Microhardness as a Thermally Activated Process: Indentation Time Dependence for an Amorphous Copolyester

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SYNOPSIS

Vickers microharness, MH, measurements have been performed on samples of a plasticized amorphous copolyterephthalate with different diluent contents. The dependence of MH on contact time is explained in terms of the Eyring equation and it has been found that the activation volume increases abruptly in the vicinity of the glass transition. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

It has been proved that hardness measurement is an adequate tool to detect transitions in polymers. As early as in the 1950s, it was found that the Rockwell hardness vs. temperature curve of poly(vinyl chloride) displays a marked softening,[1] i.e., hardness decreases greatly above the glass transition temperature, T_g. It has been shown more recently that the glass transition of polypropylene[2] and plasticized copolyesters[3] or the Curie transition of a vinylidene fluoride–trifluorethylene copolymer[4] can be precisely localized by Vickers microhardness, MH, measurements. The localization of these transitions was achieved by means of temperature-dependent MH determinations. It is expected that more information about the phase transitions can be found when contact time and temperature-dependent measurements are considered.

Not long ago, the plastic flow of high-density polyethylene (HDPE) in Vickers microhardness tests was described as a thermally activated process.[5] Particular attention was paid to the agreement between the values of the activation parameters reported in the literature for tensile tests and those that were obtained from MH measurements. The

consistency of the results supported the applicability of the Eyring model to study the unrecoverable deformation of HDPE under the penetration of a Vickers indentor. Further evidence to prove the validity of the proposed model[5] depends on its ability to provide a description of the time-dependent behavior. With the purpose of analyzing our previous results on temperature-dependent MH measurements,[3] we will apply to them the Eyring model, originally developed to study the yielding of polymers in stress–strain tests.[6]

The first aim of this paper was to examine the application of the thermal activation theory to the description of the viscoelastic creep of polymers in MH tests. If the model fits the data, it would be possible to obtain a confident estimation of the activation parameters. As a second aim, the values of these parameters will allow a deeper insight into the nature of the transitions because they may give some indication of the underlying molecular mechanisms.

EXPERIMENTAL

A commercially available amorphous copolyester (COP) of poly(ethylene terephthalate) (PET) and poly(1,4-cyclohexylene–dimethylene terephthalate) (PCHDMT) with a composition of 75 wt % in PET was studied. Plasticized samples were obtained by blending COP with different amounts of tricresyl

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phosphate (TCP), following the procedure that has been established elsewhere.[3] The molded sheets were around 1 mm in thickness.

DSC measurements were performed in a Mettler TA 3000 calorimeter and the diluent content, w_1, of the plasticized specimens was determined from a calibration curve T_g vs. w_1, obtained previously.[7]

A Vickers indentor attached to a Leitz microhardness tester was used to carry out microindentation measurements. Microhardness values were calculated according to the relation

$$MH = 2 \sin 68° P/d^2 \qquad (1)$$

where P (in N) is the contact load and d (in mm) is the length of the diagonal of the indentation. All the measurements were undertaken at room temperature (20–22°C) and a contact load of 0.049 N was selected. The experimental results for different indentation times, t, are collected in Table I and it can be seen that the half-widths of the confidence intervals (confidence level 95%) are smaller than 0.05 times the corresponding mean values.

RESULTS AND DISCUSSION

It has been demonstrated in a recent paper[5] that the flow of high-density polyethylene under the action of a Vickers microindentor can be explained in terms of a modification of the high-stress approximation of the Eyring equation.[6] The mathematical expression that has been proposed to describe this phenomenon reads

$$\dot{\delta} = \dot{\delta}_0 \exp\left(\frac{vMH - \Delta H}{kT}\right) \qquad (2)$$

where $\dot{\delta}$ is the strain rate; $\dot{\delta}_0$, a preexponential factor; v and ΔH, the activation volume and enthalpy, re-

spectively; T, the absolute temperature; and k, the Boltzmann constant. The preexponential factor includes the entropic contributions to the strain rate, so ΔH appears in the exponent instead of the activation free energy. The strain rate has been defined as

$$\dot{\delta} = \dot{d}/d \qquad (3)$$

$\dot{d}$ being the derivative of d with respect to t.

To determine the underload dimensions of the indentation and, consequently, $\dot{\delta}$, it has been assumed that the length of the diagonal of the impression when the load is acting equals that of the residual impression, i.e., after releasing the indentor. It has been previously proved for metallic,[8] ceramic,[8] and polymeric materials[9] that whereas the indentation depth recovers the indentation diagonals do not.

For dealing with isothermal sets of data, eq. (2) can be rewritten in the form

$$\dot{\delta} = \dot{\delta}_0(T) \exp\left(\frac{vMH}{kT}\right) \qquad (4)$$

which must be modified in order to calculate the dependence of MH on t. Taking into account eqs. (1), (3), and (4), we get

$$M\dot{H} = -2MH\dot{\delta}_0(T) \exp\left(\frac{vMH}{kT}\right) \qquad (5)$$

an ordinary differential equation with the following solution:

$$2\dot{\delta}_0(T)t = \int_{vMH/kT}^{\infty} \frac{\exp(-x)}{x} dx \qquad (6)$$

Table I   Vickers Microhardness, MH, at Various Indentation Times, t, for Copolyester Samples with Different Diluent Contents, w_1

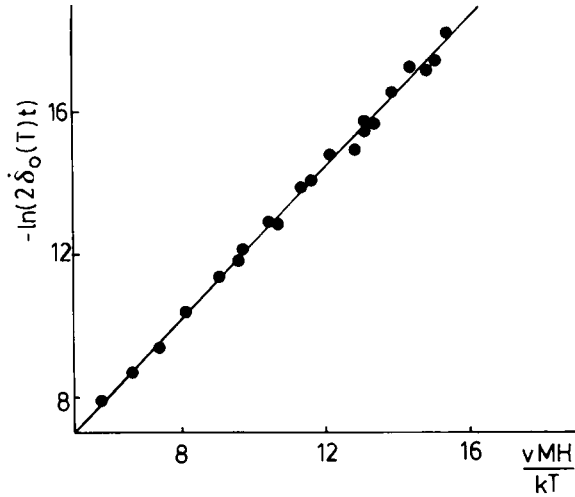| Sample	w_1 (%)	$T - T_g$ (K)	MH/MPa			
			$t = 5$ s	$t = 15$ s	$t = 30$ s	$t = 60$ s
1	0	−54	119.5 ± 2.0	114.5 ± 2.5	108 ± 2.0	101.5 ± 1.5
2	2.5	−46	106.5 ± 2.5	100.5 ± 2.0	94.5 ± 2.0	90.5 ± 1.0
3	7.5	−30	90 ± 3.0	85 ± 3.0	78.5 ± 1.0	75.5 ± 1.5
4	16	−8	82 ± 2.0	77.5 ± 2.0	70.5 ± 1.5	65.5 ± 1.0
5	19	−3	74 ± 2.0	68.5 ± 3.0	63 ± 1.5	57.5 ± 1.0
6	30	11	2.04 ± 0.05	1.20 ± 0.04	0.92 ± 0.04	0.70 ± 0.04
7	29	13	0.38 ± 0.01	0.35 ± 0.01	0.31 ± 0.01	0.27 ± 0.01

Figure 1 Proof of the validity of eq. (8) of the text, relating microhardness and indentation time.

The analysis of our previous data of time-dependent MH at room temperature for different polyethylenes and polypropylenes shows that the dimensional ratio vMH/kT ranges[10] from 7 to 20. The examination of the information available in the literature about v and MH for different polymers, including poly(methyl methacrylate),[11-16] polycarbonate,[11,17-19] polystyrene,[11,18,20] and poly(vinyl chloride),[11,15,18] reveals that even greater values for the quotient can be expected in other cases. All these values justify the high-stress approximation [sinh $(vMH/kT) = \frac{1}{2} \exp(vMH/kT)$] that has been assumed for the modified Eyring equation. It can be proved by means of numerical methods that

$$\ln \int_\alpha^\infty \frac{\exp(-x)}{x} dx = -1.69 - 1.07\alpha$$

$$(5 < \alpha < 20) \quad (7)$$

Hence, combination of eqs. (6) and (7) yields

$$MH = \frac{kT}{1.07v} (-2.38 - \ln \dot{\delta}_0(T) - \ln t)$$

$$= a - b \ln t \quad (8)$$

Figure 1 shows the excellent agreement between the theoretical predictions of eq. (8) and the experimental results for all the plasticized COP specimens except for sample no. 6, which is not represented in Figure 1 because the estimated value of vMH/kT for this sample is lower than 4 and, then, the high-

stress approximation is not valid. To deal with such low values, eq. (4) must be modified by substituting $\exp(vMH/kT)$ for $2 \sinh(vMH/kT)$. By a mathematical treatment analogous to the previous one, it is possible to obtain an expression similar to eq. (8) and to calculate the activation volume.

At this point, it is interesting to remark that the dependence of MH on t defined by eq. (8) is different from the previously reported one[21-23]:

$$MH = MH_0 t^{-n} \quad (9)$$

However, it can be demonstrated by means of regression techniques that both fittings of the experimental results yield correlation coefficients very close to unity and that the differences between the MH values calculated from either eq. (8) or (9) are lower than the experimental errors. Even more, for any sample, the difference between each pair of v values that can be estimated from both equations does not exceed 10% and the same result is obtained for each two $\ln \dot{\delta}_0(T)$ values. Although eqs. (8) and (9) explain the results, the first option has been selected to deal with the data of this work because the parameters that are obtained from the fittings are directly related to fundamental physical quantities, whereas eq. (9) is the result of a phenomenological study.

Figure 2 shows the dependence of v on $T - T_g$. It can be seen that v is approximately constant (0.57 ± 0.04 nm³) for $T < T_g$ and increases abruptly to 86 nm³ when $T - T_g$ rises from −3 to 13. This result parallels that obtained from compression tests for poly(methyl methacrylate) (PMMA)[13,14]: If T is
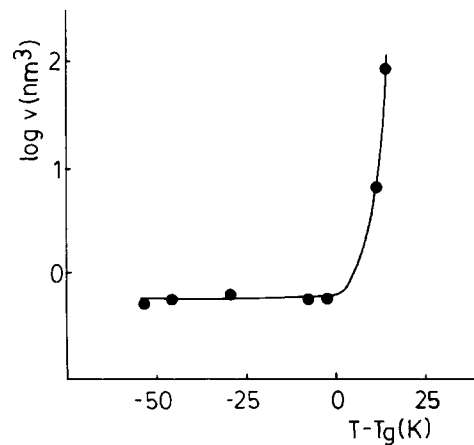

Figure 2 Activation volume of the Eyring equation as a function of the difference between the indentation and glass transition temperatures for each copolyester sample.

sufficiently lower than the secondary relaxation location ($T \simeq 300$ K), the activation volume is T-independent ($\simeq 0.11$ nm^3), and when T approaches the temperature of the secondary relaxation, the activation volume increases markedly.

The activation volume is usually related to the size of the activated unit, i.e., to the number of segments activated coherently in a successful thermal fluctuation. For the plasticized copolyester samples, the volume occupied by a segment is approximately 0.3 nm^3 (the ratio of the comonomer unit weight to the macroscopic density). Then, for $T < T_g$, the activation volume is in the order of 2 comonomer units. This fact points out the localized character of the segmental motions that are responsible for the plastic deformation of glassy polymers, i.e., cooperative movements of segments are frozen below T_g. When T rises above T_g, a new deformation mode that implies a greater number of segments is activated, as can be expected.

It is interesting to compare the thermal expansion coefficient, β, of the activation volume for two different amorphous polymers: PMMA and a plasticized copolyester. In the former case, β will be considered in the vicinity of the secondary relaxation, whereas in the latter one, the temperature interval is around the glass transition. Having taken into account the data in Ref. 13, a mean value of 1.7 $\times$ 10^{-2} K^{-1} is estimated for β_{PMMA}, and from the results of this work, an averaged value of 7 $\times$ 10^{-1} K^{-1} is obtained for β_{COP}. This fact illustrates the difference between a secondary relaxation and a glass transition: The increase of the cooperativity in the segmental motions when T rises is lower for the former. This result can be emphasized if the number of segments that participate in an elemental deformation process is estimated. For PMMA, it raises from 1.5 to 10 monomer units if T increases from 200 to, approximately, 350 K. In the case of plasticized COP, the ratio of the activation volume to the volume estimated for one comonomer unit jumps from 2 to 300 for an increase of only 16 K in $T - T_g$. It is important to report these results because the concepts of cooperativity or coherency of segmental motions are qualitative ones. However, from the results reported here, the evaluations of activation volumes or those of the thermal coefficient of v represent a quantitative measurement of the previous concepts.

If these results are compared with those of Ref. 3 where plain MH values of these copolymers were related to $T - T_g$, it can be seen that the analysis developed in this paper, based on the Eyring's theory

of thermal activation, not only allows one to obtain information about the localization of the transition, but also about the molecular mechanism.

CONCLUSIONS

The two main conclusions of this paper are the following:

- The dependence of microhardness on contact time, for the plasticized copolyester samples that have been studied, can be described by the expression

$$MH = a - b \ln t \qquad (8)$$

obtained from a modification of the Eyring's thermal activation theory for the plastic deformation of polymers.

- One of the coefficients in eq. (8), b, is directly related to the activation volume, v. This activation parameter can be used to quantify the cooperativity of segmental movements in the vicinity of the glass transition.

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