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Thermal Conductivity of Polytetrafluoroethylene

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Synopsis

Measurements of thermal conductivity of heat-treated and γ-irradiated polytetrafluoroethylene (PTFE) are reported for the 10–180°C. temperature range. Conductivity of PTFE is observed to be largely temperature-independent with a value of about 6.5×10^{-4} cal./cm.-sec.-°C. for the as-received material. Slight anomalous changes in conductivity data occur in the 20 and 125°C. temperature regions. The former is assumed to be associated with the first-order crystalline transitions which occur near 19 and 30°C., while the latter may be associated with a relaxation process near 400°K. The anomaly in the conductivity which occurs near 20°C. is affected by annealing or radiation treatments, and is correlated with crystallinity and specific volume changes previously reported. The overall conductivity level is observed to decrease for annealed, quenched, or irradiated samples. From estimates of crystallinity, it is noted that the thermal conductivity is not a simple function of per cent crystallinity in these cases.

I. INTRODUCTION

Cherkasova,[1] Kline,[2] Hattori,[3] and Eiermann[4] have studied the thermal conductivity of polytetrafluoroethylene (PTFE) as a function of temperature. Cherkasova[1] found that the thermal conductivity of a fluoroplastic sample of 2.1 g./cm.^{3} density was nearly constant over the temperature range from 25 to 95°C. and on the order of 5×10^{-4} cal./cm.-sec.-°C. Using PTFE of density 2.19 g./cm.^{3} and approximate crystallinity of 65%, Kline[2] reported similar thermal conductivity values which were also largely independent of temperature from 0 to 70°C.

Hattori[3] measured the thermal conductivity of quenched and annealed PTFE samples in the temperature range of 10–110°C. The conductivity values were higher for the annealed than for the quenched PTFE, suggesting that the thermal conductivity increased with crystallinity. The conductivity values for the quenched PTFE were approximately constant for the temperatures below 60°C. but increased with temperature above 60°C. For the annealed sample, the conductivity was nearly independent of temperature over the entire temperature range with a value of about 10.5×10^{-4} cal./cm.-sec.-°C. Eiermann[4] measured the conductivity of annealed commercial PTFE in the temperature range −180 to 90°C., and found that it gradually increased with temperature from about 5.4×10^{-4}

cal./cm.-sec.-°C. at −180°C. to about 6.1×10^{-4} cal./cm.-sec.°C. at approximately 20°C. Near 20°C. the thermal conductivity made a sharp drop to 5.8×10^{-4} cal./cm.-sec.-°C., after which there was a general increase with temperature. The sharp drop in conductivity near room temperature was assumed to be associated with a crystalline lattice transformation which occurs in PTFE at 20°C.

Studies of the effect of nuclear radiation on the thermal conductivity of PTFE have not been reported in the literature, and general investigations have been limited to temperatures below 120°C. This paper is based on a study of the effect of γ-radiation and heat treatment on the thermal conductivity behavior of PTFE over the 10–180°C. temperature range.

II. EXPERIMENTAL PROCEDURES

The apparatus used for these experiments was a modification of that reported earlier.[2] Heat was released at a measured rate at the center of a tubular specimen by means of a resistance heating element (0.250 in. diameter) and flowed radially through the specimen into a coaxial heat sink (0.378 in. inside diameter) which was maintained at a constant temperature. On the basis of the sample geometry, the temperature differential, and the power input, the thermal conductivity was calculated. Measurements were made about every 12 min. for temperature intervals which were about 5°C. The temperature differential across the sample was about 2C.°

The PTFE was received in the form of $^1/_2$-in. diameter rods. Number-average molecular weight was of the order of 10^7, and as-received density was near 2.154 g./cm.^{3}. Crystallinity was estimated at 54% by using the equation of Sperati and McPherson.[5] The 6-in. test samples were machined in three 2-in. pieces with 0.250-in. inside diameters and 0.378-in. outside diameters.

Sample 2 was held above the melting point at 340°C. for 2 weeks and then cooled in 5C.° decrements at the rate of 0.15C.°/min. After each decrement the sample was maintained at the reduced temperature for 24 hr. This procedure was repeated until reaching 100°C., at which time the specimen was cooled continuously to room temperature at the rate of 0.15C.°/min. The density increased from 2.154 to 2.235 g./cm.^{3} as a result of this annealing procedure. This indicates an increase in crystallinity from 54 to 78%, if the equation of Sperati and McPherson[5] is used.

Sample 3 was maintained at 350°C. for 18 hr. and then quenched in liquid nitrogen. The density and indicated crystallinity by the density method decreased from the original value of 2.154 g./cm.^{3} and 54% to 2.132 g./cm.^{3} and 45%, respectively.

Samples 4 and 5 were irradiated in a Co^{60} γ-ray source at the National Bureau of Standards in Washington, D. C. in a radiation field where the dose rate in air was approximately 10 Mr/hr. at the irradiation date. This corresponds to a dose rate in PTFE of about 8.4 Mrad/hr. The radiation doses for samples 4 and 5 were 4.7 and 190 Mrad, respectively.

TABLE I
Characteristics of PTFE Samples Tested

Sample	Treatment	Dose, Mrad	Density, g./cm.[3] [a] Before test	After test	Indicated crystallinity, %[b] Before test	After test	Approximate number-average molecular weight
1	Untreated	—	2.154	2.154	54	54	10^7 [c]
2	Annealed	—	2.235	2.233	78	77	10^7 [c]
3	Quenched	—	2.132	2.138	45	47	10^7 [c]
4	Irradiated	4.7	2.198	2.210	67	71	6.4×10^5 [d]
5	Irradiated	190	2.222	2.245	74	81	1.7×10^4 [d]

[a] Average as-received density was 2.154 g./cm.[3] for all samples.
[b] Determined by density method by using equation of Sperati and McPherson.[5]
[c] Estimated original average molecular weight.
[d] Estimated by using $G = 0.3$.[6]

This can be noted in Table I where characteristics of the PTFE samples tested are given.

Prior to heat-treating, samples 2 and 3 were made into tubes of 0.200-in. inside diameter and 0.430-in. outside diameter. A 0.200-in. diameter aluminum rod was put through the center of the tubular samples and the assembly was then placed in an aluminum tube having an inside diameter of 0.430 in. This was done to insure uniform temperature distribution and form stability during heat treatment. The samples were subsequently remachined to exact diameters for testing.

III. EXPERIMENTAL RESULTS

Figure 1 shows the thermal conductivity versus temperature for the control sample and samples 2 (annealed) and 3 (quenched). The over-all conductivity of the annealed sample is less than that for the untreated sample while the thermal conductivity of the quenched sample is, in turn,

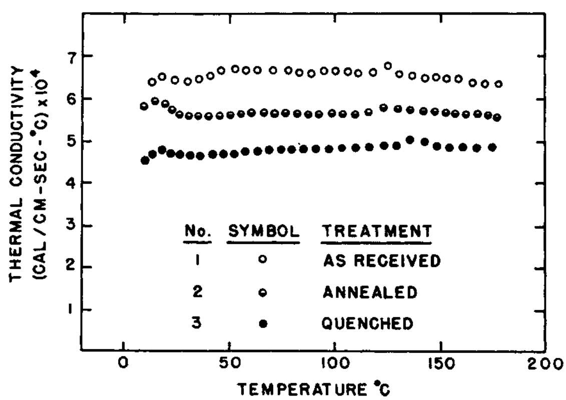

Fig. 1. Thermal conductivity vs. temperature for heat-treated PTFE specimens.

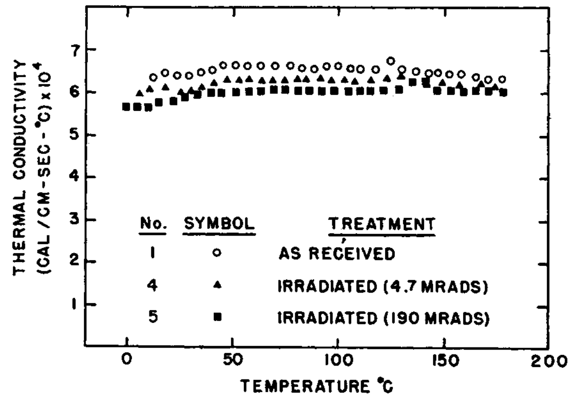

Fig. 2. Thermal conductivity vs. temperature for irradiated PTFE specimens.

less than that of the annealed sample. A slight maximum occurs in each curve near 18°C., with the most prominent peak occurring in the curve for the annealed sample. In the 50–115°C. range the conductivities of all three samples are nearly independent of temperature. In the 115–150°C. region, a slight bump occurs near 125°C. for samples 1 and 2 and near 135°C. for the quenched sample. Beyond about 150°C. the curves for samples 1 and 2 decrease very slightly.

Figure 2 presents the thermal conductivity as a function of temperature from 10 to 180°C. for the untreated sample (1) and the two irradiated samples (4 and 5). The overall level of the thermal conductivity decreases with increased radiation dose. As the temperature increases from 10°C. the local maximum is observed near 15°C. for sample 2 (4.7 Mrad). There is only a slight indication that such a maximum might occur at a lower temperature for sample 5 (190 Mrad). In the range between 50 and 115°C. the thermal conductivity is still rather independent of temperature, and the slight maximum which occurs at 125°C. for the untreated sample appears to occur at higher temperatures for the irradiated samples.

Further comparisons of the thermal conductivity behavior of all five specimens indicate: (*1*) the untreated sample had the highest thermal conductivity of the series (on the order of 6.5×10^{-4} cal./cm.-sec.-°C.); (*2*) the annealed sample had a thermal conductivity value which was lower than either of the irradiated samples for all temperatures above 20°C.; (*3*) the quenched sample had the lowest conductivity of all samples tested; (*4*) the annealed sample had the most pronounced bump in the curves at the 18°C. region.

IV. DISCUSSION

General

As can be noted in the figures, the thermal conductivity of the untreated PTFE (sample 1) is only slightly temperature dependent in the 10–180°C.

temperature range. This is consistent with results reported in the literature.[1,2,4] The data also show that near 20°C. the conductivity for the untreated sample begins to dip slightly with temperature. As suggested earlier by Eiermann,[4] this drop is assumed to be associated with the two first-order transitions in PTFE near 19 and 30°C.[7] The volume change in the 30°C. transition is minor compared to the 19°C. transition. Theory has shown that the thermal conductivity can be directly related to the heat capacity and the sound velocity for the material, and the mean free path for phonon collision. Furukawa[8] observed a sharp peak in the heat capacity of PTFE starting near the 19°C. transition, and dynamic mechanical studies[9–13] have shown that the dynamic modulus, and thus the sound velocity, undergoes a considerable drop in this region. The effects are believed to be a result of changes occurring in the crystallites at the transition temperature. However, it should be noted that all data reported are for polycrystalline material. If the theory is correct in describing the thermal conductivity behavior in this region, the changes in the heat capacity and the sound velocity, along with possible changes in the phonon mean free path, must be largely cancelling to result in the rather slight changes noted in the thermal conductivity.

Data for sample 1 (Fig. 1) indicate a slight upturn in the conductivity curve near 125°C. A bump also appears on the curves for all of the other samples in the same general temperature region. From dynamic mechanical studies,[9,11–13] PTFE is known to undergo a relaxation process in the region of 125°C. At present the process is not well understood, but it appears, from x-ray studies that this may not be related to a crystalline phase change, since no distinct changes are noted in the x-ray pattern. McCrum[13] associated this relaxation with the amorphous regions of the polymer, because his data indicated a decrease in damping with decreasing amorphous content. Tsuge, et al.[14] questioned the validity of this interpretation, because they noted that E'', the complex modulus, as calculated from this data, increases with decreasing amorphous content.

Effects of Heat Treatment

Data shown in Figure 1 indicate that the annealed sample 2 (78% crystalline) had a higher over-all conductivity as compared to the quenched sample 3 (45% crystalline). This is consistent with the behavior of PTFE noted by Hattori[3] for quenched and annealed samples. However, it is interesting that the conductivity of the annealed sample (2) is lower than that of the as-received sample. (1), even though the indicated crystallinity is higher in the annealed sample. Hattori[3] did not specifically report the values for the as-received material. If the heat treatment carried out in air resulted in a significant amount of chain scission (See experimental procedures), it would be conceivable that the over-all path for heat conduction along valence bonds was disrupted sufficiently to be partly responsible for the decrease in conductivity of sample 2 in spite of the increase in crystallinity during annealing. Since little degradation is expected at these temperatures (340°C.) this appears rather unlikely however.

The data for the annealed sample 2 also show a somewhat higher bump in the thermal conductivity curve near 20°C., as compared to samples 1 and 3. This is attributed to the annealing process which resulted in an increase in indicated crystallinity. It may also be related to the degree of crystalline perfection or other crystallite characteristics because sample 5 (Fig. 2), which increased to the same range of indicated crystallinity (Table I) as a result of irradiation, does not show this somewhat more prominent bump in the 20°C. region. However, for irradiated samples the effect could occur at lower temperatures, as will be noted later.

It is interesting to note that the slight bump which occurs at 125°C. for the untreated and the annealed samples appears near 130–140°C. for the quenched sample. A similar shift is also noted in the data for the irradiated samples. At this time these effects are not explained.

Irradiation Effects

Polytetrafluoroethylene has been found to be particularly sensitive to irradiation by nuclear particles in the presence of air, while when irradiated in vacuum its sensitivity has been shown to be somewhat less.[15,16] In the presence of air, irradiation is believed to result in molecular scission. Since many of the properties of PTFE are attributed to its high molecular weight, a rather low radiation dose accompanied by chain scission leads to significant changes in these properties. A moderate average G value for scission, such as G (scission) = 0.3, implies that a radiation dose of about 5 Mrads would reduce the number-average molecular weight from an original value of about 10^7 to about 6×10^5, while a dose of 200 Mrads would reduce the molecular weight to about 1.6×10^4 (Table I). It is quite probable that the G value for scission changes with dose and dose rate.

The thermal conductivity data shown in Figure 2 indicate that γ-irradiation of samples 4 and 5 resulted in an overall decrease in the conductivity level with dose while the data of Table I indicate that the crystallinity, as estimated from the density, increases. For samples machined from the same type of PTFE, infrared measurements confirmed the per cent crystallinity increase with increasing dose at these levels,[17] and similar effects have been noted before.[18,19] This increase in density and crystallinity at relatively low doses is contrary to results usually noted for partially crystalline polymers.

The decrease in conductivity level with increasing crystallinity as shown for samples 4 and 5 might be somewhat unexpected, since the thermal conductivity of materials including PTFE has been typically observed[3,4,20,21] to increase with increasing crystallinity, and theoretical considerations predict that crystalline regions should have a somewhat higher conductivity than amorphous regions. In the case of irradiated PTFE other effects apparently offset the increase in per cent crystallinity. Apparently such factors as scission of the valence bonds and the presence of voids are important in hindering energy flow. It has been shown that the void content increases with increasing radiation dose.[11]

After testing to 180°C. the per cent crystallinity of the irradiated samples (4 and 5) increased further (Table I). This is consistent with the specific volume measurements of Licht and Kline,[17] for heat-treated, γ-irradiated samples. In this investigation thermal conductivity tests could not be carried out on the irradiated samples after heat treatment because of the extreme fragility of the material.

Licht and Kline[19] have shown with specific volume measurements that the PTFE first-order transition near 19°C. shifts to lower temperatures and loses definition with increasing radiation dose. A dose of about 5 Mrad (such as received by sample 4) resulted in a shift of 1°C. or less, while a dose of 190 Mrad (such as received by sample 5) resulted in a shift of about 14°C. In Figure 2 it can be noted that the slight bump in the thermal conductivity data which appears near 19°C. for the unirradiated sample shifts only slightly to lower temperatures for sample 4. Likewise, the bump in the curve appears to have shifted to a somewhat lower temperature for sample 5 as predicted from the specific volume data.[19] The extent of the shift is difficult to estimate from the thermal conductivity data, however.

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Résumé

On donne le résultat des mesures de conductivité thermique du polytétrafluoroéthylène (PTFE) traité à chaud et irradié au moyen de rayonnements gamma dans un domaine de températures allant de 10 à 180°C. On a observé que la conductivité du PTFE était essentiellement indépendante de la température et avait une valeur d'environ 6.5 × 10^{-4} cal/cm-sec-°C pour le matériau étudié. De faibles changements anormaux dans les résultats de la conductivité ont lieu dans les régions de température de 20 et 125°C. On admet que le premier changement est associé aux transitions cristallines du premier ordre qui ont lieu aux environs de 19 et de 30°C tandis que le dernier changement peut être associé à un processus de relaxation qui a lieu aux environs de 400°K. L'anomalie dans la conductivité qui a lieu aux environs de 20°C est influencée par les traitements de recuit ou par l'irradiation et est reliée aux changements de cristallinité et de volume spécifique décrits antérieurement. On a observé que le niveau global de la conductivité diminuait pour les échantillons recuits, trempés ou irradies. A partir des estimations concernant le degré de cristallinité, on note que la conductivité thermique n'est pas une fonction simple du pourcentage de cristallinité dans ces cas.

Zusammenfassung

Wärmeleitfähigkeitsmessungen an hitzebehandeltem und γ-bestrahltem Polytetrafluoräthylene (PTFE) wurden für den Temperaturbereich von 10 bis 180°C mitgeteilt. Für das ursprüngliche Material erweist sich die Leitfähigkeit von PTFE als weitgehend unabhängig von der Temperatur mit einem Wert von etwa 6.5 × 10^{-4} cal/cm-sec-°C. Schwache anomale Leitfähigkeitsänderungen treten in den 20 und 125°C-Temperaturbereichen auf. Erstere wird auf die Kristallumwandlung erter Ordnung bei 19°C und 30°C zurückgeführt, während die letztere mit einem Relaxationsprozess in der Gegend von 400°K verknüpft sein kann. Die Leifähigkeitsanomalie bei 20°C wird durch Temperung oder Strahlungsbehandlung beeinflusst und steht in Beziehung zu den früher mitgeteilten Kristallinitäts- und spezifischen Volumsänderungen. Die Bruttoleitfähigkeit nimmt für getemperte, abgeschreckte oder bestrahlte Proben ab. Aus Kristallinitätsbestimmungen wird festgestellt, dass die Wärmeleitfähigkeit in diesen Fällen keine einfache Funktion der prozentuellen Kritallinität ist.

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