length[14]. Details of these investigations will be forthcoming in future publications.

Acknowledgement

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Stress whitening in polyethylene

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Introduction

The origin of stress whitening in thermoplastics is a matter of some controversy. Although Breuer, Haaf and Stabenow[1] have pointed out that the optical inhomogeneities which give rise to opacity may be caused by fluctuations in density (e.g. voids or crazes) or by fluctuations in structure (e.g. changes in crystal orientation) most authors have preferred to attribute stress whitening to fluctuations in density. The object of this communication is to cast some doubt on this for polyethylene at least.

Vincent, Willmouth and Cobbold[2] found in the stress whitened region of a propylene/ethylene co-polymer, holes up to 2 μm in diameter. Kambour[3] in the stress whitened region of a specimen of polypropylene found crazes extending throughout the 'millimetre or two' of stress whitening. Jareki and Meier[4] in ultra high modulus polyethylene observed two different forms of voids whose axes were either parallel or perpendicular to the stress direction and discussed the whitening of the drawn polyethylene as corresponding to an extensive formation of internal voids. The void formation described by the above authors[1–4] differs from the micro-voids described by Zhurkov and Kuksenko[5] or by Wendorff[6] since their micro-voids are in general less than 50 nm in diameter.

However the void formation described above is not easily reconciled with the observations made by some authors who have worked with semicrystalline polymers and observed a decrease in volumetric strain with time. Carmichael[7] working with low density polyethylene observed a negative plastic volume change for plastic extensions of less than 10% and Benham and McCammond[8] observed in creep experiments on polypropylene negative volumetric strains at tensile strains of about 3%*. Powers and Caddell[9] in constant strain rate extension experiments on high density polyethylene observed a contraction ratio greater than 0.5 and hence a negative volumetric strain for all values of tensile strain in the region of 0–8% tensile strain (the extent of their measurements).

It therefore seems possible that stress whitening may be caused by fluctuations in structure and some recent observations in this laboratory may be put forward to support this view.

Experimental

The polymer used was high density polyethylene (HDPE) supplied by Hoechst Australia Pty. Ltd. and designated GA7260 ($M_w = 6.1 \times 10^4$, $M_n = 9.5 \times 10^3$). It came in powder form with no additives. The HDPE was compression moulded at 180°C between induction heated platens for 5 min after which it was left to cool to room temperature, while still in the press. The HDPE plaque was then milled to a thickness of 2.54 ± 0.01 mm. Dumbell shaped specimens of gauge length 20 mm and width 5 mm were made using a polymer router. The sides of the specimen were cleaned with silicon carbide polishing paper (grade 800) to remove machinery marks and surface scratches.

In order to examine simultaneously the development of stress whitening and the volumetric changes in the specimen during creep a sample of polyethylene was examined in an apparatus of the form shown in *Figure 1*. Two solar cells were used to detect stress whitening. One of them was used to serve as a reference. Stress whitening was detected by noting the decrease in transmitted light intensity through the specimen. An ordinary fluorescent lamp was used as the light source. Three linear voltage displacement transducers (LVDT) were used to measure

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* The actual volumetric strains are more negative than those shown in Benham and McCammond's paper since these authors neglected terms of the order of ε_x^2 and higher in calculating their volumetric strain and this neglect is not justified in the region in which they worked

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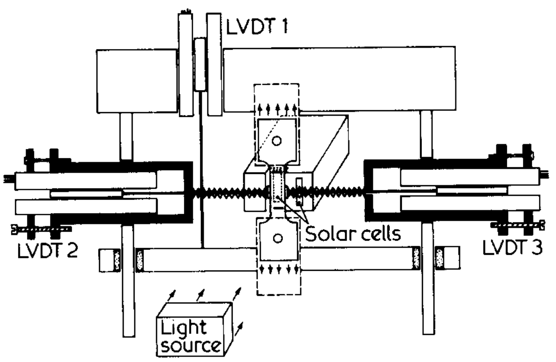

Figure 1 **Schematic drawing of the apparatus used to measure lateral contraction, longitudinal extension and stress whitening simultaneously**

the volumetric strain. LVDT 1 measured the longitudinal extension while the outputs of LVDT 2 and 3 were connected in series to measure the lateral contraction. It was found by attaching a clip gauge extensometer along the gauge length of the specimen and correlating this extension measurement with the longitudinal extension measurement of LVDT 1 that an effective gauge length of 22.5 mm could be used when calculating the longitudinal strain using the output from LVDT 1. (A clip gauge extensometer was not used to measure the longitudinal strain because the specimen tended to break at the points where the clips were attached.)

The creep contraction ratio (v) which is defined as the ratio of lateral strain (e_w) to longitudinal strain (e_L) was calculated by determining the slope, using linear regression analysis, of a plot of lateral strain *versus* longitudinal strain. All the linear correlation coefficients were greater than 0.998. The volumetric strain (e_v) was calculated by using the equation

$$e_v = [(1 + e_w/v)(1 + e_w)^2 - 1] \times 100$$

The longitudinal strain at onset of stress whitening (e_{sw}) was determined by noting the strain at which the transmitted light intensity first dropped.

Results and Discussion

The variation of volumetric strain with log (time) is shown in *Figure 2*. The onset of stress whitening is indicated by two parallel bars (I---I). The majority of the specimens have a creep contraction ratio greater than 0.5, except for one specimen where the creep contraction ratio is less than 0.5, labelled X in *Figure 2*. The possibility that this result could be caused by slip in the friction grips cannot be completely eliminated. Even then the onset of stress whitening is detected only after the volumetric strain starts to decrease. If the onset of stress whitening is due to micro-voiding which is a dilatational process then one would expect stress whitening to be detected when the volumetric strain is increasing with time, but this was not observed. Nevertheless, it is inevitable that a structural change will be accompanied by micro-voiding possibly in the interlamellar regions[10]. However, the results in *Figure 2* indicate that the volume changes resulting from such micro-voids are small compared to the changes associated with the structural transormation, and are unlikely to be the major cause of the stress whitening.

It has also been found that the onset of stress whitening does not start immediately on application of the load but that there is a delay period where no stress whitening is detected (region I, *Figure 3*). Region II corresponds to a region where the specimen undergoes a growing intensity in stress whitening. The delay time for onset of stress whitening decreases with increase in applied stress.

The apparatus in *Figure 1* also permits the determination of the total energy input per unit volume for the onset of stress whitening. This energy (E_{sw}) is calculated by multiplying the applied stress (σ_{ap}) and the strain (e_{sw}) at which stress whitening was first detected. This is shown in *Table 1*. The results in *Table 1* show that the energy per unit volume for the onset of stress

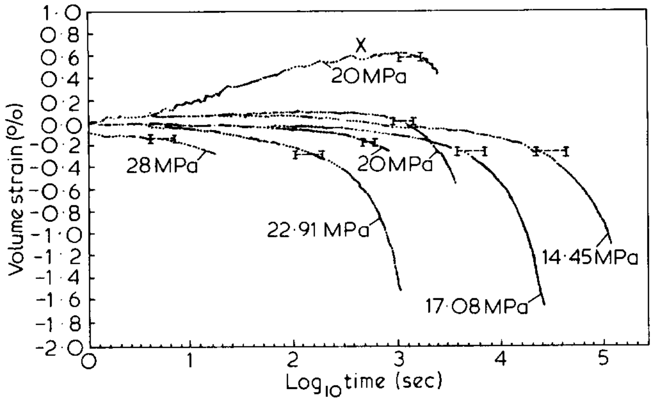

Figure 2 **Volumetric strain *versus* log (time). (I— — —I) indicates region of onset of stress whitening**

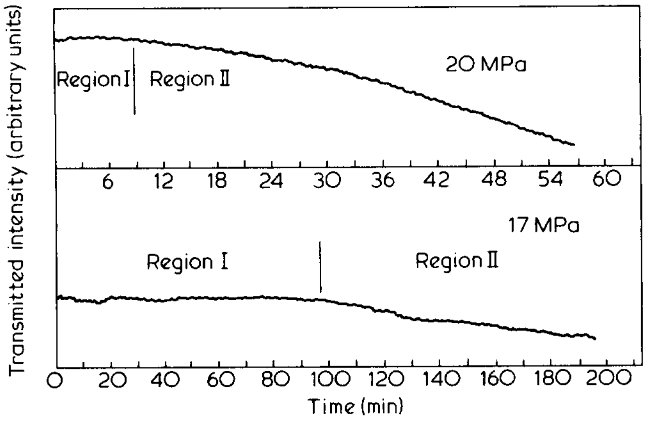

Figure 3 **Transmitted light intensity *versus* time**

Table 1 **Energy for the onset of stress whitening**

Applied stress (σ_{ap}) (MPa)	Stress whitening strain (e_{sw}) (%)	Stress whitening energy ($E_{sw} = \sigma_{ap} \times e_{sw}$) (MJ m^{-3})
14.45	6.2–7.7	0.90–1.11
17.00	8.2–8.8	1.40–1.50
17.08	6.2–6.7	1.06–1.14
20	4.3–4.5	0.85–0.90
20	4.7–5.4	0.90–1.10
20	4.0–4.5	0.80–0.90
20	6.0–6.5	1.20–1.30
20	6.0–6.5	1.20–1.26
20	6.0–6.5	1.20–1.30
22.91	4.9–5.1	1.12–1.17
23	3.5–4.3	0.80–1.00
24.5	4.9–5.3	1.20–1.43
26	4.6–5.4	1.20–1.40
28	3.3–3.6	0.92–1.00
		Mean = 1.12 ± 0.20 MJ m^{-3}

whitening is almost a constant value (1.12 ± 0.20 MJ m^{-3}). This is important evidence to suggest that the onset of stress whitening could follow an energy criterion similar to the Reiner Weisenberg energy criterion of failure[11] which has recently been used by Brüller[12] for the characterization and prediction of failure of some thermoplastics.

Conclusions

Stress whitening is caused by variations in refractive index which themselves may be caused either by variations in structure or by the presence of voids. However since the voiding is a comparatively small effect, it seems likely that stress whitening results primarily from the changes in structure associated with permanent plastic deformations.

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Chain conformational defects in polyvinylidene fluoride

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Introduction

There is an increasing interest in the study of polyvinylidene fluoride (PVDF) due to its important technological applications and in recent years much progress has been made using a variety of approaches for the understanding of its structure and electrical properties[1–15]. Nevertheless, the correlation between structure and electrical properties is still not clearly understood. Therefore, it seems that detailed investigations of structural aspects in various conditions using transmission electron microscopic studies may further help in understanding structure–property relationships. Chain and lattice defects in PVDF crystals may influence its electrical behaviour as well as the phase transformation process, as both the processes are susceptible to conformational changes. The purpose of this communication is to report electron microscopy results of thin PVDF films (approximately 100 nm) containing both the phases (α-form and β-form) in fine dispersions and to present evidence deduced from electron diffraction patterns for a very high density of conformational defects in the α-forms of PVDF crystals.

Experimental

PVDF, Dyflor-2000 obtained from Dynamit Nobel was used for the study. Highly oriented thin films of PVDF are prepared in high longitudinal flow fields by orienting thin molten films (≈ 1 μm) according to the method developed by Petermann and Gohil[16]. The molten thin film of PVDF is prepared by spreading a 0.5% solution in dimethyl formamide (DMF) onto a glass slide kept at the preparation temperature (135°–160°C). The solvent is allowed to evaporate and the resulting molten thin film is drawn vertically upward from the glass slide at a speed (v) of 1 cm s^{-1}. The adhesion of the film to the glass slide causes a high degree of orientation in the resulting films which are thin enough (100 nm) for direct observation in the transmission electron microscope without any further treatment. Also, for X-ray, mechanical and thermal studies, thick samples can be prepared by winding the films on glass substrates. A JEM 200A electron microscope, operated at 100 kV was used for the present investigation.

Results

Different morphologies of PVDF, highly oriented lamellar crystals of the α-form (*Figure 1a*) and the needle like crystals of the β-form (*Figure 1b*) can be obtained by our method depending on the experimental conditions such as preparation temperatures and drawing rates. If intermediate conditions of preparation are chosen, ($T = 135$°C, $v = 1$ cm s^{-1}), a mixture of both forms is obtained in which the β-form has a ribbon like dispersion in the matrix of the α-form (*Figures 2a–c*). If the film contains a proportion of the β-form, a remarkable difference in diffraction patterns is sometimes seen (*Figure 3*). Strong streaking of (110) diffraction spots of the α-form (*Figure 3a*) extend in the [001] direction. Also, in some cases strong streaking of both the (110) and the (020) diffraction spots as seen in the *Figure 3b* are observed. Additionally, streaking of the (002) spot in the α-form

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