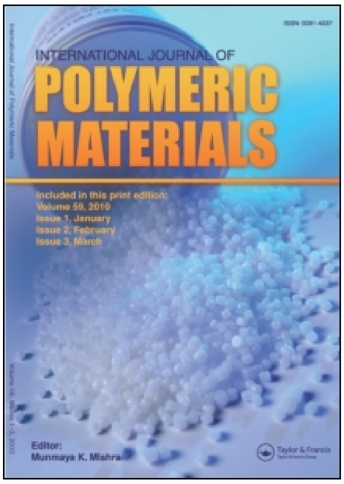

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Krisyuk, B. E. , Marikhin, V. A. , Myasnikova, L. P. and Zaalishvili, N. L.(1993) 'Structure of Drawn Gel-Crystallized UHMWPE as Revealed by Spin-Probe Technique', International Journal of Polymeric Materials, 22: 1, 161 — 166

To link to this Article: DOI: 10.1080/00914039308012070

URL: http://dx.doi.org/10.1080/00914039308012070

Intern. J. Polymeric Mater., 1993, Vol. 22, pp. 161–166
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Printed in Malaysia

Structure of Drawn Gel-Crystallized UHMWPE as Revealed by Spin-Probe Technique

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The volume distribution and molecular dynamics of spin-probe (nitroxyl radical) in the gel-crystallized UHMWPE of different draw ratios (DR = 12, 100) have been investigated. The spin-probes were found to occupy approximately 50% of the polymer volume in the necked samples and 20–30% in the samples drawn up to DR = 100. The mobility of the spin-probe in the samples studied is higher than that in the drawn and even in the undrawn samples of conventional melt-crystallized PE. This fact along with a low value of activation energy of spin-probe rotation (less than 10 kJ/mole) enables a conclusion that the regions of spin-probe localization are those with a significantly reduced density, such as pores, for examples. The analysis of the data obtained and the results of the structural study of the gel-crystallized samples by a SAXS and WAXS technique suggest that these pores are localized in interfibrillar space.

KEY WORDS ESR spin-probe technique, drawn gel-crystallized UHMWPE, microfibrils, microvoids.

1. INTRODUCTION

During the last decades considerable progress has been made in obtaining high strength and high modulus polyolefines. However, in spite of significant property enhancement achieved, for ultradrawn UHMWPE in particular, their mechanical characteristics still remain below the theoretical predictions.[1] The heterogeneities, such as the molecular chain length, micro- and macrofibrils, chain ends, various conformational defects and disordered regions, are expected to be responsible for the reduction of ultimate properties.

The aim of this work was to study the heterogeneities of the drawn and ultradrawn UHMWPE samples in order to establish the structural base of a discrepancy between the theoretical and experimental values. The spin-probe ESR technique which is a powerful tool for investigating of structural nonuniformity has been used for these purposes.

2. EXPERIMENTAL

The specimens investigated were prepared from UHMWPE GUR 412 ($\bar{M}_w = 1.5 \times 10^6$) by the gel-technology proposed by Smith and Lemstra.[2] Dried gel-crystallized films were oriented by multistage zone drawing technique up to different draw ratios (DR). The samples drawn up to DR = 12 were oriented in one stage at the drawing temperature $T_{dr} = 110°C$ and speed 20% per minute. The ultradrawn samples with DR = 100 were produced with the same deformation speed in three stage, T_{dr} at the first, second and third stages of drawing having been 110, 115, and 120°C, respectively. Sample crystallinity was calculated from DSC curves recorded by a Perkin–Elmer calorimeter and the melting enthalpy of an ideal crystal H_0 was taken to be 4.1 kJ/mol (see Reference 3).

X-ray analysis was carried out to estimate the geometrical parameters of supermolecular structure. The longitudinal D_{002} and transverse D_{110} sizes of crystallites along with the paracrystalline lattice distortions (g) were calculated from the integral halfwidth of correspondent wide angle X-ray reflexes (002, 110, and 220). The WAXS measurements were made using MoK$_\alpha$-radiation with a diffractometer GUR-2 fitted with an asymmetrical quartz monochromator. The SAXS technique was used to calculate a long period L and get information on the nonperiodic heterogeneity of the structure. SAXS photographs were taken using CuK$_\alpha$-radiation in a flat camera with a point collimation system. X-ray patterns were further analyzed with a photodensitometer IFO-451. Molecular dynamics were investigated by the 3 cm ESR spin-probe technique, nitroxyl radicals (2, 2, 6, 6-tetramethyl-piperidine-1-oxyl) having been used as a probe. The radicals were introduced into oriented samples from vapor at room temperature to attain an appropriate concentration. The latter was determined from the ESR data. The ESR spectra were recorded by a ESR-spectrometer SE/X-Radiopan in a wide temperature range (from 77 K up to 360 K). The probe local concentration was calculated from concentration dependence of dipole-dipole broadening of ESR spectra central line at liquid nitrogen temperature.[4] The correlation time of probe rotation τ_c was calculated from the ESR spectra along the standard procedure[5] at nitroxyl concentration not higher than 10^{-3} mol/kg. Tensile strength (σ) of the samples investigated was measured in a lab-scale device of the Instron-type at the 20% per minute stretching speed. The modulus of elasticity E was calculated for the strain level of 0.1% from the slope of stress-strain curve of drawn samples obtained at room temperature during static step-wise loading .

3. RESULTS AND DISCUSSION

Table I presents the structural and mechanical data for both types of samples under study. In the gel-crystallized samples the longitudinal sizes of crystallites D_{002} are seen to exceed the value of long period L already after the neck formation at DR = 12 (PE-I samples). The phenomenon implies a coherent position of neighboring crystallites in microfibrils[6] as well as possible existence of a certain amount of taut tie molecules that bridge these crystallites.[7,8] It is observed in drawn melt-crystallized PE only at ultimate DR. Probably it is these specific features of microfibrillar structure in a neck region that allow to obtain a perfect structure during further drawing up to DR = 100 (PE-II samples) and provide extremely high mechanical properties of the ultradrawn gel-crystallized material. The

TABLE I
Mechanical characteristics and structural parameters of PE samples

Draw ratio	D_{002} (nm)	D_{110} (nm)	L (nm)	g_{110}	κ (%)	σ (GPa)	E (GPa)
12	26.0	13.4	24.0	0.067	66	0.5	20
100	70.0	21.0	absent	0.109	85	6.0	150

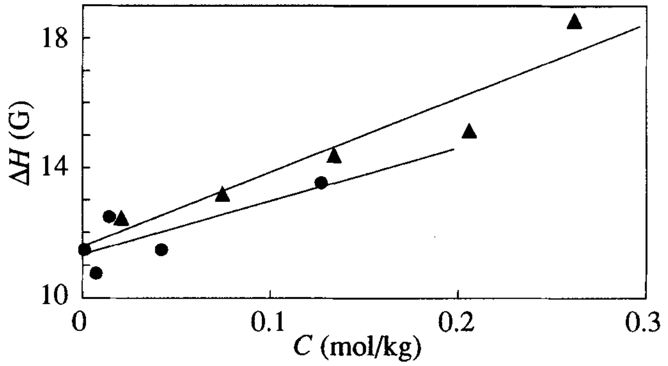

FIGURE 1 Dependence of linewidth of ESR spectra ΔH at 77 K on probe concentration C for PE-I (▲) and PE-II (●) samples.

longitudinal sizes of crystallites and their distortions is greater in PE-II samples than those in PE-I. The ESR study of the same samples also reveal the difference in their structure.

Figure 1 represents the dependence of the width of ESR spectra of nitroxyl central line ($S = 0$) versus probe concentration for the samples investigated. It is obtained for the samples initially saturated up to the ultimate probe concentration with subsequent nitroxyl radical removal due to evaporation. In accordance with theoretical estimates this dependence is to be linear, which is confirmed by the experiment. In the case of uniform probe distribution in a sample, a slope of such dependence should be less by a factor of two[4,9] than that observed in the experiment for the PE-I sample, which evidences that the local probe concentration is twofold higher than an average value. It enables the suggestion that the probes occupy nearly 40–50% of the polymer volume in the PE-I sample. The change in a slope of the dependence for PE-II sample implies porosity decreasing as low as 20–30%.

It is well known that in semicrystalline polymers a nitroxyl radicals can penetrate only in more loosely packed noncrystalline regions, crystallites being impervious for the probes. Therefore one may suggest that in the necked gel-crystallized UHMWPE a portion of disordered regions is as high as about 50% of its volume. However, the degree of crystallinity in the PE-I samples as revealed by DSC is as high as 66%, (see Table I) which allows to assume that a half volume of this polymer is made up of pores or at least of regions with a low chain density. So the value of mass crystallinity measured by DSC corresponds to that of a dense part of the samples. Thus ESR technique enables the detection of an empty space in a polymer volume. Our hypothesis related to the porous structure of drawn gel-crystallized UHMWPE samples correlates with the data previously obtained by Lemstra and Smith[10] who demonstrated the existence of pores already in the

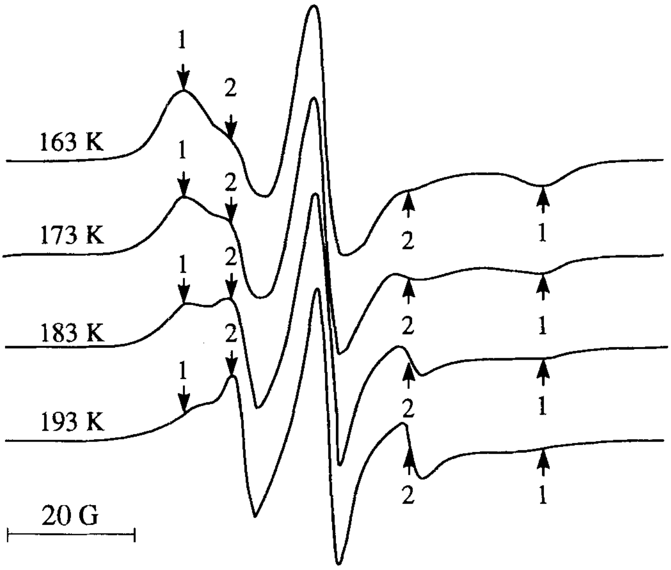

FIGURE 2 ESR spectra of PE-I sample with DR = 12 at different temperatures. Arrows 1 and 2 indicate the slow and fast components of the spectra, respectively.

initial undrawn gel-crystallized UHMWPE. They showed that the apparent density of such PE samples does not exceed 500–700 kg/m^3 but can be increased to be as high as the density of highly crystalline PE (940–960 kg/m^3) by simple compression at room temperature.

A question arises where these pores are localized in the drawn samples. Figure 2 shows several ESR spectra for PE-I samples recorded at different temperatures below 210 K. These spectra in a definite temperature range comprise a superposition of the spectra of probes rotating at two different correlation times, which follows from the splitting of the 1st and 3nd lines of observed spectra (as indicated by arrows in Figure 2). To subdivide these superimposed spectra the following procedure has been used: the nonsplitted spectra recorded at low temperature were subtracted from the experimental one with different statistical weight and the correlation time for a fast component was calculated from the resulting spectrum that no longer contained the slow component. To eliminate some distortions due to the subtracting procedure the resulting spectrum has been corrected by computer simulation. The correlation time for a slow component was calculated after the subtracting of the corrected spectrum from the experimental one.

It was found that the temperature dependence of τ_c for these two components is quite different. The slow component has the temperature dependence which resembles the one usually obtained for many polymers.[11] The activation energy E_a calculated from the slope of the Arrhenius-type dependence at high temperature which can be described by an expression $\tau_c = 2.2 \times 10^{-19}\exp(43/kT)$, reaches 43 kJ/mol (see Figure 4, dashed line) and a bend point is observed near T_g. At the temperature lower than T_g, E_a drops as low as 12 kJ/mol ($\tau_c = 7 \times 10^{-10}\exp(12/kT)$). This behavior is typical of polymers with intermediate M_w and not very high DR.[11] Taking into account the existence of the distinctly pronounced meridional reflection in SAXS pattern from these samples (Figure 3) one may suggest that this component (the slow one) is due to the probes localized in intrafibrillar

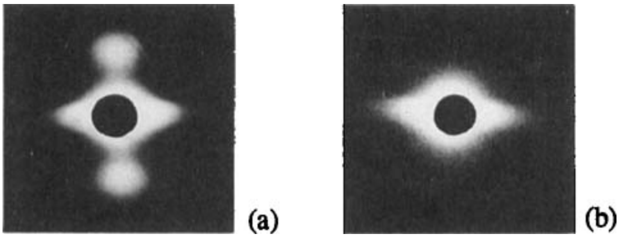

FIGURE 3 SAXS pattern of (a) PE-I and (b) PE-II samples.

disordered regions. For the fast component its Arrhenius curve is linear within the whole temperature range (Figure 4a) and can be described as $\tau_c = 1.9 \times 10^{-11}\exp(5.9/kT)$, i.e the fast component activation energy $E_a \approx 6$ kJ/mol is lower and the rotational frequency of the probes is higher than those in conventional polymers, which implies that these probes are localized in pores. It is additional evidence for the porous structure of oriented PE samples prepared by the gel-technique. The localization of these pores can also be deduced from the SAXS data. On the same SAXS pattern from PE-I samples (Figure 3a) one can see an intense diffuse scattering around a primary beam which can be caused by the existence of pores or the regions of very low electron density. The intensity distribution of this scattering evidences that these regions of reduced density should be oriented along the drawing direction and their transverse size should be smaller that the longitudinal ones. It would be reasonable to suggest that these elongated pores are located between microfibrils which are formed in a neck region at drawing.

In contrast to the necked samples the ESR spectra of ultradrawn samples (PE-II) only consists of a fast component. From the temperature dependence of τ_c (see Figure 4) described by the expression $\tau_c = 2.91 \times 10^{-14}\exp(24.5/kT)$ follows that rotation of the spin-probe in these samples occurs with $E_a = 24.5$ kJ/mol, which is higher than that for the PE-I. The rotation frequency of spin probe in PE-II is much higher in comparison with this value found for conventional melt-crystallized polymers and PE-I samples (slow component) but is lower than that determined for PE-I (fast component). All other specific features of probe mobility in ultradrawn samples are similar to those of fast component in the necked PE samples. These imply that in ultradrawn PE spin probes only occupy pores between microfibrils and they can not penetrate inside microfibrillar units. It is obviously caused by a dramatic change in an internal microfibrillar structure. The disordered regions of microfibrils actually disappear, which is evidenced by the increase in crystallinity calculated from DSC data up to the value close to that of the PE single crystal (see Table I). At the same time the intensity of SAXS reflection in the PE-II samples drops to zero (Figure 3b), which can also be explained by a reduction of difference between the density of crystalline and noncrystalline regions inside of microfibrils.

ESR-data show that irrespective of the perfectness of the internal microfibrillar structure in the ultradrawn samples PE-II the porosity of polymer is maintained, being reduced, however, up to 20–30% as follows from the calculation of the local probe concentration for these samples. The shape of pores is obviously changed with drawing. It is deduced from the analysis of the diffuse scattering distribution in SAXS pattern (Figure 3a, b) and confirmed by the increase of activation energy and the decrease of probe rotational frequency in PE-II samples. The above observations enable us to draw a conclusion that

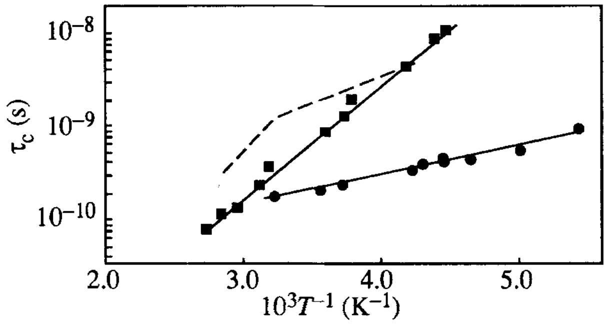

FIGURE 4 The Arrhenius type curves $\tau_c = f(T^{-1})$ for fast components of the spectra from PE-I sample (●), PE-II sample (■) and for a slow component (dashed line).

the interfibrillar pores become more narrow and longer. The relative freedom of probe rotation in pores allows one to estimate the lower limit of their sizes. Their transverse size cannot be less than 10 Å, which is an approximate transverse size of nitroxyl radical.

4. CONCLUSIONS

From the data obtained a conclusion can be made that the drawing of gel-crystallized UHMWPE filaments leads to a crystallization of intrafibrillar disordered regions. The microfibrils become comparable by their structure with unidimensional single crystals. Interfibrillar pores of these samples persist throughout all the range of drawing but they change their shape and volume with drawing. These appear to be very important for understanding of discrepancy between experimentally observed and theoretically calculated values of modulus of elasticity and tensile strength. It can partly be due to ignoring the existence of pores when calculating the samples cross section. We only measure an apparent cross section that is greater than the real one. The potential resource for the further enhancement of mechanical properties of this polymer material is an elimination of porosity of the drawn samples.

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