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A new viscoelastic method for detection of paracrystalline aggregates in ethylene–propylene elastomers

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Abstract

A method for characterization of paracrystalline structures in ethylene–propylene copolymers is proposed, based on classical dynamic mechanical measurements performed at different temperatures and frequencies, and on a particular analysis of the resulting modified Cole–Cole plots. A collapse function relative to the disappearance of all ordered structures is evaluated, from which the differential distribution of mechanically effective constraints in the polymer samples may be obtained. At each temperature the total amount of ordered structures present appears to be determined by copolymer compositions and microstructure, and not by thermal treatments. The contribution of paracrystalline structures is revealed from the comparison of the mechanically effective distribution functions with the calorimetric crystalline transitions in the same sample.

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Keywords: Ethylene–propylene elastomers; Paracrystallinity; Cole–Cole plots

1. Introduction

The rheological properties of polymers are often described by means of reduced viscoelastic variables, according to the so-called time–temperature superposition principle [1]. A direct consequence of the above principle is that for a *viscoelastically simple* amorphous polymer the values of loss modulus, G'', at different frequencies and temperatures may be plotted against the corresponding storage modulus, G', on a double logarithmic scale usually called modified Cole–Cole plot [2,3], giving a temperature-independent master curve.

Ethylene–propylene rubbers (EPR) are commonly considered amorphous materials [4], however, depending on ethylene content, different samples may show different Cole–Cole plot behaviours. Low-ethylene EPR samples behave as viscoelastically simple, which means that tan δ curves are well superimposable and Cole–Cole plots form a single master curve. High-ethylene EPRs, on the other hand, have Cole–Cole plots at the different temperatures which are not superimposable until sufficiently high temperatures are reached. Such samples cannot be considered as viscoelastically simple [5], and the reason may be attributed not only to the presence of low-melting crystallinity [6] but also to different interactions which may develop between ethylene sequences, giving rise to low amounts of paracrystalline regions otherwise also defined as thermo-reversible gels [7]. Complete melting of all possible ordered structures is only obtained at sufficiently high temperature, and below that temperature the modified Cole–Cole plots are displaced on the right side of (log G', log G'') plane.

The distance between Cole–Cole plot at a temperature lower than complete melting and the master curve where all Cole–Cole plots are stacked together must depend on the amount of paracrystalline aggregates still present at that temperature. This peculiar behaviour can be therefore employed to investigate morphological details of high-ethylene EPR samples. How such samples attain complete melting will depend on their structures and thermal history, each situation resulting in different distributions of para-crystalline aggregates and defects. Moreover, since total superposition of plots usually occurs at temperatures that are well above those commonly considered as true melting, this approach may be used to reveal high-temperature segmental

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interactions which cannot be normally detected with DSC measurements but are likely to play a role in the polymer mechanical transformations.

A new method, based on classical viscoelastic measurements and appropriate treatment of Cole–Cole plots data, is proposed in this work for the characterization of differences in type and distribution of the high-melting paracrystalline structures in high-ethylene EPR samples, and for investigating their time evolution effects.

2. Experimental part

The samples investigated were ethylene–propylene copolymers or terpolymers with ethylidene norbornene (ENB). All samples were obtained by homogeneous Ziegler-Natta polymerizations with vanadium based catalysts, and had a high ethylene content, >78% molar (Table 1). Chemical compositions were determined on a Perkin–Elmer (Norwalk, CT) 1750 FT-IR instrument. The absorption bands at 1379 and 1464 cm^{-1} were used for propylene and ethylene content, respectively, whereas ENB was determined from measurements of the absorbance of peak at 1685 cm^{-1} [8,9]. Molecular weight characterization was performed by size exclusion chromatography (SEC), on a Waters 150-C apparatus with a DRI detector (Waters Corp., Milford, MA) at 135 °C in *o*-dichlorobenzene. Separations were obtained with four 30 cm × 0.78 PL gel, 10 μm columns (PL Laboratories, Shropshire, UK). Polymer solutions, 0.25% w/v concentrations, were prepared by heating the samples in the solvent at 150 °C for 1 h. Average molecular weight values were calculated using the universal calibration approach. Narrow distribution polystyrenes were used as primary standards, and Mark-Houwink coefficients for the EPDMs were calculated from those of linear polyethylene and of polypropylene taking into account sample compositions according to the method of Scholte [10].

Thermal properties were determined with a Perkin–Elmer DSC 7 differential scanning calorimeter, at a heating rate of 20 °C min^{-1}. The first scan was considered in all cases, in order to account for thermal history after equilibration or ageing.

Viscoelastic measurements have been performed in shear mode with a Polymer Laboratories DMTA MKII (Shropshire, UK), on 12 mm diameter disks. Samples were moulded at 120 °C and equilibrated at various conditions in order to obtain different thermal histories; frequency sweeps were carried out with low strain level (linear viscoelasticity domain) at different temperatures, in the range 35–130 °C, heating and equilibrating the same sample. Frequencies from 0.1 to 100 Hz (0.628 to 628 rad s^{-1}) were used to minimize the test time at each isotherm.

Table 1
Molar composition, molecular weight distributions and DSC melting temperatures of EPR co- and terpolymers

Sample	M_w	M_n	$M_\mathrm{w}/M_\mathrm{n}$	Ethylene (mol%)	ENB (mol%)	DSC peak (C°)
A	194,000	77,000	2.5	79.7	–	46.1
B	164,000	50,000	3.3	79.8	1.3	47.4
C	171,000	59,000	2.9	78.6	1.2	45.0
D	173,000	67,000	2.6	79.0	1.1	–

3. Results and discussion

The modified Cole–Cole plots relative to EPR samples C and D, obtained from different polymerization batches but having similar monomer composition and molecular mass distribution, are plotted In Fig. 1(a) and (b) respectively. It is evident that the log G'' vs log G' curves are not superimposed, although sample C is approaching the convergence more rapidly. Let's call Tmc the temperature of complete disappearance of every ordered structure within the polymer, beyond which the Cole–Cole plots form a single master curve. Considering the behaviour near the melting, the rate of approaching such temperature may be simply expressed by the difference between the maximum log G'' of the master curve and the corresponding maximum value at each other temperature:

$$\Delta\log G''_{\mathrm{Tmc}} = \log G''_{\mathrm{Tmc}} - \log G''_{T} = \log(G''_{\mathrm{Tmc}}/G''_{T}) \qquad (1)$$

The $\Delta\log G''_{\mathrm{Tmc}}$ values relative to the samples of Table 1 are plotted in Fig. 2, and the different viscoelastic behaviours are clearly reflected from the curves relative to the different samples. The investigated EPR samples not only approach

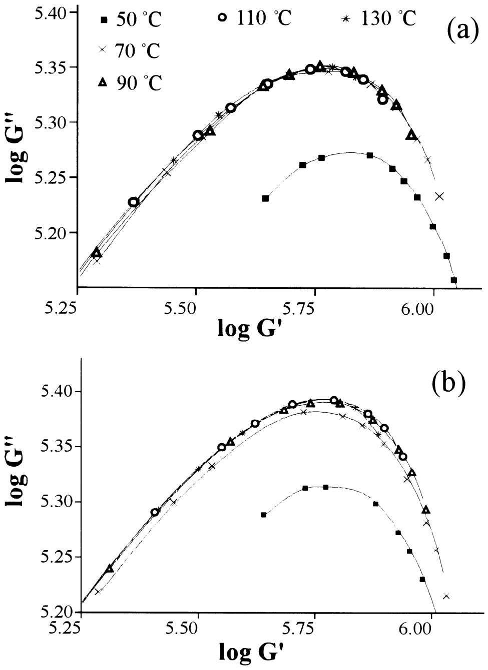


Fig. 1. Cole–Cole plots relative to (a): sample C of Table 1; (b): sample D of Table 1.

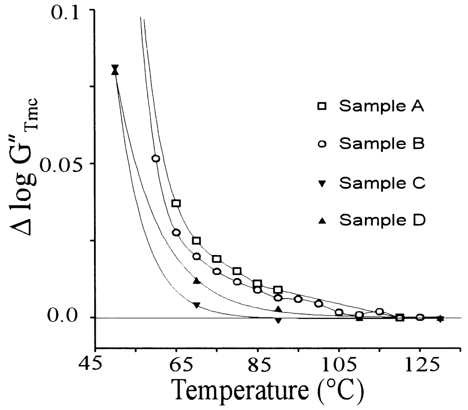


Fig. 2. Values of vertical distances between maxima of the Cole–Cole plots at the different temperatures for the samples of Table 1.

their zero $\Delta\log G''_{\mathrm{Tmc}}$ value with different rates, but they also attain different Tmc values. For each sample the resulting behaviour may be attributed to the presence of specific amounts, types and distributions of aggregates and ordered structures, still active at temperatures higher than the end of the melting peak revealed by DSC measurements, i.e. in regions where such polymers are commonly considered as melts. The aggregates practically behave as high-melting paracrystalline regions and it may be expected that they can affect the mechanical behaviour of the polymers. Therefore indications about their presence turn out to be important for a full characterization of the material properties. Similar informations are not visible from classical calorimetric determinations, whereas are obtained from the properly accomplished viscoelastic measurements and data analysis which is herein proposed.

The procedure adopted can be extended at lower temperatures, and the approach towards the complete melting master curve may be better represented by the values of the segments joining the maximum of each isotherm with the maximum of the master curve, as shown in Fig. 3 for sample B in the range 35–120 °C. Based on simple geometrical considerations the distance between Tmc and the maximum at each temperature T is given by the equation:

$$Y(T) = [(\log G''_{\max\mathrm{Tmc}} - \log G''_{\max T})^2 + [(\log G'_{\max(G'')\mathrm{Tmc}} - \log G'_{\max(G'')T})^2]^{1/2} \qquad (2)$$

where $\log G''_{\max T}$ is the value of the maximum $\log G''$ at temperature T, and $\log G'_{\max(G'')T}$ the corresponding abscissa.

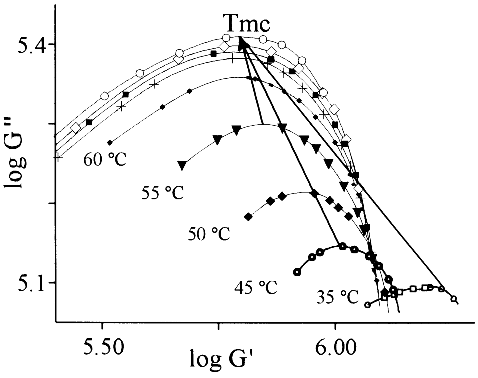


Fig. 3. Cole–Cole plots relative to sample B in the temperature range 35–120 °C, and segments expressing the distance between curves. At the highest temperatures isotherms are closely spaced and for better readability in the plot are shown only those at 65 °C (+), 75 °C (■), 95 °C (○), and 120 °C (◇).

The values of such distances for the Cole–Cole plots of Fig. 3 are plotted in Fig. 4, and a fitted curve $Y(T)$ is obtained, showing an inflection point and then an almost exponential decay towards Tmc, whose value is in this case 120 °C. This curve may be considered as a measure of the viscoelastic effects deriving from ordered structures still present at temperatures $T <$ Tmc and, being a description of the way such ordered structures approach complete disappearance, we define $Y(T)$ a ‘collapse function’.

The distribution of paracrystallinity in a EPR sample may be essentially considered a distribution of defective structures with respect to the ‘pure’ ethylene–ethylene interactions. The $Y(T)$ function, on the other hand, is a measure of the cumulative distribution of all aggregates which act as viscoelastically ‘effective’ constraints. An empirical correlation between the shape of the collapse function and the thermal properties of the samples is given by the full agreement between the temperature of inflection point in the $Y(T)$ curve (47 °C in Fig. 4) and the DSC peak maximum (47.4 °C, sample B in Table 1). This correlation holds also in the case of a polymer with different ageing histories, as it can be seen from the examples reported in Figs. 5 and 6, relative to sample A. In Fig. 5 the inflection point of the $Y(T)$ curve is at 47 °C, and the corresponding DSC melting peak temperature at 46.1 °C. The same polymer, after 20 days annealing at room temperature, shows the behaviour seen in Fig. 6, with $Y(T)$ inflection temperature and DSC peak at 49 °C. At the same time the temperature of complete melting shifts from 130 to 107 °C.

The above results indicate that, by making measurements on the same polymer sample at different time intervals, this technique is capable of highlighting the morphological differences produced by molecular rearrangements occurring

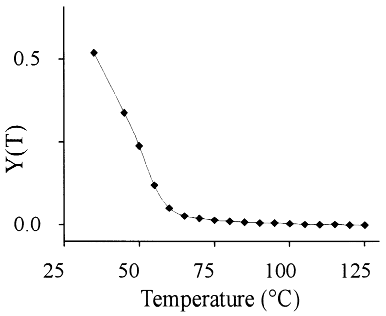


Fig. 4. Collapse function relative to sample B, obtained from the distance values between Cole–Cole plots of Fig. 3. Tmc = 120 °C.

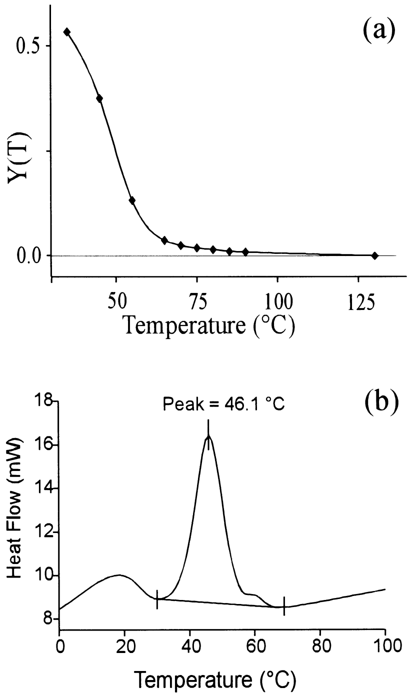


Fig. 5. (a) Collapse function of sample A. Tmc = 130 °C. (b) DSC melting peak of sample A.

at room temperature. A further evidence is shown by the results in Fig. 7, where the $Y(T)$ curves for polymer B, determined immediately after processing and after 10 days of room temperature ageing, are plotted. Differences are quite small at temperatures around the inflection point, but they become evident at higher temperatures, where the $Y(T)$ function has smaller values in the aged sample, and vanishes at a lower (100 °C instead of 120 °C) Tmc value. This indicates that the distribution of aggregates has changed with ageing and, particularly, that the highest-melting structures have disappeared.

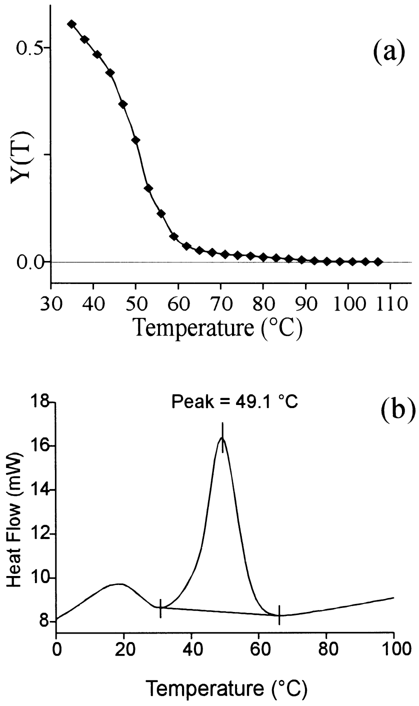


Fig. 6. (a) Collapse function of sample A Tmc = 107 °C. (b) DSC melting peak of sample A after 20 days ageing at room temperature.

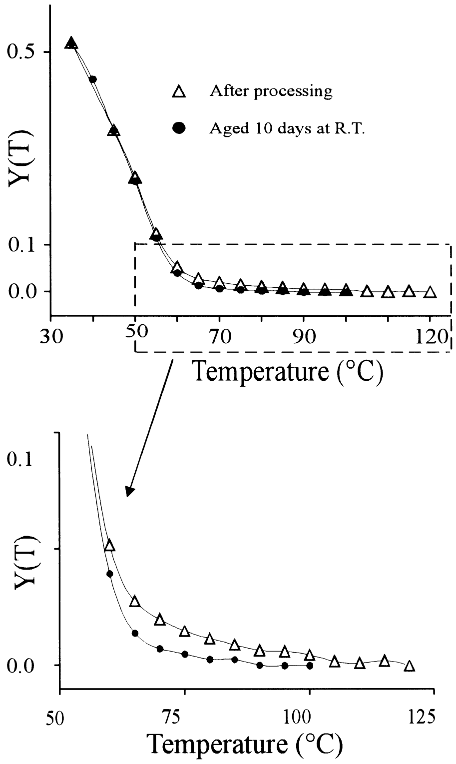


Fig. 7. Collapse function of sample B from measurements immediately after processing (Tmc = 120 °C) and after 10 days at room temperature (Tmc = 100 °C).

‘High-melting’ structures should be intrinsically strong, but here their effect is seen to decrease or disappear upon keeping the sample at room temperature for sufficient long time. The only possible motions in ‘cold flow’ are long-range relaxations due to rearrangements of polymer chain segments. Residual stresses deriving from sample processing (molding, milling, etc.) may be present in the polymer, and relaxation of these stresses occurring through chain motions can be strong enough to reduce and finally destroy the paracrystalline interactions. During such process the collapse function, $Y(T)$, will take lower values and also Tmc will decrease.

3.1. Influence of thermal history

The formation and evolution of crystalline structures in a polymer is generally investigated with DSC measurements, and is well-known to depend from the sample thermal history [11,12]. The effect is clearly seen in the case of the EPR sample A when, after the equilibration at 23 °C previously discussed in connection with Fig. 6, it has been annealed at 40 °C for 48 h. The DSC curve of the sample immediately after the treatment (Fig. 8) shows the presence of a new endothermic peak at temperatures higher than those of the main peak. The annealing has induced the formation of a new distribution of the ordered structures, in comparison with the situation of the sample before the annealing (see Fig. 6(b)). How this different morphological organization is reflected in the viscoelastc behaviour may be examined by comparing the respective collapse functions. In Fig. 9 the $Y(T)$ curve obtained from measurements on the annealed sample reveals a clear difference in respect of that shown in Fig. 6(a): the Tmc value has decreased from 107 to 101 °C, two inflection points are present after annealing, and their temperatures, 41 and 51 °C, are in good agreement with the peak maxima of the DSC curve (Fig. 8).

The values of the $Y(T)$ function are determined by the amount of ordered structures still present at each temperature and we have already defined the $Y(T)$ curve as an integral distribution of every type of ordered structures in the sample. By taking the derivative of this function we obtain the differential distribution curve, $\Phi(T)$, which represents the *mechanically effective* distribution function, and can be directly compared with the differential calorimetric curve relative to the same polymer sample. In Fig. 10 are plotted the $\Phi(T)$ distribution curves relative to sample A before and after the annealing treatment. In the former case a monomodal distribution is seen, and in the latter a bimodal, similarly to what is shown by the DSC curves of the same samples (Figs. 6 and 8). The total area under the two different distributions is identical, indicating that the total amount of possible ordered structures is not determined by the different thermal histories but by the polymer structural features. At the same time, the ordered regions may be more displaced towards high or low temperatures of melting, in dependence of sample ageing or annealing. When the EPR sample A has been annealed at 40 °C, for example, the amount of mechanically effective paracrystalline structures melting at 55 °C is much higher than in the untreated polymer, and at the same time there are less effective structures melting at 45 °C.

By comparing the DSC peaks with those of the $\Phi(T)$ distribution, as shown in Fig. 11, it is seen that the relative peak sizes are inverted: there is an higher weight fraction of low-temperature melting structures but the lower fraction of high-melting structures is the one more mechanically effective. This comparison emphasizes the difference between thermal and mechanical effects of the polymer morphological organization, and is at the base of the $\Phi(T)$ distribution definition.

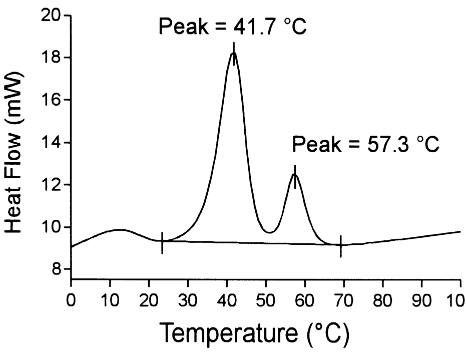


Fig. 8. DSC curve of sample A annealed at 40 °C for 48 h.

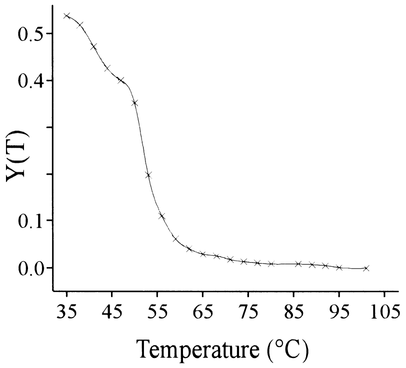


Fig. 9. Collapse function of sample A annealed at 40 °C for 48 h. Tmc = 101 °C.

The correlations between mechanical and calorimetric measurements may be explained in the following way. Both are ‘dynamical’ tests, and the obtainable distributions reflect the characteristics of the techniques. The viscoelastic responses of polymer structures are not always proportional to the thermical ones, even if so happens in the majority of cases. For example, it has been recognized that ethylene sequence length distributions can lead to different morphologies within the same sample, giving rise to different melting temperatures [13]. At the same time, crystalline aggregates melting at the same temperature but present in macromolecular chains with higher molecular masses may give larger ‘mechanical losses’.

The importance of type and distribution of ethylene sequences along the chains or in the various molecular weights is graphically illustrated in Scheme 1. Different distributions of interacting sequences will have, in general, different melting temperatures but the dynamic moduli will be similar if the ordered structures are present in comparable positions and molecular masses of the polymer chains. On the other hand, different positions of ordered structures along the polymer chains, or position on chains with

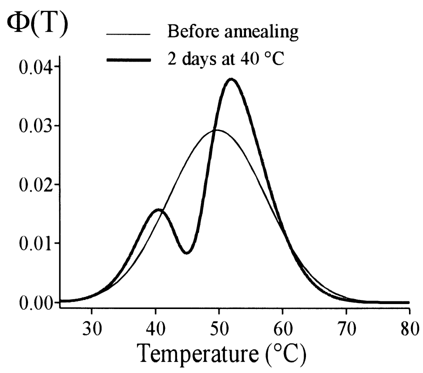


Fig. 10. Mechanically effective differential distribution function of ordered structures in sample A before and after annealing at 40 °C for 48 h.

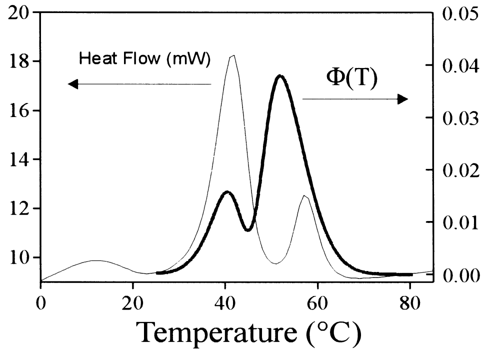


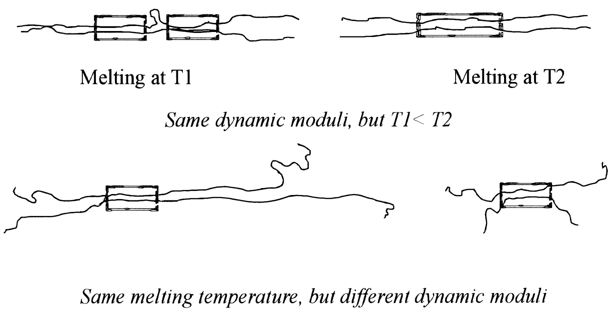
Fig. 11. Comparison between DSC and $\Phi(T)$ distribution curve for sample A annealing at 40 °C for 48 h.

different molecular masses, may produce same melting temperature but quite different dynamic moduli. Furthermore, one should consider that there will be morphologies which do not contribute to the melting peaks but contribute to mechanical effects and can be detected by the viscoelastic analysis here described. Among the particular structures which have been postulated one can recall the clusters of loosely packed ethylene sequences, suggested by Monte-Carlo simulations [14] but not yet experimentally demonstrated.

4. Conclusions

In this work it is shown that by means of classical dynamic mechanical experiments on ethylene–propylene copolymers with high-ethylene content and proper analysis of their modified Cole–Cole plots, a collapse function $Y(T)$ relative to the disappearance of all ordered structures in the sample may be evaluated. Analysis of such functions give detailed information, not immediately detectable with other methods, on the morphological characteristics and transformations taking place in the polymers. The viscoelastic behaviour of such samples appears to be controlled not only by their low-melting crystallinity but also by the effect of paracrystalline structures which remain still active at temperatures higher than the crystalline melting.

The morphological differences may be among samples having the same average composition but different distribution of ordered structures, or within the same polymer with different thermal ageing or stress relaxation histories.



Scheme 1.

The derivative of the collapse function represents the differential distribution of all ordered structures in the polymer which are effective from the mechanical point of view. Such distributions depend on the thermal history or ageing of the samples whereas the total amount of ordered structures within a same sample is only determined by copolymer composition and microstructure. Comparison between the mechanically effective and the calorimetric crystallinity peaks reveals the contribution of the paracrystalline ordered structures present in a given sample.

It is expected that with the proposed characterization approach and in correlation with detailed molecular characterization of polymer samples a better understanding of the paracrystallinity phenomenon in ethylene–propylene elastomers may be obtained, and eventually a reliable method for quantification of paracrystalline aggregates in polymer samples. Further work along this line will be carried out by extending the comparison of viscoelastic and calorimetric behaviour of samples properly prepared.

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References

[1] Ferry JD. Viscoelastic properties of polymers. New York: Wiley; 1980.
[2] Harrel ER, Nakajima N. J Appl Polym Sci 1984;29:995.
[3] Demaio M, Caldari S, Chiantore O. Int J Polym Anal Charact 1999;5:85.
[4] Baldwin FP, Ver Strate G. Rubber Chem Technol 1972;45:709.
[5] Boudewijn J, Scholtens R. J Polym Sci: Polym Phys Ed 1985;23:1325.
[6] Pizzoli M, Righetti MC, Vitali M, Ferrari P. Polymer 1998;39:1445.
[7] Christophe D, Tze-Chi J, Bauer BJ, Amis EJ. Macromolecules 1999;32:8938.
[8] Tosi C, Simonazzi T. Angew Makromol Chem 1973;32:153.
[9] Gardner IJ, Ver Strate G. Rubber Chem Technol 1973;46:1019.
[10] Scholte ThG, Meijerink NLJ, Scoffelers HM, Brands AMG. J Appl Polym Sci 1984;29:3763.
[11] Mathot VBF, editor. Calorimetry and thermal analysis of polymers. New York: Hanser; 1994.
[12] Wright KJ, Lesser AJ. Macromolecules 2001;34:3626.
[13] Vanden Eynde S, Mathot V, Koch MHJ, Reynaers H. Polymer 2000;41:3437.
[14] Mathot VBF, Scherrenberg RL, Pijpers MFJ, Engelen YMT. In: Hosoda S, editor. The new trends in polyolefin science and applications. Research Signpost, Kerala, India 1996.