

Low Temperature Slow Rate Penetration Test: Evidence for Its Sensitivity to the Thermomechanical Relaxations in the Case of Ethylene–Vinyl Acetate Copolymers

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SYNOPSIS

The sensitivity of a low temperature slow rate penetration test to the dynamic mechanical response of ethylene–vinyl acetate (EVA) copolymers with different compositions is clearly evidenced. The β -molecular relaxation process occurring around -10°C controls the slow puncture behavior. The penetration resistance reaches a maximum value at this temperature and the type of rupture involved in the perforation mechanism varies on both sides of this critical temperature (brittle or ductile rupture). The parallel variations of the slow puncture resistance and of the high speed tensile impact strength with temperature, as well as with the vinyl acetate content, point to the reliability of the low temperature slow rate penetration test. This test thus appears as an efficient tool to simulate static mechanical deformations undergone by polymer films used in the sealed packaging of frozen food. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Slow rate penetration resistance measurements at low temperature may be a fruitful tool to assist in the development of polyethylene-based films, dedicated to the frozen food packaging market. Slow puncture simulates a condition commonly encountered when a polyethylene bag is filled with irregularly shaped objects.

Little attention has been devoted in literature to the mechanical response of polymers punctured at low speed. The detailed review of Seyler is, however, worth noting, with special emphasis on probing the geometry and penetration rate¹; the influence of probe shape (needle or cylindrical plunger) is also discussed by Agarwal and Kumta.² While the temperature dependence of the Charpy or Izod impact energy is mainly investigated for injection-moulded parts, there seems to be a lack of data regarding the temperature variation of low velocity puncture re-

sistance in the case of blown films. This lack of data led to the development in the laboratory of a test able to provide such information. Its sensitivity and its reliability are assessed on ethylene–vinyl acetate copolymers (EVA), since these copolymers are among the applications used for the packaging of chilled food.^{3,4}

The analysis was conducted according to the following approach: for EVA copolymers, the temperature variation of the tensile impact strength showed a maximum around 0°C , whatever the vinyl acetate content. The higher this content, the better the impact resistance for identical Melt Flow Index (MFI) grades. All these results are illustrated in Figure 1.

The main concern of this work was to examine whether a static test, such as slow rate penetration, exhibits behaviors analogous to those observed at higher frequency, that is, to answer the following questions:

- Is there a maximum in the slow puncture resistance of an EVA film as a function of temperature?

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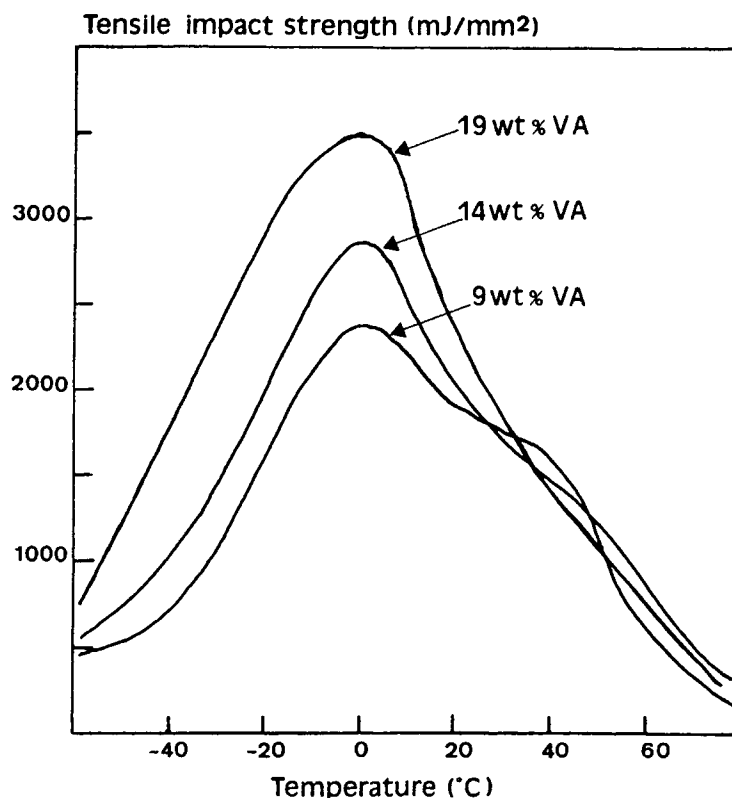


Figure 1 Effect of the vinyl acetate content on the tensile impact resistance for EVA copolymers with the same MFI.

- Does the critical temperature of this maximum depend on the comonomer concentration?
- Does the perforation energy increase with the vinyl acetate content?

These questions are addressed in reference to the observed dynamic mechanical behavior of these EVA copolymers.

EXPERIMENTAL

Materials

EVA copolymers under investigation were the three Greenflex grades from EniChem Polimeri, as de-

scribed in Table I. The vinyl acetate content varied between 9 and 19% by weight. The degree of crystallinity was determined by Differential Scanning Calorimetry on a DSC-7 Perkin-Elmer apparatus. The Melt Flow Index was measured on a MPS-E Göttfert melt indexer, at 190°C and under a 2.16 kg load. EVA copolymers were chosen with comparable MFI to avoid any potential influence of this parameter on the final results. The density was obtained by a floatation method on specimens taken from the melt indexer, annealed in boiling water for 30 min and cooled to room temperature in about 2 h. These EVA grades contained neither slip agent nor anti-block additive and the thickness of the blown films was 50 μm .

Table I Characteristics of Ethylene-Vinyl Acetate Copolymers

Materials	Vinyl Acetate (wt %)	MFI (g/10 min)	Density	Degree of Crystallinity
Greenflex FF 35	9	0.81	0.9324	33
Greenflex FF 45	14	0.63	0.9371	28
Greenflex FF 55	19	0.66	0.9442	22.5

Puncture Procedure

The slow rate penetration test consisted of measuring the resistance of a film to penetration by a probe driven at a constant velocity. In this study, we use a hemispherical-ended probe (130 mm in length and 12 mm in diameter). The constant perforation rate was 500 mm/min; Figure 2 shows the slow puncture test in terms of the deformation rate among mechanical tests currently performed in the laboratory.

The experimental device is shown in Figure 3. The specimen was clamped between pneumatic grips with a pressure of 5 bars and was then perfectly stretched before testing. Samples (12 cm × 12 cm square) were cut off along the same generating line of the film reel. Puncture tests were done on the same side of the film, in the temperature range of $-40^{\circ}\text{C} < T < +37^{\circ}\text{C}$. To achieve thermal homogenization, samples were maintained in the thermal chamber for 20 min before being perforated; temperature was regulated within $\pm 2^{\circ}\text{C}$ accuracy.

Analysis of Perforation Curves

The evolution of the force against deformation was recorded during the penetration test. A typical curve is shown in Figure 4. The area under the force–penetration curve represents the perforation energy; it is computed either by hand or by using an integrator.

Each deformation curve was analysed in the following way:

- The elastic part was determined from the maximum slope of the load–extension curve. This enabled correction of any initial nonlinearity associated with a bad contact between the film and the plunger.
- It had been carefully verified that perforation of the specimen occurred as early as the first drop appeared on the load–deformation curve. As a consequence, the portion of the curve beyond the peak force is not taken into account for the calculation of the puncture energy.

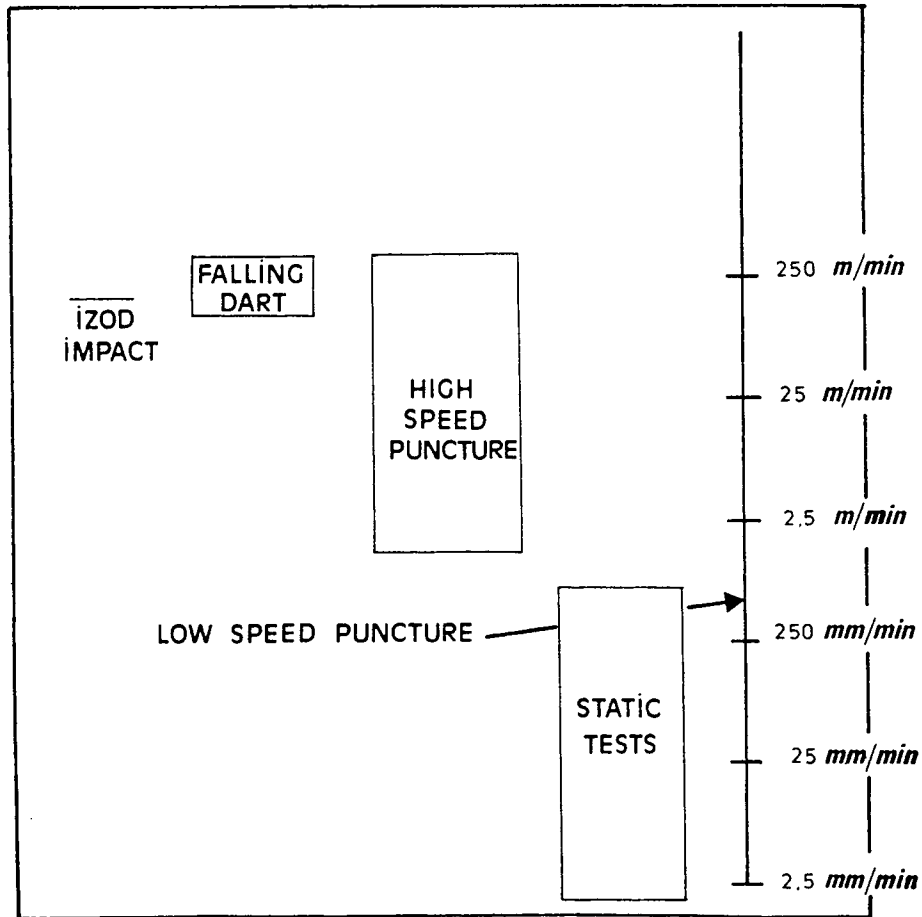


Figure 2 Deformation rates of some usual mechanical tests.

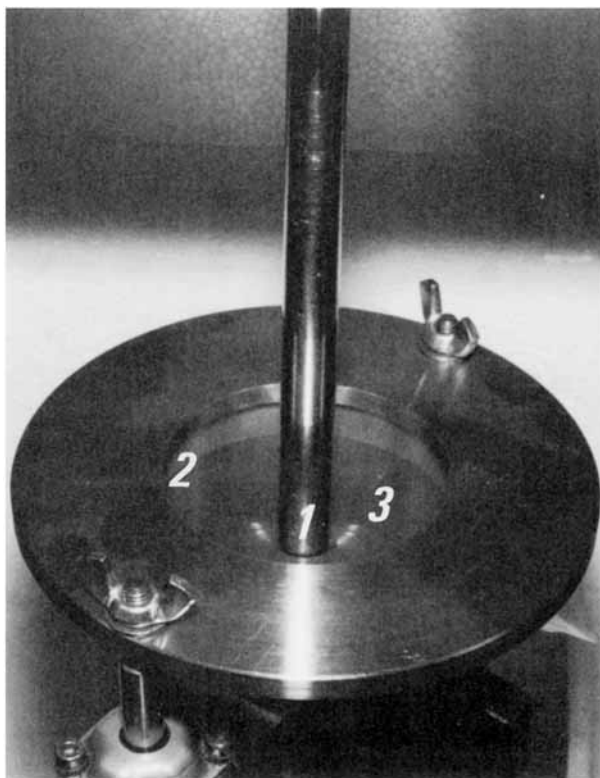


Figure 3 Slow rate puncture of a film: experimental device. (1) hemispherical-ended probe, (2) pneumatic grips, and (3) sample.

The behavior after initial perforation strongly depends on the testing temperature, as discussed below.

Dynamic Mechanical Spectrometry

This test is of great interest, since it enables identification of the various thermomechanical transitions occurring in the material in a given temperature-frequency range. The relaxations refer to motions of specific molecular groups. For a particular

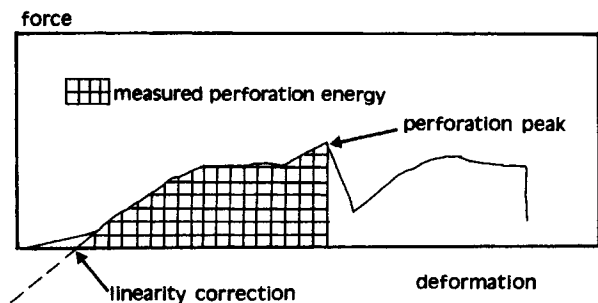


Figure 4 Analysis of a perforation curve.

test frequency, these are evidenced through peaks on the $(\tan \delta, T)$ curve, where the mechanical loss factor $\tan \delta$ relates to the damping capacity of the material, that is, it stands for its ability to absorb energy; $\tan \delta$ is defined by the ratio between the loss modulus and the storage modulus (E''/E' in a tension-compression test and G''/G' in a torsion-shear test).⁵

The temperature variation of $\tan \delta$ for the three EVA films was determined on a Rheometrics RSA II solid-state analyzer, between -120°C and $+50^{\circ}\text{C}$, at frequencies in the range of 0.1–10 Hz. Rectangular strips (50 mm \times 10 mm) have been tested in a tension-compression mode with auto tension monitoring to avoid specimen bending during the compression part of the cycle.

MOLECULAR RELAXATIONS IN EVA COPOLYMERS

Much work has been devoted to the mechanical relaxations observed in polyethylenes and ethylene-based copolymers. An extensive review and study by Popli et al.⁶ provided experimental evidence and molecular interpretations of these relaxations.

In EVA copolymers, three relaxations were observed between -140°C and $+60^{\circ}\text{C}$; this feature is common to other ethylene-based copolymers.^{7,8} Regarding the EVA, the temperature maxima of these

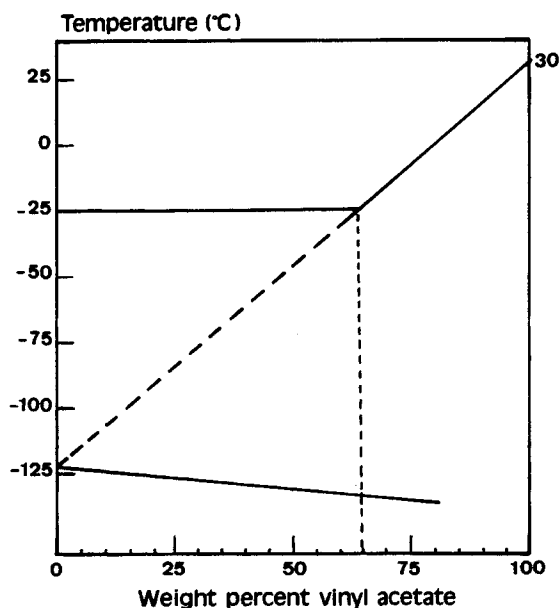


Figure 5 Transition temperatures as a function of vinyl acetate concentration (after Ref. 7).

relaxations depended on the vinyl acetate content as schematically indicated in Figure 5 (after Ref. 7).

With respect to the slow rate penetration measurements, the following discussion will be mainly concerned with the β -relaxation, which roughly spreads between -25°C and $+30^{\circ}\text{C}$. The γ -transition, located around -130°C , corresponds to the glass transition of the polyethylene. Its temperature maximum decreases linearly as the vinyl acetate content increases and the transition even totally disappears when the material becomes too rich in vinyl acetate (for vinyl acetate contents higher than 80 wt %).

The 1 Hz-temperature maximum of the β -transition varied with the comonomer composition in the following way: it decreased linearly from $+30^{\circ}\text{C}$ down to -25°C as the vinyl acetate concentration diminished from 100 down to 65%. Below this

value, the transition temperature remained constant at -25°C . According to Ref. 7, the β -transition observed in this concentration range was assigned to molecular motions of isolated $-\text{CH}_2-\text{CHR}-\text{CH}_2-$ sequences, where R is the acetate group. The number of sequences involved would not depend on the composition of the copolymer.

Another molecular interpretation for the β -transition is suggested by Popli et al.^{6,9} This transition was attributed to segmental motions of disordered chains, occurring within the interfacial regions associated with the lamellar crystallites. This point of view is supported by Glotin and Mandelkern,¹⁰ who propose a quantitative evaluation by Raman spectroscopy of the interfacial content for EVA copolymers with vinyl acetate concentration between 5 and 28% by weight. It was shown that a decrease in the degree of crystallinity from 39% down to 12%

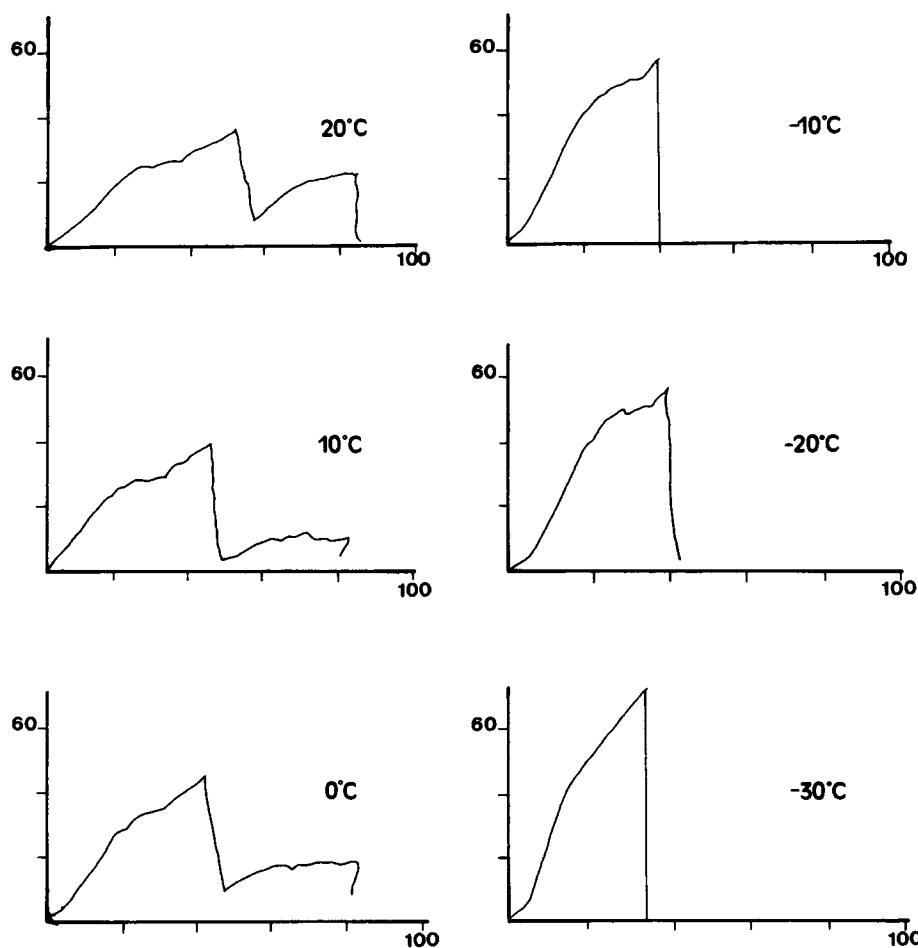


Figure 6 Variation with temperature of the force-deformation curve for a 14 wt % vinyl acetate copolymer (the force is indicated in Newton; the deformation in mm).

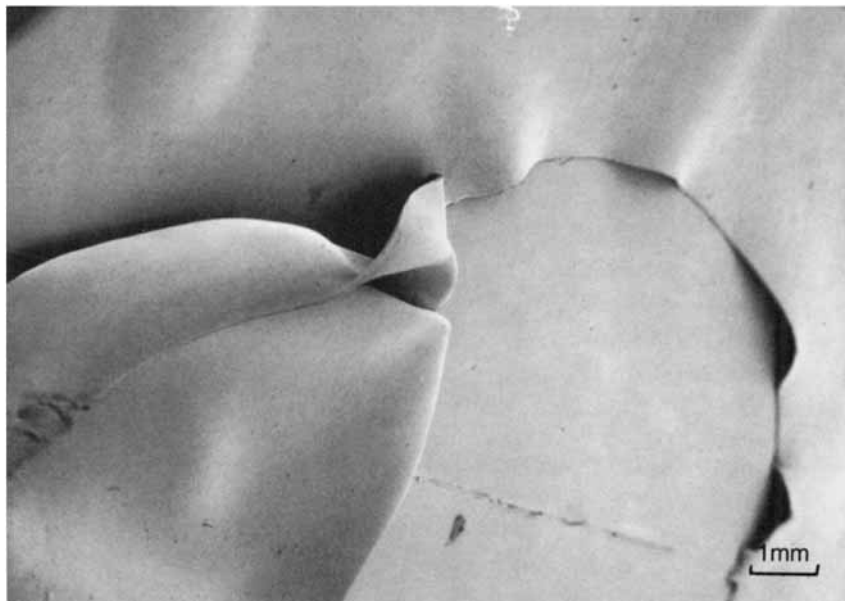


Figure 7 Punctured area at $T = -40^{\circ}\text{C}$.

only induced minor variations in the interfacial content (from 16% to 21%). The constancy of the β -transition temperature, observed in the low vinyl acetate concentration range, together with the slight variation in the interfacial content, led to the assumption that this transition related to relaxations of chain units located in the interfacial region. The requirement of a minimum interfacial content for the β -transition to be observed is also discussed by Popli et al.⁶

Regarding the α -relaxation, Popli et al.⁶ showed that it depends primarily on crystallite thickness.

RESULTS AND DISCUSSION

Figure 6 gives a general view of the penetration curves obtained at different temperatures for the 14 wt % vinyl acetate copolymer. For temperatures

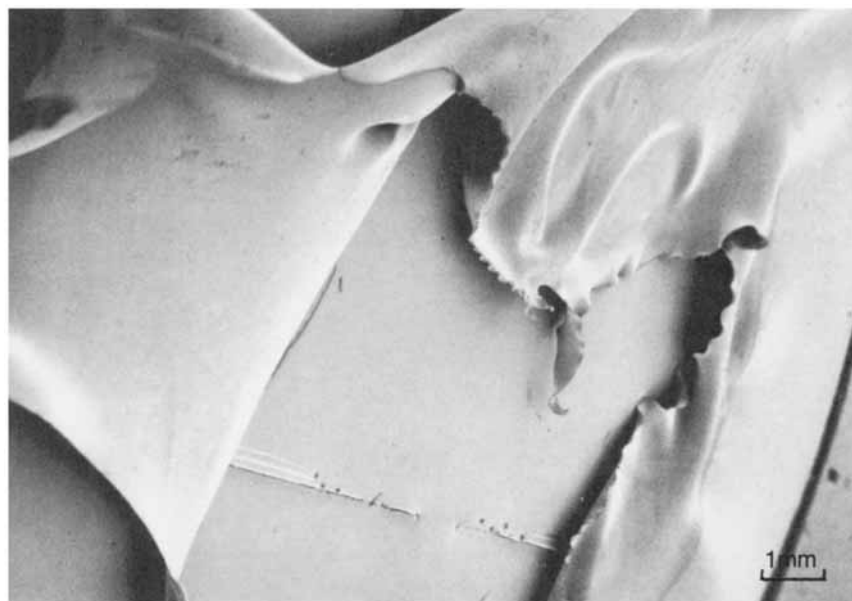


Figure 8 Punctured area at $T = 0^{\circ}\text{C}$.

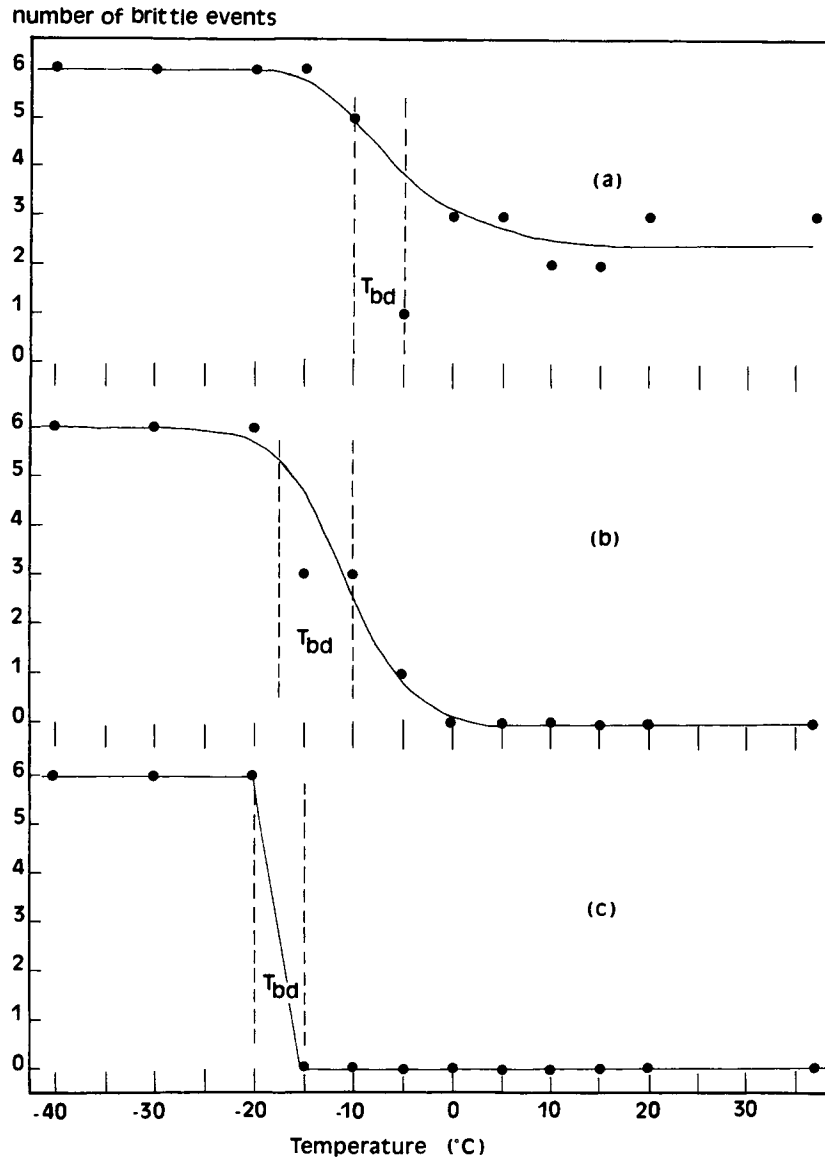


Figure 9 Evolution of the rupture behavior with temperature; for each temperature, six specimens were tested. (a) 9 wt % VA, (b) 14 wt % VA, and (c) 19 wt % VA.

higher than -10°C , the force tended to increase again after the initial drop, indicative of the film perforation. It is not the case for temperatures lower than -10°C .

Figure 7 gives evidence of the clearly delineated punctured region for a specimen deformed at -40°C ; such a rupture may be called a brittle rupture. For a sample tested at 0°C , the perforated area is less regular, as shown in Figure 8; in this case, a friction effect between the film scraps and the probe explains the force increase observed beyond the breaking point. An examination of the two other copolymers yielded similar results.

A closer look at the perforation curves enabled the determination for each experimental temperature of the number of brittle ruptures obtained when six specimens were tested. As suggested by Figure 9, two behaviors may be defined on both sides of a brittle-ductile transition temperature T_{bd} .

A consideration of how the perforation energy is affected by temperature follows. Results are gathered in Table II and may be alternately viewed in Figure 10. A maximum in the puncture resistance is evidenced for each copolymer at a temperature T_p in good agreement with the T_{bd} range, as indicated in Table III. This observation parallels the evolution

Table II Perforation Energy Values (mJ) in Function of Temperature

<i>T</i> (°C)	9 wt % VA	14 wt % VA	19 wt % VA
37	594 ± 27	1044 ± 98	1033 ± 57
20	662 ± 198	1001 ± 98	1258 ± 179
15	642 ± 153	1088 ± 154	1176 ± 107
10	727 ± 115	1109 ± 95	1320 ± 180
5	893 ± 105	1441 ± 120	1376 ± 260
0	807 ± 97	1180 ± 137	1677 ± 257
-5	1070 ± 120	1614 ± 140	1474 ± 237
-10	1030 ± 50	1366 ± 276	1348 ± 121
-15	1044 ± 80	1283 ± 90	1708 ± 313
-20	930 ± 124	1448 ± 173	1500 ± 113
-30	870 ± 100	1353 ± 170	1565 ± 116
-40	875 ± 183	1156 ± 123	1320 ± 210

of the impact resistance recalled in Figure 1; note that the shift in the temperature of the maximum may originate from the difference in the frequency characteristic of each impact test.

As seen in Figure 11, the slow rate perforation energy increases with vinyl acetate content at a given temperature in the same way as does the high speed tensile impact resistance.

The next step of the discussion deals with the temperature dependence of the mechanical loss factor $\tan \delta$. Figure 12 shows the evolution with vinyl acetate content of the composite α , β damping peaks, measured at a frequency of 10 Hz. The three curves are differentiated from each other beyond -40°C .

Table III Critical Temperatures Controlling the Slow Rate Penetration Resistance for EVA Copolymers

Temperature	9 wt % VA	14 wt % VA	19 wt % VA
T_{bd}^a	-10 ↔ -5	-17 ↔ -10	-20 ↔ -15
T_p^b	-10	-10	-15
T_β^c	-10	-11	-13

^a T_{bd} , Transition temperature between brittle and ductile rupture.

^b T_p , Temperature of maximum perforation energy.

^c T_β , Temperature of the β -peak maximum.

The curve obtained for the 9 wt % vinyl acetate film exhibits two peaks: the β -maximum is located around -10°C ; the α one (seen around $+30^\circ\text{C}$) is more prominent.

For the 14 wt % vinyl acetate copolymer, the β -peak at -11°C is more clearly defined, while the α one is both decreased in magnitude and shifted towards lower temperatures.

In the case of the 19 wt % vinyl acetate composition, a strong β -peak is seen at -13°C , and its high temperature shoulder suggests the presence of a small α component, but with a temperature maximum still decreased as compared to the 9 and 14 wt % compositions. The increase in the amplitude of the β -peak, as the vinyl acetate content is varied from 9 wt % up to 19 wt %, together with the decrease in the amplitude of the α -peak, agree with results previously published.^{6,11}

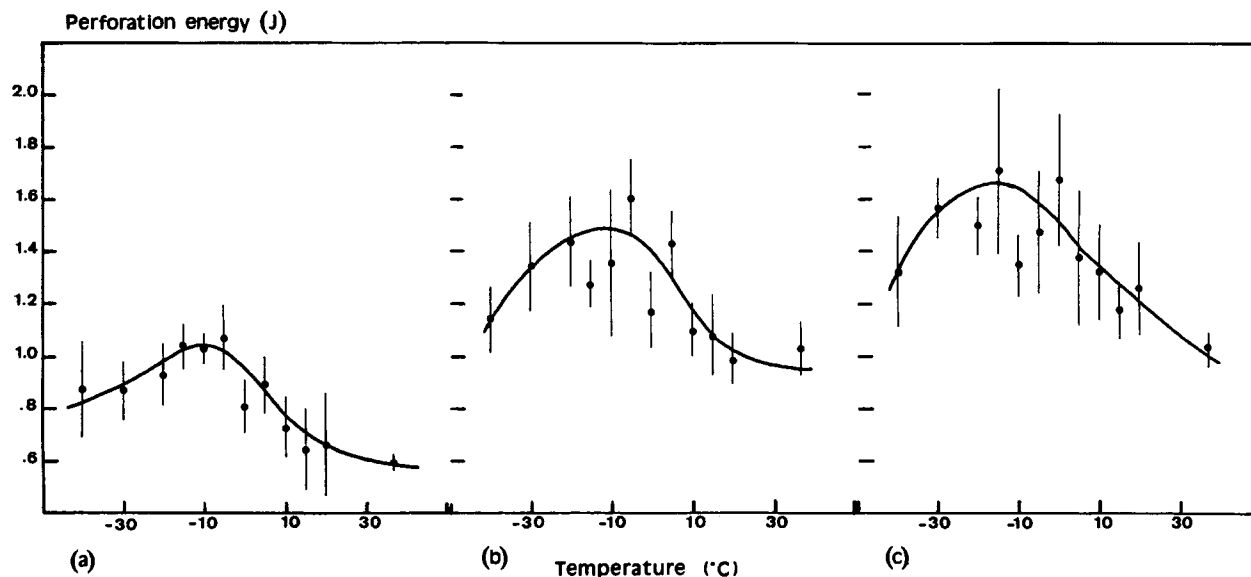


Figure 10 Temperature dependence of the perforation energy: (a) 9 wt % VA, (b) 14 wt % VA, and (c) 19 wt % VA.

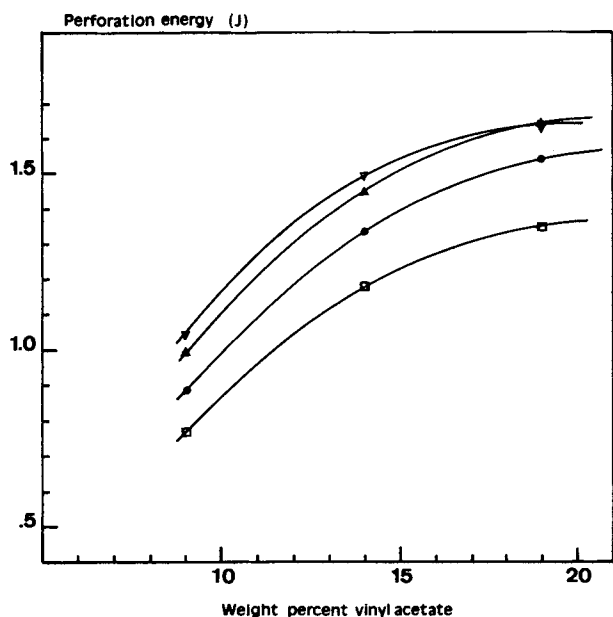


Figure 11 Variation of the perforation energy with the vinyl acetate concentration: (\square) $T = +10^{\circ}\text{C}$, (\bullet) $T = -30^{\circ}\text{C}$, (\blacktriangle) $T = -20^{\circ}\text{C}$, and (∇) $T = -10^{\circ}\text{C}$.

It is worth noting that the constant β -peak temperature maximum shows closer agreement with the data of Popli et al.⁶ as compared to those of Reding

et al.⁷ No explanation is offered for such discrepancies.

Figure 13 compares the temperature evolutions of the perforation energy and of $\tan \delta$ in the temperature range -40°C to $+37^{\circ}\text{C}$. Whatever the copolymer, the temperature T_p associated with the highest puncture resistance value coincides with the temperature T_p of the damping peak. The crystalline α damping peak does not show any correlation with the perforation energy.

The connection between damping β -peak and puncture resistance is also shown in Figure 14: the higher the vinyl acetate content is, the greater the damping ability of the material and the better the resistance to a perforation impact.

The general agreement for a given vinyl acetate concentration between critical temperatures, derived from perforation and dynamic mechanical behaviors, is clearly seen in Table III.

CONCLUSION

The preceding results show that a low temperature slow rate penetration test is able to differentiate behaviors of EVA copolymers with varying vinyl acetate concentration in the same way as does a high

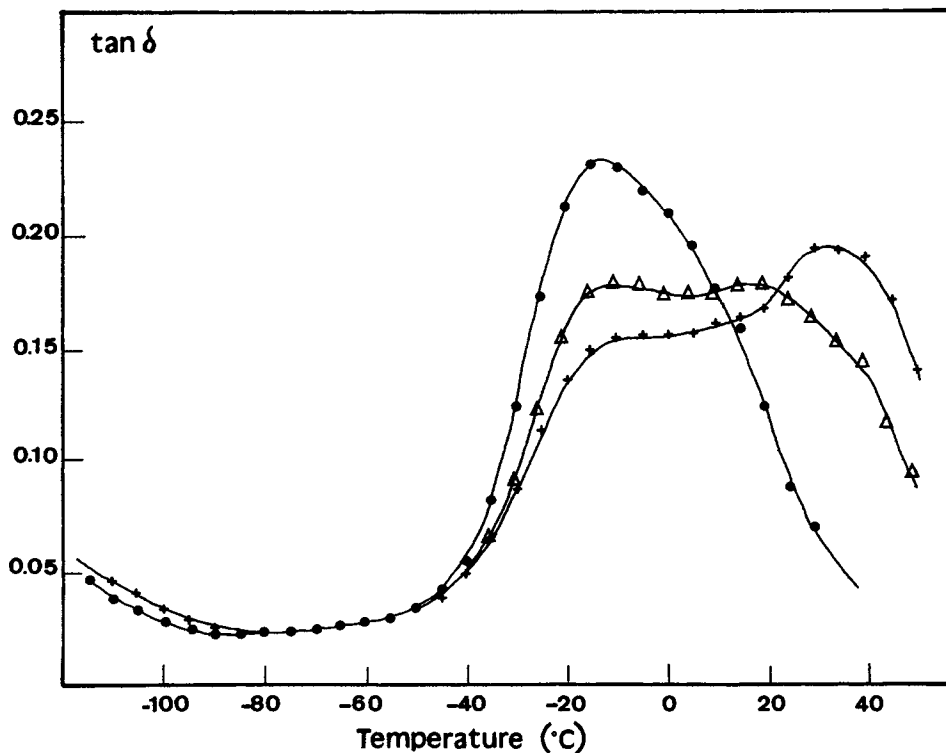


Figure 12 Mechanical damping measured at a frequency of 10 Hz: (+) 9 wt % VA, (Δ) 14 wt % VA, and (\bullet) 19 wt % VA.

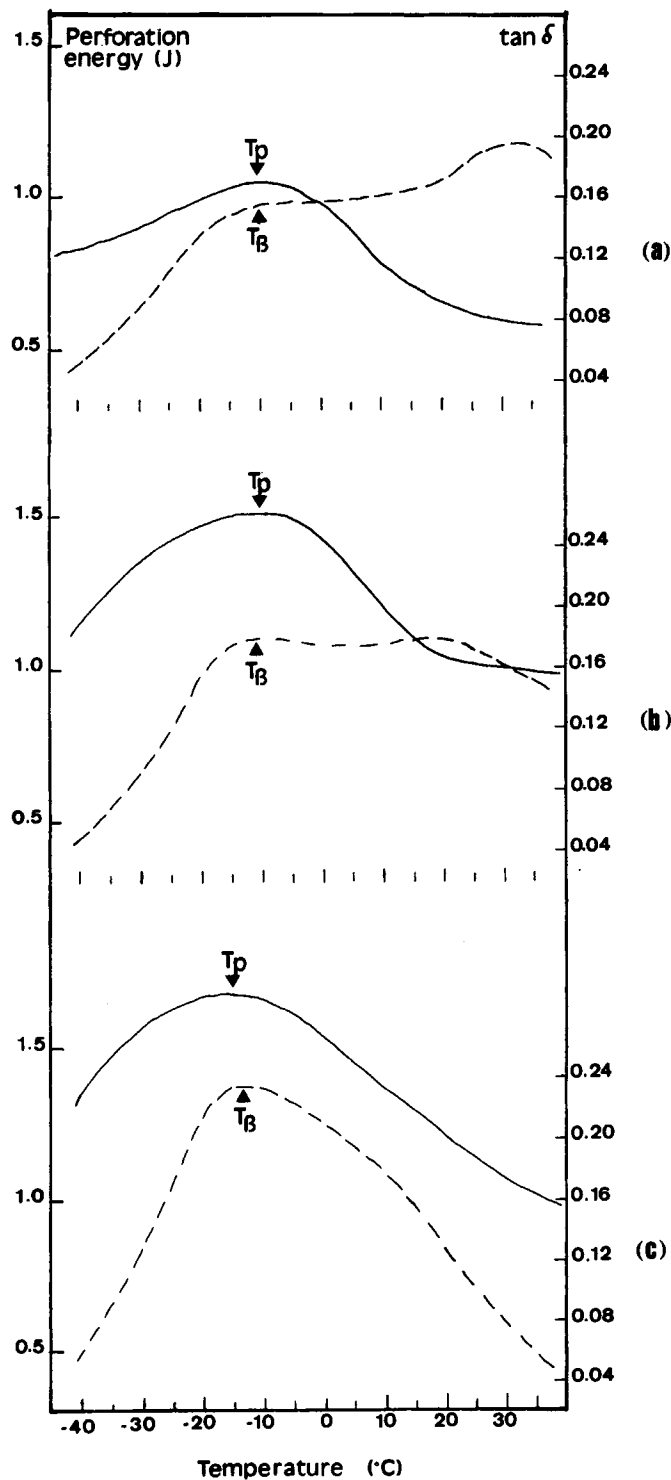


Figure 13 Temperature dependence of the perforation energy (—) and of the mechanical loss factor $\tan \delta$ (---): (a) 9 wt % VA, (b) 14 wt % VA, and (c) 19 wt % VA.

speed impact test. The existence of a key temperature, controlling the mechanical response to such a test, is clearly established. However in both tests, assessing the elementary deformation frequency is

still under debate. This latter point limits the possibility of quantifying the observed correlation with the dynamic mechanical response.

In any event, the critical temperature in the per-

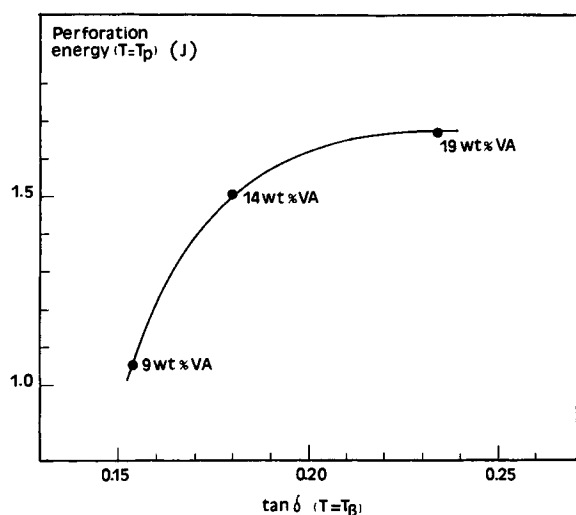


Figure 14 Correlation between the puncture resistance and the mechanical loss factor.

formation behavior is located between -10°C and -15°C , according to the comonomer composition. This temperature corresponds to the temperature at which the penetration resistance is the highest and the damping ability related to β -motions is the most efficient, as deduced from dynamic mechanical spectrometry. This agreement reflects the sensitivity of the low temperature slow rate puncture test to the molecular dynamics.

The perforation procedure described here thus appears as an effective and reliable tool to provide a static mechanical characterization of films devoted to packaging applications for the frozen food market.

In comparison with the well-known free-falling dart method (standard ASTM D 1709), the slow puncture test has the advantage of simulating more

closely the mechanical deformation of a packaging film during use. In addition, this test may be achieved more easily at low temperature and may consequently improve the characterization of the material for a particular range of applications.

The authors are indebted to N. Chaumont for performing the penetration resistance measurements during an undergraduate research project, and to Dr. O. Darras for his kind assistance in the dynamic mechanical testing.

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Received May 6, 1992

Accepted July 27, 1992