

Glass-Transition Temperature Determination by Microhardness in Norbornene–Ethylene Copolymers

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ABSTRACT: Vickers microhardness as a function of temperature was determined in a series of norbornene–ethylene copolymers synthesized with a metallocene catalyst. The norbornene content in the samples ranges from 31 to 62 mol %, and all of them were found to be amorphous. The possibility of studying the glass-transition temperature by plotting the microhardness–temperature dependencies is discussed in addition to the limits and the reliability of the

suggested method. Moreover, a linear dependency between microhardness at different temperatures and glass-transition temperature was established. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3666–3671, 2003

Key words: norbornene–ethylene copolymers; microhardness; glass transition;

INTRODUCTION

An extensive demand for materials with tailor-made properties to be used as engineering polymers is occurring at present time. Industry continuously tries to modify commercial polyolefins. In recent years, the use of single-site metallocene catalysts has allowed important advances in polyolefins technology because a new and large variety of polyolefins may now be obtained, that is, ethylene and propylene modified with α -olefins or cycloolefins.

Cyclic olefinic copolymers (COCs) are a new class of polymeric materials whose properties profiles can be changed with the comonomer content during the polymerization. When the content of norbornene is above 30 mol % these copolymers are amorphous and transparent materials. Metallocene catalysts permit to

copolymerize cycloolefins (norbornene, for instance) and ethylene units in the whole range of composition with control of molecular weight (MW) and molecular weight distribution (MWD). In addition, changing the catalyst system can attain copolymers with different properties. These distinct properties are dependent upon the abilities of metallocenes to form blocks of cyclic monomer units and different stereoregularities within the norbornene blocks.^{1,2} Thus, the microstructure of COCs plays an important role in their properties. Copolymers containing a high norbornene content do not necessarily exhibit a glass-transition temperature T_g higher than that of others with a lower content in the rigid comonomer.² In the case of copolymers made up of predominately alternating/isolated norbornene, the T_g measured is relatively low. This feature can be attributed to the flexibility increase in the polymer backbone. The reverse situation is also observed. A higher T_g is obtained when longer norbornene sequences predominate due to the augment in stiffness introduced in the material backbone. Therefore, it is important to utilize the same catalyst system in the polymerization of cyclic olefins copolymers if a correct composition-properties relationship is desired to be reached. In a previous work, we found a linear relationship between the amount of norbornene incorporation and the T_g for a given catalyst in the polymerization.³ On the contrary, a linear correlation does not appear when copolymers with high norbornene content and different microstructures are considered.² Few studies can be found in the literature about the properties of this type of polymers because synthesis with metallocene catalysts is quite recent.⁴ Moreover, microhardness (MH) measurements are

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particularly scarce in the copolymers studied in this work.^{3,5}

The Vickers microindentation hardness test measures the resistance of a given material to a plastic deformation produced by the impact of an indenter. Therefore, amorphous and crystalline polymers provide a different response, related to the rigidity of the system. Microhardness tests allow a rapid evaluation of variations in mechanical properties that are affected by changes in chemical or processing conditions.⁶⁻⁸ In addition, MH results can be related to mechanical parameters such as the elastic modulus and yield stress.⁹

The goal of this work is to determine the glass transition temperature of norbornene-ethylene copolymers by microhardness and attempt to find a microhardness/norbornene content relationship. Their behavior with temperature and their stability when they are used at high temperatures are also analyzed. The copolymers used in this work have been prepared using *rac*-Et(Ind)₂ZrCl₂ and characterized by differential scanning calorimetry, DSC, x-ray diffraction, RX, and dynamic mechanical thermal analysis (DMTA).

EXPERIMENTAL

The synthesis and NMR characterization were carried out in the laboratory of Dr. Tritto (CNR, Milan, Italy). An autoclave under high-pressure conditions and a Bruker AM-270 spectrometer (Bruker Instruments, Billerica, MA), operating at 67.89 MHz, in solutions of C₂D₂Cl₄ at 103°C were used, respectively. To prevent the catalysts decomposition used for polymerization, all manipulations of air- and/or moisture-sensitive compounds were carried out under a dry nitrogen atmosphere with using of standard Schlenk or vacuum-line techniques and by means of a glove-box. MAO (10 wt % in toluene; Witco) was used after previously removing the solvent (Crompton GmbH, Bergkamen, Germany) and subsequently drying the resultant powder (50°C) for 3 h in a vacuum (0.1 mm Hg). Toluene was dried and distilled from sodium under a nitrogen atmosphere. *Rac*-Et(Ind)₂ZrCl₂ was purchased from Witco.

All the polymers were obtained with a conversion lower than 20% to maintain constant the norbornene/ethylene relative concentration in the mixture. Molecular weights were obtained by GPC in *o*-dichlorobenzene, at 135°C. The polydispersity index, M_w/M_n , ranged from 1.5 to 2.

Thermal, dynamic mechanical and hardness measurements were carried out on films obtained using a Collin hot-press, heated to a temperature of 40° above the glass transition and held under a pressure of 50 bar. The films were kept under such conditions not more than 3 min to avoid a possible thermal degradation, especially at high norbornene contents. The cool-

ing process was carried out with water-cooled plates by quenching.

DSC measurements were made with a Perkin-Elmer DSC7 (Perkin Elmer Cetus Instruments, Norwalk, CT) at a scanning rate of 20°C/min. The sample mass ranged from 6 to 10 mg. The glass-transition temperature estimation was taken as three different criteria: (1) $T_{g\text{ middle}}$: the temperature at which the specific heat increment was half of the total value at the transition; (2) $T_{g\text{ onset}}$: the temperature of departure from the specific heat line of the glassy state before the transition; (3) $T_{g\text{ offset}}$: the temperature of reaching the line for the rubbery state above the transition. All these determinations were made on the second heating run of the sample.

MH measurements were made by using a Vickers indenter (Vickers Instrument, Malden, MA) attached to a Leitz microhardness tester (Leitz, Wetzlar, Germany). A load of 100 g was used, with a loading cycle of 25 s. The temperature was raised in steps of 5 or 10°C, allowing 3 min for temperature equilibration, and then performing MH determination. The experimental values are the average of three measurements. MH values (in MPa) were calculated according to the following relationship:

$$\text{MH} = 2 \sin 68(P/d^2) \quad (1)$$

where P (in N) is the contact load and d (in mm) is the diagonal length of the projected indentation area. The heating control was made with a hot-stage Linkam TM S 92 and an aluminum adaptador. All samples were initially heated above T_g to refresh. As described for DSC measurements, the glass-transition temperature estimation was accomplished under three different criteria: (1) $\text{MH}_{T_{g\text{ middle}}}$: the temperature where MH diminishment was half of the total value at the transition; (2) $\text{MH}_{T_{g\text{ onset}}}$: the temperature of MH departure from the line obtained before the glass transition; and (3) $\text{MH}_{T_{g\text{ last}}}$: the last temperature at which MH can be determined. It is important to notice that measurement of MH above T_g cannot be performed because elastic deformation dominates under the empirical conditions used and reversibility of the imprints is so fast that the measurement of the indentation diagonals in the frame of an admissible accuracy could not be attained.

It was found that, at the end of the MH experiments, sample CNE10 appears to be brown, in contrast to its initial transparency. The interpretation of this feature is that some kind of degradation (crosslinking, oxidation, etc.) occurred in the sample, provoked by its exposure at high temperatures during the MH experiments. Therefore, no reliable MH data can be obtained for this sample in the glass transition region and only the MH results at low temperatures have been considered for this sample (see Fig. 1). No ap-

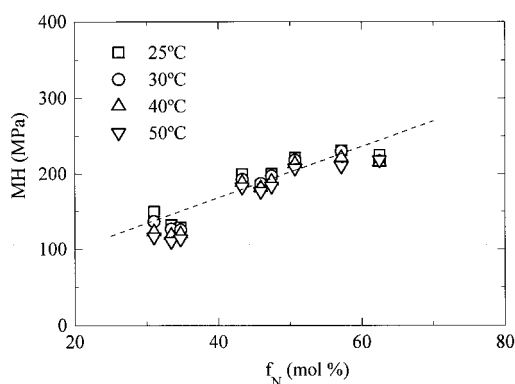


Figure 1 Dependency of Vickers microhardness on the norbornene content at different temperatures.

parent degradation seems to have occurred in the other samples because their transparency is maintained along MH measurements.

Dynamic mechanical measurements were carried out with an MK II dynamic mechanical thermal analyzer (Polymer Laboratories, Poole, UK) working in the tensile mode. The complex modulus and loss tangent of the samples were determined at 1, 3, 10, and 30 Hz over a temperature range from -140 to 230°C . The heating rate was $1.5^{\circ}\text{C}/\text{min}$.

RESULTS AND DISCUSSION

The amorphous norbornene–ethylene copolymers were characterized by X-ray diffraction in a previous work⁵ and the results obtained from the characterization of the different norbornene–ethylene copolymers by DSC and DMTA are shown in the Table I. The DSC scan of each sample was recorded at $20^{\circ}\text{C}/\text{min}$, as mentioned in the Experimental section, after a cooling at $20^{\circ}\text{C}/\text{min}$ from the rubbery state to remove any thermal history developed within samples below T_g . The copolymers under study show a single DSC glass transition and the T_g value increases as norbornene

content is raised. These results are similar to those previously reported by us and other authors for different norbornene–ethylene copolymers.^{3,5,10,11}

Figure 1 shows the microhardness for the samples studied as a function of the norbornene content f_N measured at four temperatures (25 , 30 , 40 , and 50°C) lower than the glass transition of all the specimens. It can be seen that microhardness increases as f_N does, as expected, because norbornene segments incorporate a considerably much higher rigidity into the macromolecular chains.^{5,12} It seems that at lower norbornene contents, MH decreases significantly on passing from 25 to 50°C and that difference becomes smaller as the norbornene content increases, so that different straight lines could be drawn for the various temperatures. However, and considering the scattering of the data and the uncertainty of the experimental results, we have drawn a single line in Figure 1. This line extrapolates to a value of MH of about 275 MPa for $f_N = 100$ (i.e., for PN homopolymer), whereas its value is very small (around 10 MPa) for $f_E = 0$ (i.e., for PE homopolymer). This value should represent the one for PE totally amorphous and measured below its glass transition, as it happens for all of the samples here considered. However, this is quite unrealistic, because for values of f_N below around 20% the glass transition of such a copolymer will be below room temperature and if f_N is even lower, the sample will crystallize to some extent, as occurs with other ethylene copolymers with low comonomer content.

More realistic appears to be the value extrapolated for PN homopolymer, leading to a very high MH, which reflects the very high rigidity of this polymer even in the amorphous state. In fact, previous *ab initio* calculations on this polymer show its very high packing efficiency.¹³

Figure 2 displays the temperature dependence of microhardness for all of the copolymers studied. The measurements are performed from room temperature

TABLE I
Molar Composition, Molecular Weight, Polydispersity Index, and Glass-Transition Temperature for the Different Samples

Sample	mol % N ¹³ C-NMR	M_w (10^{-3})	M_w/M_n	T_g ($^{\circ}\text{C}$)	
				DSC ^{middle}	DMTA (E'' , 3 Hz)
CNE1	31.0	166	2.6	63	62
CNE2	33.7	—	—	66	49
CNE3	33.4	138	2.3	66	55
CNE4	34.8	122	1.9	78	54
CNE5	43.3	96	1.7	111	106
CNE6	45.9	122	1.9	121	120
CNE7	47.4	164	2.1	136	133
CNE8	50.7	80	1.5	147	143
CNE9	57.2	—	—	180	177
CNE10	62.5	188	2.1	221	213

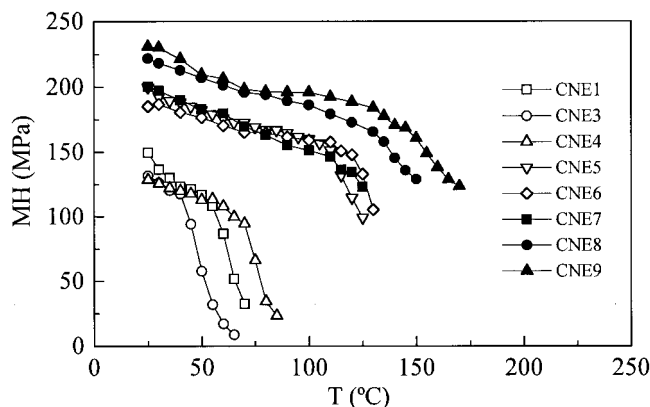


Figure 2 Vickers microhardness as a function of temperature for the different copolymers.

up to the temperature when the measurement of the Vickers microhardness is ruled out, that is, when elastic deformation dominates. Then, the reversibility of the imprints is so fast that such imprints do not allow the measurement of the indentation diagonals in the frame of an admissible accuracy, as mentioned before.

All of the curves plotted in Figure 2 consist of two characteristic regions. In the first one, at low temperatures, MH decreases slowly with increasing of the temperature. Straight lines of slope b can characterize this region. As norbornene content is increased, the slope b is lowered, indicating a MH dependence with temperature smaller than that found at the lowest comonomer compositions, as depicted in Figure 3(a).

The second characteristic region in Figure 2 involves a significantly deeper and faster decrease of MH, which occurs along the transition from the glassy to the rubbery state. This region can be characterized by

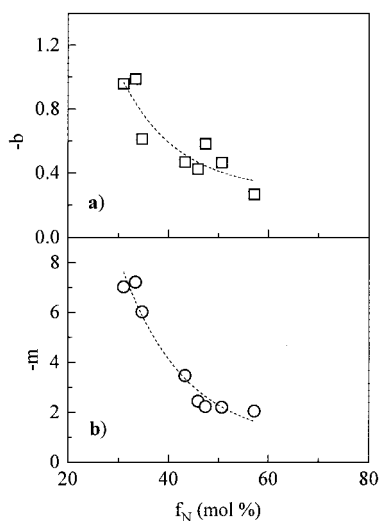


Figure 3 Values of the slopes b and m as a function of norbornene content. (For details of the slope calculation see text.)

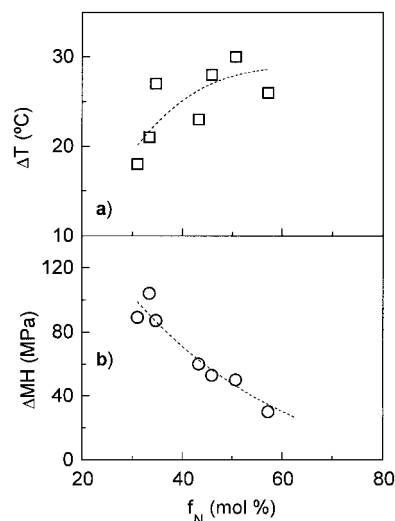


Figure 4 Influence of the norbornene content on: (a) the temperature interval of the glass transition and (b) the decrease of microhardness at the glass transition.

a sigmoidal decay and, although, as stated before, MH measurements cannot be made above glass transition, we were able to determine the maximum slope m of the corresponding decreases in MH. The values of m are plotted in Figure 3(b) for the different samples. It can be seen that in the samples with small amounts of norbornene (31–35%) the changes in microhardness, either in the region below T_g or along the temperature range at which such a transition is taking place, are larger. Samples kept their plastic contribution up to very low microhardness values because of relatively low glass-transition temperatures. As the norbornene content was increased, the m slope values decreased because of the higher hindrance caused by norbornene rings during this transition. In other words, the higher the norbornene content in the copolymer, the larger the rigidity of the chains. Accordingly, the maintenance of their mechanical strength remains over a wider temperature range.

Moreover, it can be observed in Figure 2 that the temperature interval at which the glass transition is taking place (ΔT) is broadened with the norbornene content, as shown in Figure 4(a). Because the end of the glass transition may not have been attained with these MH measurements for the higher norbornene contents, the values of ΔT might be even higher in those cases.

Regarding the decrease of MH at the transition, ΔMH , the corresponding values are plotted in Figure 4(b). It appears that smaller values of ΔMH are obtained for the higher norbornene contents. However, as mentioned above, we may not have measured all through the glass transition, so that the real variation of ΔMH with the norbornene content may be somewhat different.

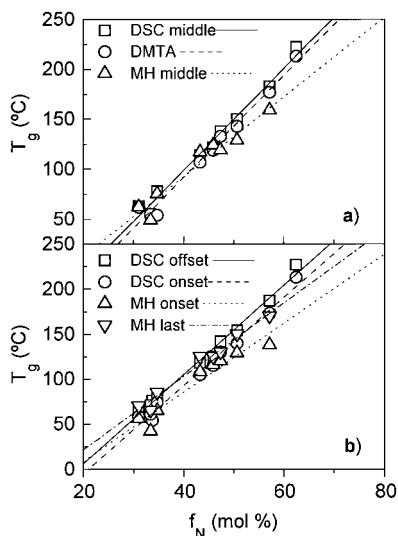


Figure 5 Influence of the norbornene content on different characteristic features of the experimental curves of calorimetric (DSC), dynamic mechanical (DMTA), and microhardness (MH) measurements.

From the previous experiments, it follows that MH measurements as a function of temperature are a useful tool to monitor the glass transition. Therefore, the T_g values estimated by different methods (DSC, DMTA, MH) is shown in Figure 5(a) as a function of norbornene content. A monotonic T_g increase, almost linear, is observed as norbornene content is raised in the copolymer. DSC and DMTA are well-known classical methods for determining this parameter. A very good agreement between the T_g values obtained for these two methods has been found.⁵ The linear fittings of the T_g values experimentally obtained by DSC and DMTA measurements as a function of f_N accomplish equations with very similar parameters:

$$\text{for DSC: } T_g = 5.1f_N - 105 \quad (2)$$

$$\text{for DMTA: } T_g = 5.1f_N - 112 \quad (3)$$

The corresponding line for the values of $MH_{T_g \text{ middle}}$ obeys the equation

$$\text{for MH: } T_g = 4.0f_N - 67 \quad (4)$$

The other two glass-transition determinations by MH, $MH_{T_g \text{ onset}}$ and $MH_{T_g \text{ last}}$ are plotted in Figure 5(b), compared with the values of $T_g^{\text{DSC onset}}$ and $T_g^{\text{DSC offset}}$. The agreement found is quite satisfactory. However, it has to be considered again that we may have not measured all through the glass transition in the MH experiments. Incidentally, the best agreement between DSC and DMTA determinations with the MH-based values is that for $MH_{T_g \text{ last}}$. It has to be considered that though $MH_{T_g \text{ last}}$ may not represent

the end of the glass transition, yet it should be considered as an important characteristic of a particular specimen reflecting a compromise between the plastic contribution and the fast elastic recovery, which rules out a reliable imprint measurement.

The larger deviations between the MH determinations and the two other methods are found for the higher norbornene contents (i.e., for the more rigid samples). This feature may be something intrinsic to those particular measurements, given that MH includes a complex combination of properties (elastic modulus, yield strength, strain hardening, toughness). In addition, MH provides an idea about the resistance of the material to plastic deformation but it has to be kept in mind that it exclusively involves local and superficial deformation instead of a bulky response as occurs in DSC and DMTA measurements.

At this point, and having into account the degradation problems in sample CNE10, it could be concluded that the microhardness method used is not appropriate for T_g determination in the high temperature interval, especially when the measurements are made in noninert atmosphere, because some undesired and uncontrolled chemical processes could take place.

Taking into consideration that, on the one hand, a linear dependence between MH and norbornene content is observed and, on the other hand, a linearity is also found between T_g and f_N (Figs. 1 and 5), a linear dependency between microhardness and glass-transition temperature can be expected. In fact, the corresponding results are plotted in Figure 6. Despite the uncertainty of the data, it seems that the slope of the lines increases with temperature of measurement, which is expected when considering that, judging from the results of the initial slope in Figure 3(a), the temperature coefficient of MH is larger for the samples with lower values of T_g .

In conclusion, the temperature dependency of Vickers microhardness of a series of norbornene–ethylene copolymers has been studied, and the following conclusions have been established:

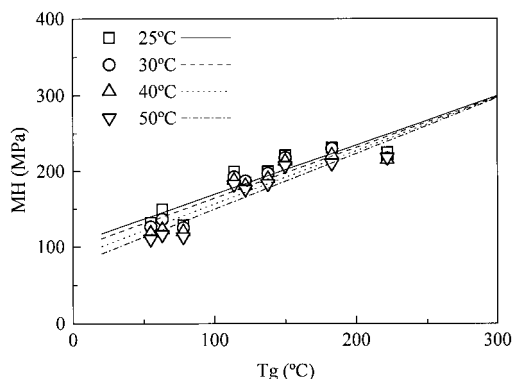


Figure 6 Variation of Vickers microhardness, measured at different temperatures, with the glass-transition temperature of the copolymers.

1. Microhardness, as an important mechanical parameter, is sensitive to the glass-transition process. The possibility of using the microhardness as a reliable method for the determination of T_g has been discussed and the limits and conditions for avoiding possible shifting of the results have been analyzed.
2. The variation of Vickers microhardness with the glass-transition temperature of the copolymers is linearly dependent. This proportionality remains also for microhardness measurements carried out at higher temperatures but before the glass-transition temperature.

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