ELSEVIER
Thermochimica Acta 272 (1996) 171–179
thermochimica
acta

Dynamic mechanical analysis (DMA) and low temperature impact properties of metallocene polyethylenes[1]

L. Woo*, Michael T.K. Ling, Stanley P. Westphal

Baxter Healthcare, Round Lake, IL 60073-0490, USA

Received 25 September 1994; accepted 12 June 1995

Abstract

As a result of the very high co-monomer content and homogeneous short branch distributions made possible by the metallocene catalyst, superior low temperature mechanical properties are possible. We have studied a series of these polymers varying in density from 0.87 to 0.92 kg l^{-1} using dynamic mechanical analysis. Compared with conventional polyethylenes, the beta relaxation was shifted to as low as –44°C. Concurrently, low temperature impact properties were evaluated from about –100°C to ambient. The impact response with temperature was in good agreement with the calculated response based on loss modulus.

Keywords: DMA; Low temperature impact; Metallocene polyethylene

---

1. Introduction

Intense research efforts in metallocene chemistry have established a new class of coordination polymerization catalysts for olefins. Compared with the traditional Ziegler–Natta catalysts from first row transition metals, e.g. Ti, Cr, V, Group IVb elements with complex d orbitals are used [1]. These metals when complexed with cyclic aromatic ligands form metallocenes with extraordinary activity. In addition, by tailoring the spatial arrangements of the ligands, exquisite control of the monomer insertion can be achieved. This level of control allows incorporation of comonomers in a very homogeneous way.

---

* Corresponding author.

[1] Presented at the 23rd North American Thermal Analysis Society Conference, Toronto, Ont., Canada, 25–28 September, 1994.

SSDI 0040-6031 (95) 02621-5

Previously, efforts to increase comonomer content beyond a few percent have yielded too much of waxy, low molecular weight fractions to be useful. When comonomers are incorporated homogeneously, very high comonomer contents are possible while the product remains solid and processible by conversion machinery. With the new technology, polymers with unprecedented properties are being commercialized.

Many of the novel properties of these materials such as flexibility, low temperature ductility and thermoplastic elastomer behavior, are important for the medical industry. Therefore we have initiated a thermal mechanical spectroscopy study of several of these polymers, compared with traditional polyethylenes (of both linear and high pressure origin). In a similar temperature range, we also evaluated the impact properties. Using a recently introduced method of calculating the impact versus temperature function from dynamic loss spectra, we compared the predicted impact temperature function with actual determinations.

2. Experimental

A Seiko dynamic mechanical Analyzer DMS-110 was used in rectangular flexure mode with compression molded samples about 1 mm thick over frequencies of about 0.5 and 100 Hz, and temperatures between −150°C and the melting point at 3°C min^{-1} temperature scanning rate. Typically, data at 1 Hz are used for comparisons, while data of all frequencies are used for activation enthalpy calculations. For the activation enthalpy calculation, $\tan\delta$ at maximum temperature in K^{-1} units (K = absolute temperature) at a given frequency is plotted against the logarithm of the frequency, and the slope of the resulting plot used for the calculation.

Impact testing was carried out on a Dynatup instrumented impact tester with 2 cm semi-spherical impact tup and a Biomation transient recorder capable of digitizing events at the rate 100 MHz. All samples were mounted on 15 cm diameter aluminum testing frames. A special computer controlled liquid nitrogen cooled environmental chamber capable to −150°C was used to condition the samples and hold the film holder during the impact event. Just prior to the experiment, an insulator gate to the chamber was first opened allowing the traveling "tup" to penetrate the sample near the top of the chamber. The velocity of the impact was measured by a 1.0 cm aluminum flag passing through an optical sensor through a Hewlett Packard universal frequency counter. The optical flag also triggered the transient recorder to digitize the strain gage signal from the impact head. Upon completion of the impact event, stress data from the transient recorder was transferred to the computer for impact energy and displacement calculations, and finally load versus displacement and impact energy versus displacement curves were plotted on a HP7470 plotter. The overall schematic set up is shown in Fig. 1. In this series of experiments, an impact velocity of about 3.3 m s^{-1} was used.

Samples chosen in this study were intended to cover a wide range of densities or comonomer contents. Designation of samples are given in Table 1. Samples A, B and C were homogeneous copolymers, while sample D was produced by a high pressure free radical initiated process, and sample E from a traditional Ziegler–Natta catalyst with heterogeneous reactivity towards comonomers.

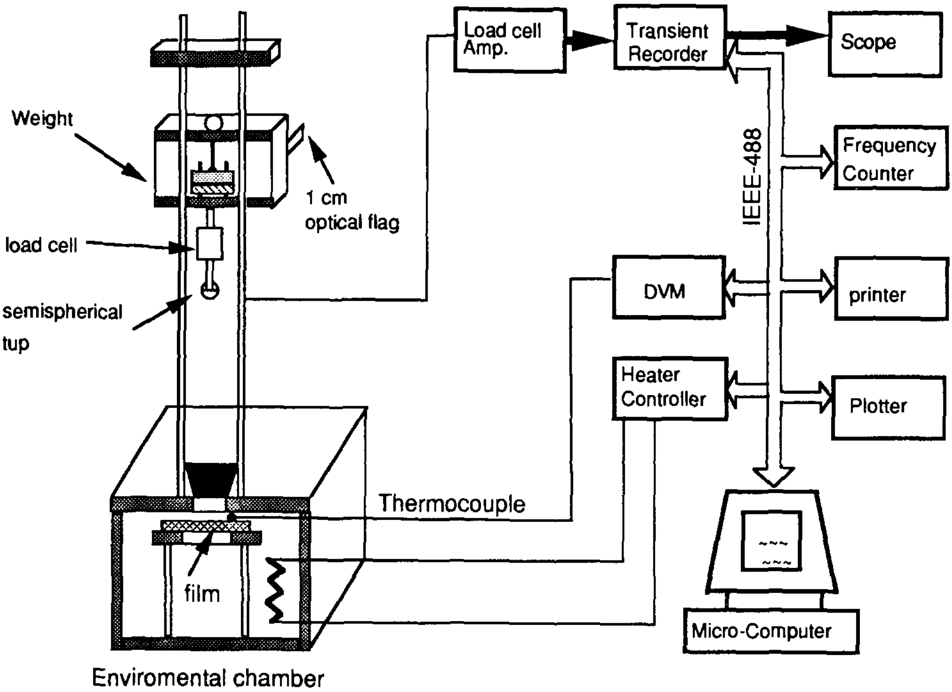

Fig. 1. Instrumented impact tester schematics.

To more completely characterize the samples, thermal properties were first determined with a TA Instruments 2100 thermal analyzer with a 2910 cell and the results are shown in Table 2.

3. Results and discussion

DSC data of the samples (Table 2) indicated that a wide range of melting points (T_m) and crystallization temperatures (T_c) were covered by the samples chosen. Crystallinity

Table 1

Sample designation

Sample	Density	MI	Process	Co-monomer
A	0.88	3.8	Solution	Butene
B	0.87	1.0	Solution	Octene
C	0.90	1.0	Solution	Octene
D	0.92	4.0	High pressure	–
F	0.912	3.3	Solution	Octene

Table 2
Thermal properties

Sample	T_m (in °C)	T_c (in °C)	Crystallinity (in %)
A	69.5	55.8	20.4
B	57.4	43.2	16.2
C	101.3	83.6	33.0
D	110.1	94.9	41.1
E	123.5	105.3	38.0

ranged between a low of 15% for sample B to the highest of about 41% for sample D. The combined dynamic mechanical 1 Hz loss spectra (tan δ) for all samples are shown in Fig. 2.

3.1. Major relaxations

The γ relaxation located between −115 and −120°C appears to increase in intensity as

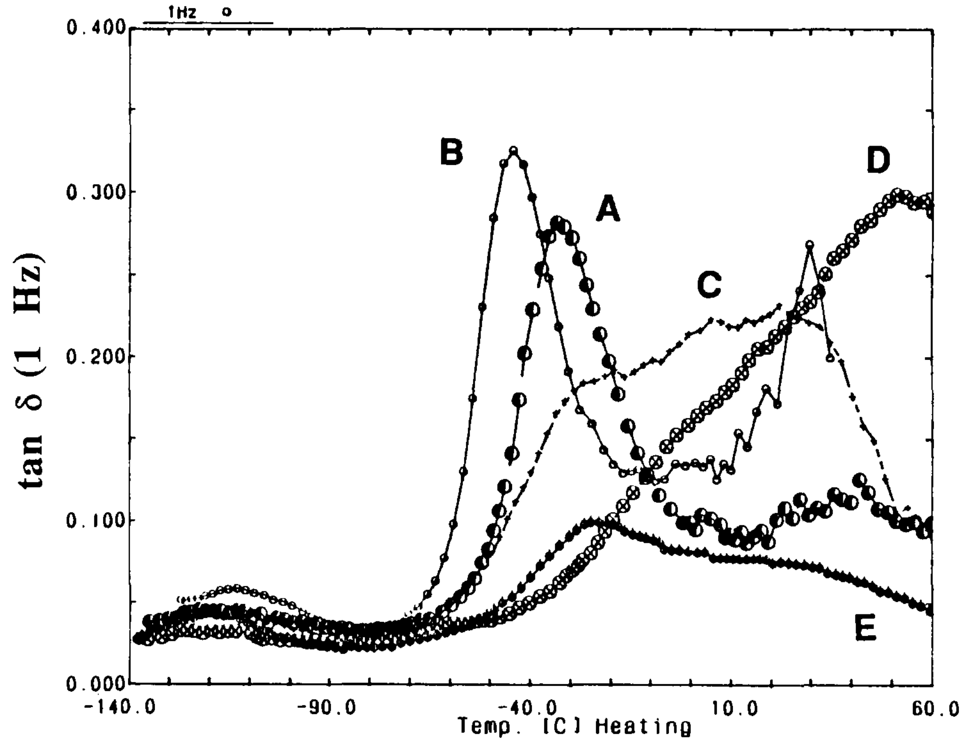

Fig. 2. Dynamic mechanical spectra (tan δ, 1 Hz).

Table 3

Dynamic mechanical analysis

Sample	β_{max} (in °C)	Tan δ (in °C)	FWHH (in %)
A	–33	0.28	26
B	–44	0.33	22
C	–26	0.18	29
D	(–5)*	(0.18)	(43)
E	–22	(0.1)	38

[a] Number in parentheses are estimates due to overlapping peaks.

the density of samples decreases or the amorphous content increases. In addition, there appears to be a slightly upward shift in temperature accompanying this trend. This observation is quite consistent with the historically assigned [2,3] local mode relaxation in the amorphous phase of polyethylene. Both the temperature shift and the increases in intensity could be the result of increased amorphous phase volume and the release of constraints from the reduced densities.

The α relaxation which occurs between 0 and 60°C is quite complex. The high pressure sample D appears to have the highest relaxation intensity, while very broad, ill-resolved relaxations are seen from samples A, C and E. If we adopt the interpretation of Mandelkern [4], where the position of the α peak is inversely related to the lamella thickness in the crystalline phase, these samples exhibited a rather broad distribution of crystal sizes. In the case of sample B, the lowest crystallinity sample in this study, the apparent sharp α transition at about 30°C indicates a narrow distribution of crystal sizes.

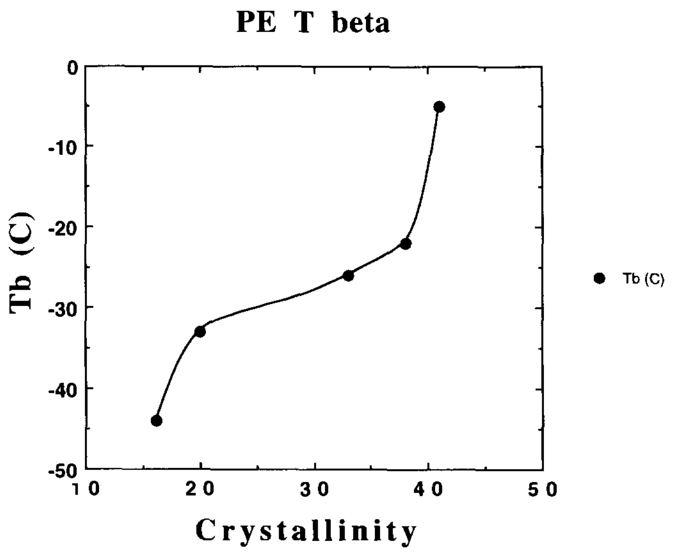

Fig. 3. Beta transition versus crystallinity.

By far, the β relaxation offered the most interesting contrast among our samples. The high pressure polymerized sample D exhibited a barely discernible shoulder on the α relaxation at about 0 to −10°C. Sample E made with conventional Ziegler–Natta catalyst showed a distinct β maximum at about −22°C, while sample C, a metallocene sample, at about −26°C. Further reduction in density led to still lower β relaxation temperatures. When the β-maxima were plotted as a function of density, or crystallinity [5], a rather steep drop from the 0°C range was seen starting at about 0.91 density. At lower crystallinities a linear dependence with density became apparent with yet another step decrease for the lowest crystallinity sample. This apparent complex dependence stands in contrast with the relative constant beta temperatures for ethylene copolymers observed by Popli and Mandelkern [4], and the parabolic function reported by the authors [6] for the ethylene vinyl acetate system. Differences in comonomer species and slightly varying thermal history of samples could be the origin of this discrepancy. Further study with the same comonomer covering similar crystallinities may be required to clarify this point.

Accompanying the shift towards lower temperatures, there is a progressive narrowing of the relaxation maxima. Since the β process is normally assigned to long main chain segments in the amorphous phase, the spectral narrowing is an indication that the local environment near the branch points (which gave rise to the amorphous phase) are becoming more homogeneous. As a consequence of this uniformity of local environments and the cooperativity of the molecular motions, the β relaxation increasingly assumes the appearance of a glass transition T_g, as evidenced by comparing $E_u - E_r$, the difference between the unrelaxed modulus and the relaxed modulus, as a function of crystallinity (Fig. 4).

3.2. Impact properties

The impact properties as a function of temperature from all samples are presented in

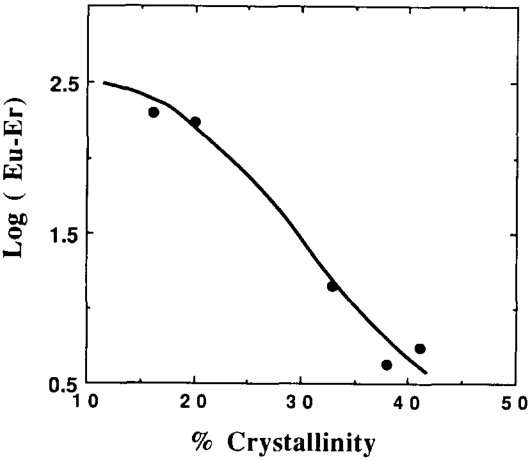

Fig. 4. $E_u - E_r$ versus crystallinity.

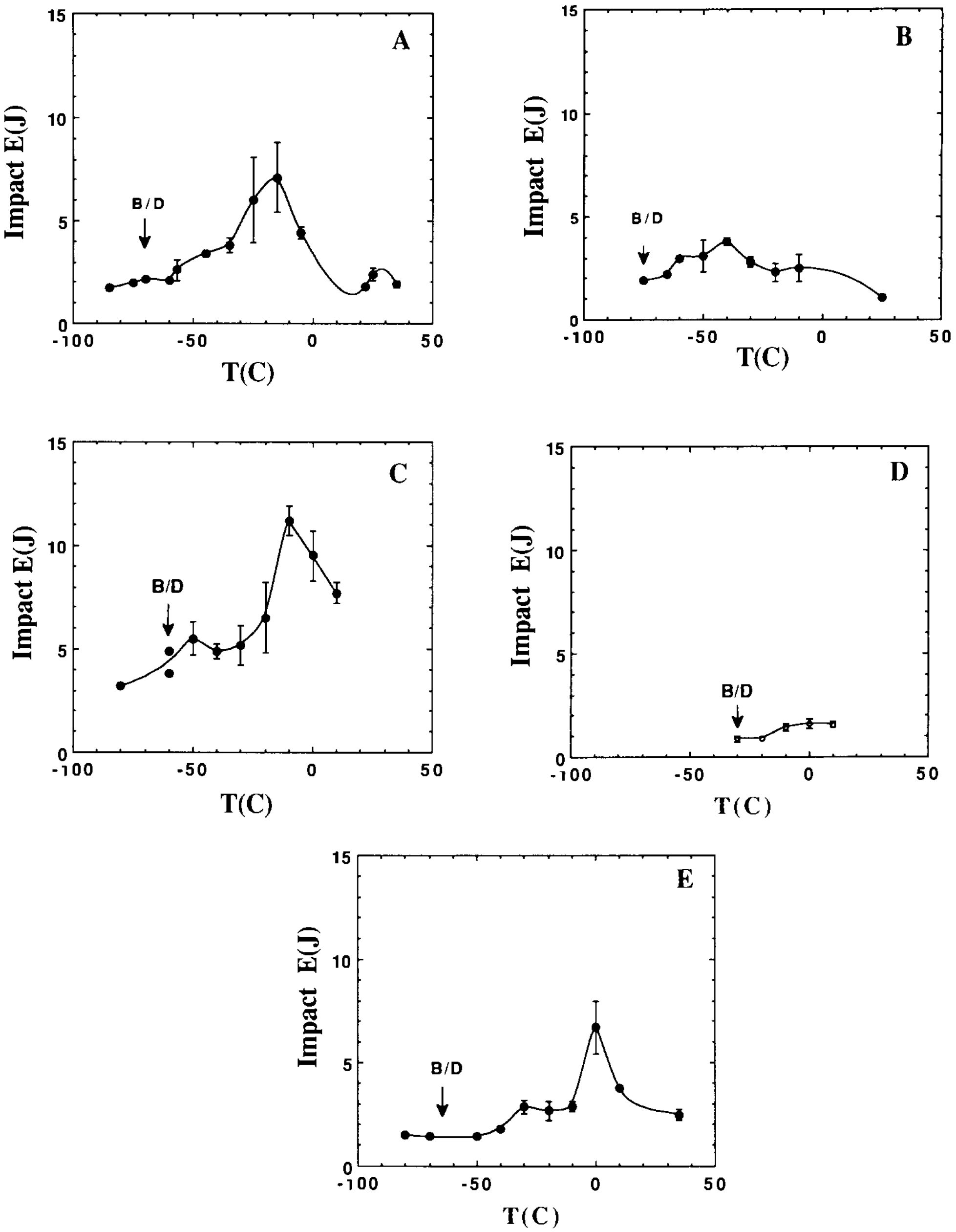

Fig. 5. Impact testing results.

Fig. 5. The brittle to ductile transition point is indicated with an arrow. The error bar represents one standard deviation from the measurement average of three separate samples. Sample A exhibited a brittle-ductile transition at −70°C, a remarkably low temperature. A slight shoulder was seen on the impact energy temperature dependence at about −55°C which may have originated from the gamma relaxation. The impact energy maximum occurred at about −22°C at about 7.1 J for the sample thickness used. Sample B, with the lowest density in this study, had the lowest B/D transition of −75°C and a pronounced shoulder on the energy plot at about −60°C. The impact energy maximum occurred at −40°C, one of the lowest impact maximum temperatures seen in many of the olefinic samples. However, perhaps due to the much reduced modulus in the temperature range, the maximum impact energy achieved was reduced to about 4 J. Sample C had a still higher B/D transition of about −60°C, reflecting the reduced effectiveness of the gamma relaxation in imparting ductility. A clear secondary impact maximum was seen at about −50°C, and the main energy maximum at about −12°C. The combination of a higher modulus and the strong beta relaxation resulted in an extremely high maximum energy value of 11.5 J. Sample D exhibited the B/D transition at about −40°C, with no indication of the contribution from the gamma relaxation. The overall impact energy was the lowest over the entire temperature range measured. Evidently, for the lower crystallinity samples, this onset in ductility resulted from the increased main chain mobility due to the γ relaxation. However, in Sample D, due to the relatively high crystallinity, the γ relaxation became suppressed and rendered ineffective between temperatures of −40°C and about −70°C. The absolute fracture energies for these samples of similar thicknesses appeared to be a complex function of the β relaxation maxima and crystallinity. The location of the impact energy maxima appeared to correspond roughly to the order of the beta relaxation temperatures.

Using a methodology introduced recently [7], the impact fracture energy function for the samples were calculated from the loss modulus (E'') spectra. Briefly, to calculate the material's dissipation capacity towards an impulse excitation, the overlap between the material's loss spectrum and the impulse spectrum is evaluated at a given temperature as a function of frequency. The comparison between measured fracture energy onset and peak temperatures is listed in Table 5. It appears that good agreement was obtained, even though the nature of deformations was very different between the two tests. There also appears to be a systematic deviation of about −8°C between the predicted and the meas-

Table 4
Impact testing

Sample	B/D transition (in °C)	Energy peak (in °C)	Peak energy[a]/J
A	−70	−22	7.1
B	−75	−40	3.8
C	−60	−12	11.5
D	−40	0	1.6
E	−65	0	6.8

[a] Film thickness = 0.23 ± 0.05 mm.

Table 5
Predicted impact function

Sample	Onset (in °C)	Peak (in °C)
A	<–60	–28
B	<–60	–39
C	–50	–21
D	–40	–10
E	<–60	–9

ured impact maxima temperatures. This offset can at least partially be accounted for by the temperature scanning rate during the frequency scan.

4. Summary

Dynamic mechanical analysis on a series of polyethylenes produced by the metallocene catalysts were compared with high pressure and Ziegler–Natta polymerized copolymers. For the sample of the lowest density in this study, the comonomer content was very high and very homogeneously distributed, resulting in beta relaxations as low as –44°C at 1 Hz. As a result of this low temperature relaxation, excellent sub-ambient impact properties were obtained. The impact results also agreed well with predicted functional behavior from a semi-quantitative method based on the mechanical loss spectra.

References

[1] S. van der Ven, Polypropylene and other Polyolefins, Polymerization and Characterization Studies in Polymer Science, Vol. 7, Elsevier, New York, 1990.
[2] N.G. McCrum, B.E. Read and G. Williams, Anelastic and Dielectric Effects in Polymer Solids, Wiley, New York, 1967, p. 371.
[3] R.H. Boyd, Polymer, 26 (1985) 1123–1133.
[4] R. Popli, M. Glotin, L. Mandelkern and R.S. Benson, J. Polym. Sci., Phys. Ed., 22 (1984) 407.
[5] B. Wundelich, Macromolecular Physics, Vol. 1, Academic Press, New York, 1973, p. 388.
[6] L. Woo, Michael T.K. Ling and S. Westphal, Thermochim. Acta, in press.
[7] L. Woo, Michael T.K. Ling and S. Westphal, Polymer Eng. Sci., 34 (1994) 420–427.