiel (DSC) permettant d'effectuer des mesures de 30 à 200°C., a montré que l'irradiation sous 600 mégarads diminue l'énergie associée à la fusion de cristallites et provoque un glissement du pic de fusion endotherme de 160 à 105°C. L'irradiation à 1800 megarads a pour conséquence une diminution additionnelle de la conductivité thermique sur el domaine de 50 à 160°C., une diminution ultérieure dans la surface du pic endotherme et un glissement de la position du pic maximum à environ 65°C. Les effets de la radiation sur la conductivité thermique du polypropylène sont comparés et reliés à des effets observés concernant la radiation sur le comportement mécanique dynamique.

Zusammenfassung

Der Einfluss von Kobalt-60-γ-Strahlung auf die Wärmeleitfähigkeit von Polypropylen (PP) wurde im Temperaturbereich von 0°C. bis 160°C. bei Strahlungsdosen von 600 und 1800 Megarad untersucht. Die Leitfähigkeit von unbestrahlten Proben steigt von $4,5 \times 10^{-4}$ cgs-Einheiten (cal./cm.-sec.-°C.) bei 0°C auf $4,8 \times 10^{-4}$ cgs-Einheiten bei 80°C. an und fällt dann mit zunehmender Temperatur auf einen Wert von etwa $3,1 \times 10^{-4}$ cgs-Einheiten bei 160°C. ab. Bei Bestrahlung bis zu 600 Megarada wird die Wärmeleitfähigkeit im Temperaturbereich von 0°C. bis 150°C. erniedrigt. Oberhalb 90°C. nimmt die Leitfähigkeit mit steigender Temperatr ab und erreicht zwischen 120°C. und 160°C. einen verhältnissmässig konstanten Wert von $3,4 \times 10^{-4}$ cgs-Einheiten. Differential-Scanning-Kalorimeter-Messungen (DSC) von 30°C. bis 200°C. zeigen, dass Bestrahlung bis zu 600 Megarad die mit dem Kristallitschmelzen verknüpfte Energie erniedrigt und das endotherme Schmelz-maximum von 160°C. auf 105°C. verschiebt. Bestrahlung mit 1800 Megarad führt zu einer zusätzlichen Erniedrigung der Wärmeleitfähigkeit im Bereich von 50°C. bis 160°C., zu einer weiteren Abnahme der Fläche unter dem endothermen Maximum und zu einer Verschiebung der Lage des Maximums zu etwa 65°C. Der Strahlungseinfluss auf die Wärmeleitfähigkeit von Polypropylen wird mit dem beim dynamisch-mechanischen Verhalten beobachteten Strahlungseinfluss verglichen und dazu in Korrelation gesetzt.

Received January 23, 1967
Prod. No. 1592