

Detection of Polymer Transitions by Measurement of Thermal Properties

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Synopsis

Thermal diffusivity, thermal conductivity, and specific heat per unit volume were measured for the following polymers: poly(ethylene terephthalate), polytetrafluoroethylene, polycarbonate, polypropylene, and three poly(vinyl chloride) samples plasticized to different levels. First- and second-order transitions can be identified and located by the following features in the thermal property-temperature curves: discontinuities, sharp inflections, broad inflections, sharp maxima, broad maxima, and change in linear slope. The results for poly(vinyl chloride) indicate the possibility of the use of plasticizer to control the thermal insulation properties of polymers, both for steady-state and unsteady-state conduction.

INTRODUCTION

The thermal properties of polymers are the thermal diffusivity, thermal conductivity, and specific heat. The relationship between them is as follows:

$$D = k/C \quad (1)$$

where D is the thermal diffusivity, k the thermal conductivity, and C the specific heat per unit volume.

The thermal diffusivity is the property which determines time-dependent heat flow through the polymer material. Thermal conductivity determines the time-independent conditions. These properties are very important from the point of view of polymer processing, where energy and time requirements have to be known with adequate accuracy. For example, in order to heat a slab of polymer to constant temperature by applying thermal energy from the surface, it is essential to know the thermal diffusivity in order to proceed in the most efficient manner. Also, the thermal conductivity should be known for any situation in which polymers are used for thermal insulation.

Equation (1) would seem to offer excellent possibilities for the determination of thermal properties. However, it has previously been very difficult and tedious to obtain any two thermal properties for the same polymer sample. Recently, however, methods have become available which enable all three thermal properties to be determined simultaneously in a time as short as a few seconds.^{1,2}

It is indicated above that a knowledge of thermal properties is important from the point of view of polymer processing. These properties are also important because they are needed for the analysis of any heat flow situation occurring in polymers. Another factor is that thermal properties measurements can provide information on the nature and location of transitions in polymers, and it is the principal purpose of this paper to investigate various polymer transitions by observing how they affect the thermal properties.

Subsidiary aims of the paper are to provide previously unknown thermal properties values (particularly diffusivity values), and to observe how they depend on temperature. It is also intended to provide sufficient identification of the experimental polymers so that interested researchers can work with material from the same source and thus provide more extensive information on well-identified polymers. For example, thermal and mechanical properties data for samples from one source could be very useful.

EXPERIMENTAL

A transient heating method suggested by Harmathy¹ has been modified by the author² for use with thin film polymers. The method is based on the fact that for a short period of time a finite solid will act like an infinite solid when subjected to a constant thermal flux.

The experimental system is shown in Figure 1. Ultrathin Constantan foil provides a constant thermal flux F , and the temperature above ambient at position x at time t is followed as a function of time. This temperature is denoted by $V(x,t)$.

Measurement by a suitable recording system enables the ratio $V(x,2t)/V(x,t)$ to be found. The dimensionless groups Dt/x^2 and $kV(x,t)/2Fx$ are obtained from such a measurement. A knowledge of F and x enables D , k , and C to be calculated.

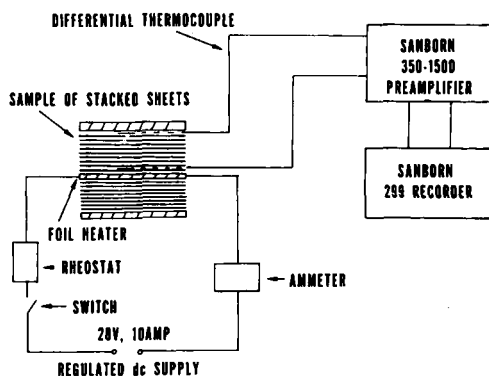


Fig. 1. Experimental system.

EXPERIMENTAL MATERIALS

The following polymers were selected for testing: polytetrafluoroethylene, poly(ethylene terephthalate), polypropylene, poly(vinyl chloride) plasticized to different levels, and polycarbonate. Four of these materials were chosen because they would show a variety of transitions and were thus suitable for the purposes of this study. All these polymers are listed in Table I together with relevant information about their source. The polycarbonate sample was chosen in order to investigate the behavior of thermal properties in a temperature region that did not contain any known transitions, and also because thermal properties information on this important class of polymers appears to be hard to find in the literature.

TABLE I
Polymers Used in Thermal Properties Measurements

Polymer	Source	Remarks
Polytetrafluoroethylene	Kaufman Glass Company, Wilmington, Delaware	Material is duPont Teflon
Poly(ethylene terephthalate)	Brownell, Inc., New York, N. Y.	Material is duPont Mylar
Polypropylene	Westlake Plastics Company, Lenni Mills, Pennsylvania	—
Poly(vinyl chloride)	Specially prepared in Armstrong Cork Company Laboratory by R. E. Singer	Prepared from Diamond PVC 40 resin. Santicizer 160 used as plasticizer. Three samples prepared with plasticizer levels of 10, 20, and 30 parts per hundred resin by weight.
Polycarbonate	Westlake Plastics Company	Prepared from Lexan resin

THERMAL PROPERTIES RESULTS

Poly(ethylene Terephthalate)

Figures 2, 3, and 4 show the thermal diffusivity, thermal conductivity, and specific heat, respectively. Previous work has shown that a glass transition is expected in the region of 70°C.^{3,4} This transition is indicated by each of the three thermal properties measurements. The thermal diffusivity shows a small but recognizable inflection point at approximately 70°C., and the thermal conductivity exhibits a discontinuity. Specific heat values remain linear with temperature but the slope of the line is changed at the transition temperature.

It is seen that the glass transition for poly(ethylene terephthalate) is identified by three different types of thermal property-temperature curves. These are (a) inflection, (b) discontinuity, and (c) change in linear slope. It must be noted, however, that the thermal conductivity results could just as easily be interpreted as evidence of a sharp change in slope.

From Figure 2 it is evident that there is the possibility of another broad

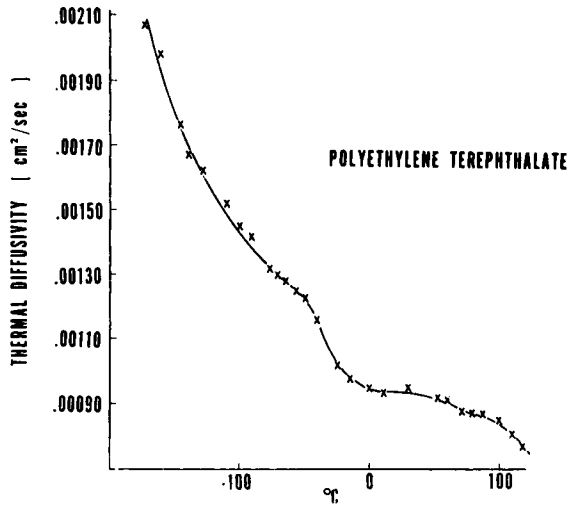


Fig. 2. Thermal diffusivity of poly(ethylene terephthalate).

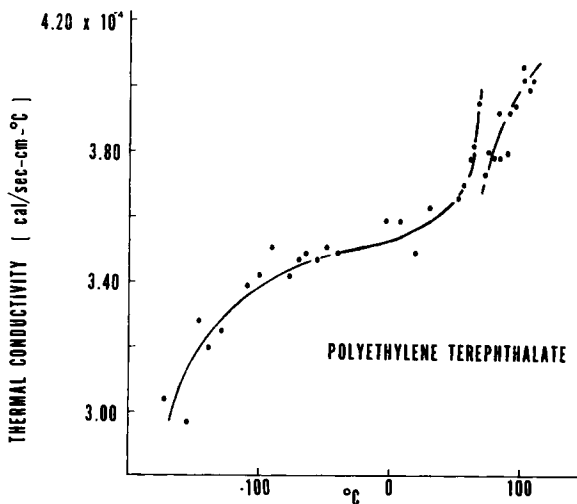


Fig. 3. Thermal conductivity of poly(ethylene terephthalate).

transition in the approximate temperature range of -50 to 0°C . This is also indicated by an almost temperature-independent range of the thermal conductivity. The specific heat, however, does not give evidence of this transition.

One point of particular interest is that the thermal diffusivity increases by about 100% between room temperature and near liquid-nitrogen temperatures. This is to be contrasted with an almost constant diffusivity from room temperature past the glass transition point.

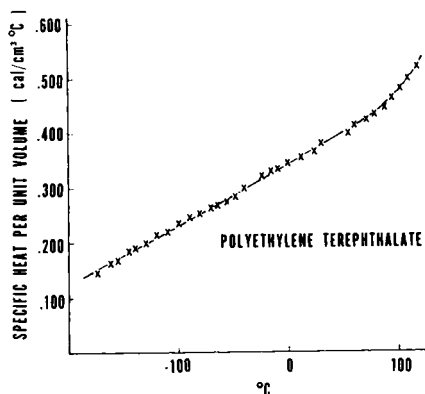


Fig. 4. Specific heat of poly(ethylene terephthalate).

Polytetrafluoroethylene

Polytetrafluoroethylene (Teflon) is known to have two transitions in the region of room temperature.⁵ The first is first order and involves a rearrangement of the helical structure of the main chains. The other transition is thought to be a minor change in the structure. They are located at 19 and 30°C., respectively. Such transitions are very different from the glass transitions and hence are interesting from the point of view of this study.

The three thermal properties of Teflon are shown in Figures 5-7. All three properties indicate the presence of the two transitions mentioned, and the characteristic result is a discontinuity in all three cases.

The specific heat shows the temperature dependence previously reported

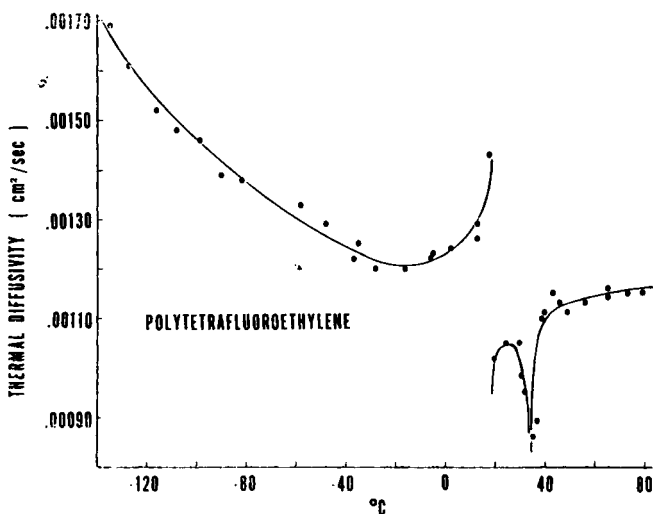


Fig. 5. Thermal diffusivity of polytetrafluoroethylene

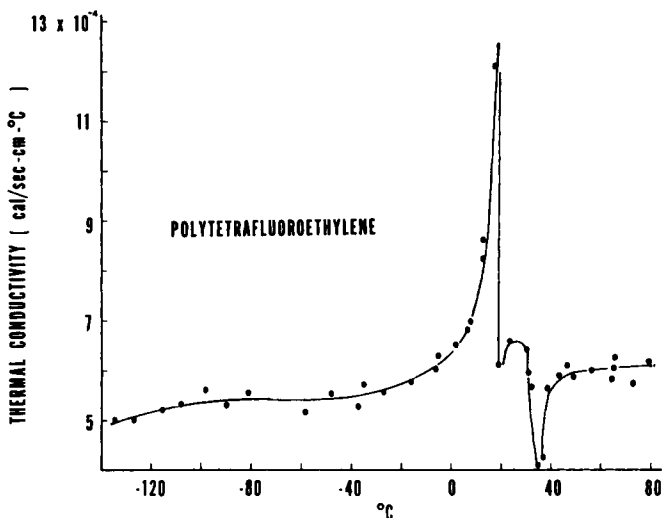


Fig. 6. Thermal conductivity of polytetrafluoroethylene.

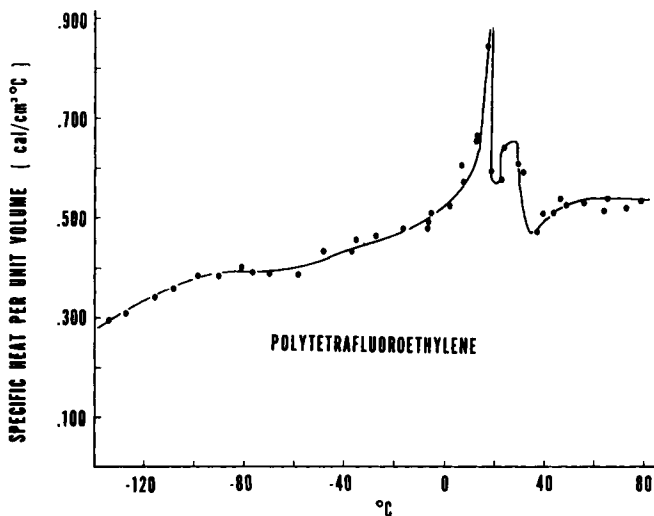


Fig. 7. Specific heat of polytetrafluoroethylene.

in two other studies.^{6,7} There is a sharp discontinuity at the major transition at 19°C. and evidence of a small maximum at the other point near 30°C. The specific heat also shows a broad transition in the approximate range -50 to -100°C. This is possibly the glass transition for Teflon.

The thermal conductivity values show some interesting results when compared with values obtained from steady-state methods.^{8,9} When steady-state methods are used, the 19°C. transition is indicated by a small discontinuity or jump in the thermal conductivity. However, the transient method requires only a few seconds, and thermal equilibrium is never

established. Under these circumstances two sharp discontinuities are observed.

This thermal conductivity curve strongly suggests a resonance type of behavior, and the tentative hypothesis can be made that perhaps these results are evidence of a "phonon resonance" for the first transition and an antiresonance for the second. Such effects cannot be seen in steady-state results because in such cases we measure an average over a rather wide temperature range.

The thermal diffusivity indicates exactly analogous behavior and has two sharp discontinuities at the two transitions. In this case however, a discontinuity has previously been observed.¹⁰

Polypropylene

The thermal properties are shown in Figures 8-10. Each property is seen to provide evidence of the existence and location of a glass transition

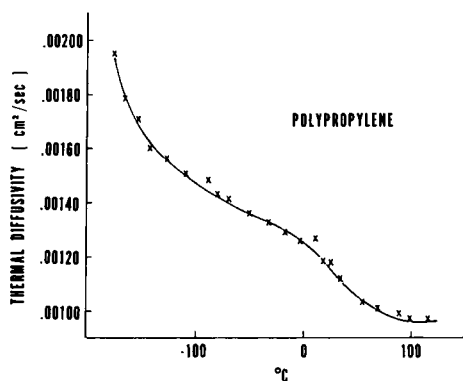


Fig. 8. Thermal diffusivity of polypropylene.

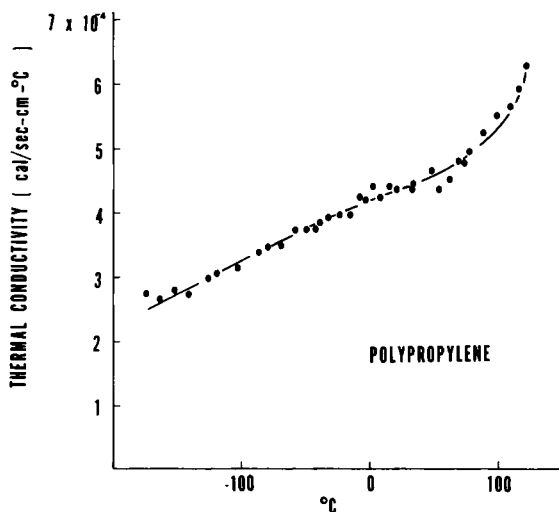


Fig. 9. Thermal conductivity of polypropylene.

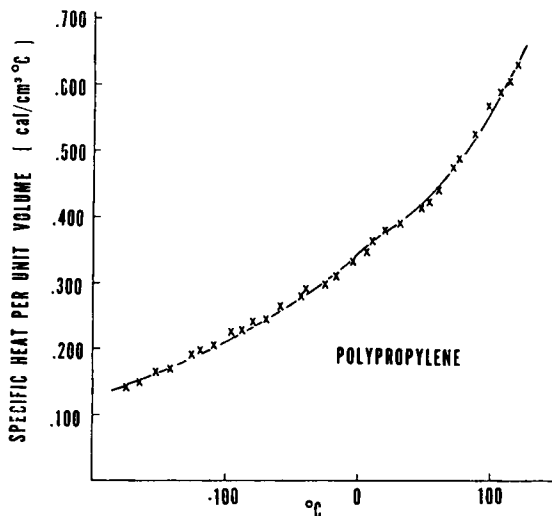


Fig. 10. Specific heat of polypropylene.

point at approximately 10°C. The three sets of data show a small inflection centered on the approximate temperature mentioned.

The form of the specific heat inflection is very similar to that observed for a sample of isotactic polypropylene used in another study.¹¹ It is also noted that the location of the glass transition is confirmed by mechanical energy loss data.¹²

Polycarbonate

The thermal properties values are shown in Figures 11–13. These curves show general trends of the thermal properties in a temperature range believed not to contain any major transitions. All three curves are approximately linear over any small temperature span such as 20°C.

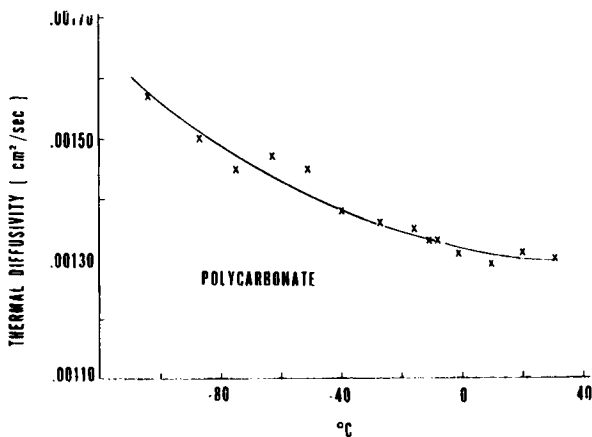


Fig. 11. Thermal diffusivity of polycarbonate.

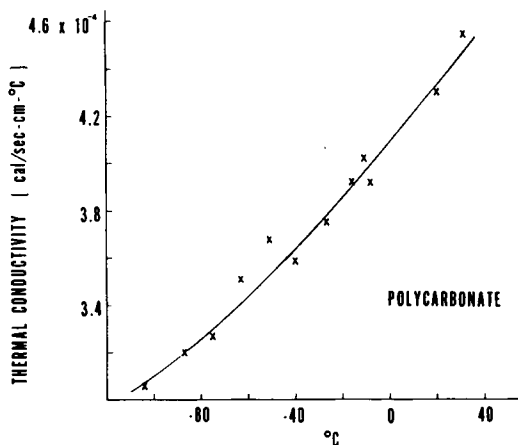


Fig. 12. Thermal conductivity of polycarbonate.

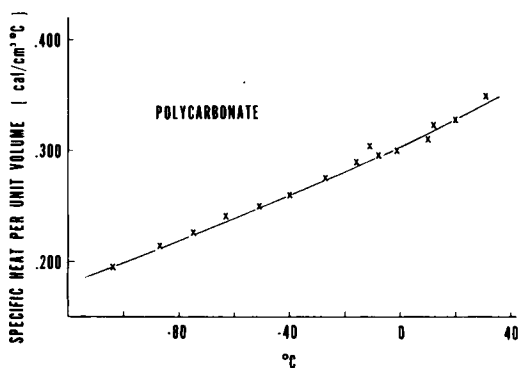


Fig. 13. Specific heat of polycarbonate.

The specific heat values compare well with those obtained in an extensive study on Lexan resin.¹³

Poly(vinyl Chloride)

Poly(vinyl chloride) is known to have a glass transition temperature of approximately 80°C. The addition of plasticizer reduces the transition temperature. For these reasons, poly(vinyl chloride) was considered suitable for the purposes of this work.

Several samples of thin film poly(vinyl chloride) were prepared at this laboratory. The basic resin was PVC 40 Diamond. These samples were plasticized to different levels. These were 10, 20, and 30 parts per hundred of resin by weight. The plasticizer used was Santicizer 160.

Thermal properties results are shown in Figures 14–16. Each set of data provides some interesting features and these will be discussed separately.

The specific heat data demonstrate that plasticizer has a great effect on the position of the glass transition. For the lowest level of plasticization the glass transition is fairly sharply defined as being about 55°C. This sharpness of transition for poly(vinyl chloride) has previously been ob-

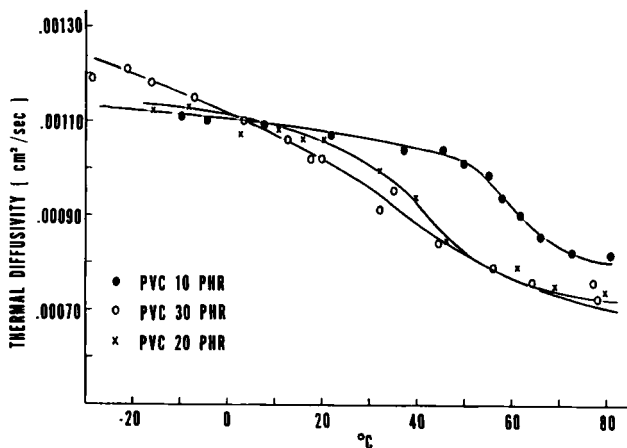


Fig. 14. Thermal diffusivity of poly(vinyl chloride).

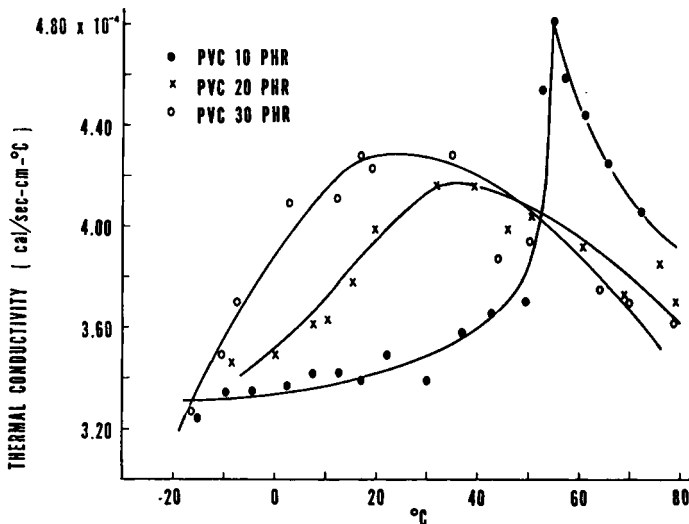


Fig. 15. Thermal conductivity of poly(vinyl chloride).

served for samples which are unplasticized or contain small amounts of plasticizer.¹⁴ However, additional amounts of plasticizer greatly broaden the transition region, and reduce the temperature we can designate as the glass transition. This point is taken to be the inflection point in the spe-

cific heat curve. For the 20 phr sample this could be approximately 30°C., and for the 30 phr sample, approximately 20°C.

From the specific heat data we can distinguish two types of curve indicating the transition. There is a sharp inflection and a broad inflection.

The diffusivity data also show inflection points which indicate the different glass transitions, and again the sharpness of the inflection decreases with increasing plasticizer level. An inflection for an unplasticized sample has previously been reported.¹⁵

The thermal conductivity values show two kinds of general behavior. The glass transition for the 10 phr sample is indicated by a maximum value which is attained very rapidly and which resembles the discontinuity observed for Teflon. The samples plasticized to higher levels show maxima

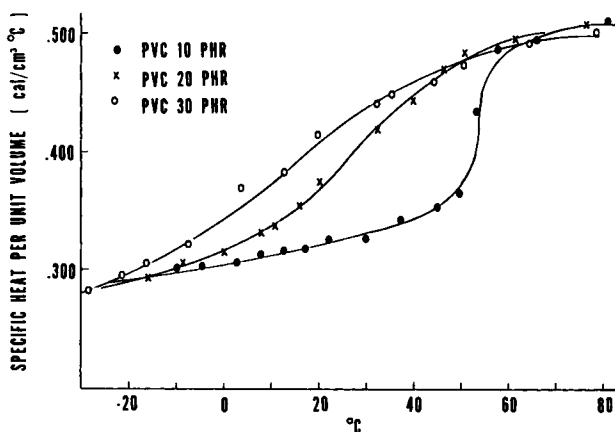


Fig. 16. Specific heat of poly(vinyl chloride).

which are not nearly so sharp. Such gradual maxima have previously been observed in plasticized poly(vinyl chloride),⁹ but the sharp maximum is apparently a new feature. The detection of this is probably due to the transient nature of the measurement.

When we consider all three sets of data for poly(vinyl chloride) it is seen that the insulation characteristics of this polymer can be radically modified by the plasticizer content.

Suppose we would want to use poly(vinyl chloride) as a thermal insulator at 30°C. Figure 15 shows that for steady-state heat flow the 10 phr sample is best because it has the lowest thermal conductivity. However, if the polymer were to be used for insulation under transient (nonsteady-state) conditions, Figure 14 shows the 10 phr sample to be the worst choice because it has the highest thermal diffusivity at 30°C.

This simple example shows that plasticizer can be used for the practical purpose of controlling the insulation characteristics of polymeric material.

CONCLUSIONS

From the results given above it is concluded that the thermal properties measurements provide an excellent method for the detection and location of transitions in polymers. Such transitions are indicated by the following forms of the thermal property-temperature curves: discontinuities, sharp inflections, broad inflections, sharp maxima, broad maxima, and change in linear slope.

From the results for poly(vinyl chloride) it is concluded that it is possible to control thermal insulation properties for polymers by the use of plasticizer.

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Résumé

La diffusion thermique, la conductivité thermique et la chaleur spécifique par unité de volume ont été mesurées pour les polymères suivants: le téréphtalate de polyéthylène, le polytétrafluoroéthylène, le polycarbonate, le polypropylène, et trois échantillons de chlorure de polyvinyle plastifiés à des degrés différents. On peut identifier et localiser les transitions de premier et second ordre par les faits suivants dans les courbes de propriété thermique-température; des discontinuités, de fortes inflections, de larges inflections, des maxima aigus, des maxima larges, et un changement dans la tangente du diagramme linéaire. Les résultats pour le chlorure de polyvinyle indiquent la possibilité d'utilisation d'un plastifiant en vue de contrôler les propriétés d'isolation thermique des polymères, à la fois pour la conduction à l'état stationnaire et l'état non-stationnaire.

Zusammenfassung

An folgenden Polymeren wurde die Wärmediffusion, die Wärmeleitfähigkeit und die spezifische Wärme pro Volumseinheit gemessen: Polyäthylenterephthalat, Polytetrafluoräthylen, Polycarbonat, Polypropylen und drei Polyvinylchloridproben mit ver-

schiedenem Weichmachergehalt. Umwandlungen erster und zweiter Art können an folgenden Merkmalen der Kurven für die Abhängigkeit der thermischen Eigenschaften von der Temperatur identifiziert und lokalisiert werden: Diskontinuitäten, scharfe Wendepunkte, breite Wendepunkte, scharfe Maxima, breite Maxima und Änderung der linearen Neigung. Die Ergebnisse für Polyvinylchlorid zeigen die Möglichkeit der Verwendung eines Weichmachers zur Kontrolle der Wärmeisolationsefähigkeit von Polymeren bei stationären und nichtstationären Leitungsbedingungen.

Received May 17, 1966

Prod. No. 1409