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Orientation effects in injection-moulded rubber materials studied by X-ray scattering

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In this work orientation effects in rubber materials have been studied by X-ray scattering measurements. The rubber materials were made by injection moulding and were anisotropic as judged from mechanical and swelling measurements. In X-ray diffractograms it was possible to detect preferred orientation of both rubber molecules and zinc oxide. It may also be concluded that zinc oxide acts as an indicator of macromolecular orientation in an anisotropic rubber material.

(Keywords: rubber material; zinc oxide; orientation; X-ray scattering)

INTRODUCTION

X-ray scattering studies on rubbers have been dominated by the characterization of natural rubber in the stretched state, i.e. evaluation of the orientation of the crystallites formed under strain, as reviewed by Stevenson[1]. However, the orientation of the amorphous phase in a stretched natural rubber has also been studied[2]; a general discussion about the use of X-ray scattering to study order in amorphous polymers, including natural rubber, has been given by Mitchell[3].

Anisotropy in the physical properties of rubber materials has not been extensively studied, in contrast to anisotropy in thermoplastics. The reason for this may be the relatively long processing time in conventional rubber production, allowing the majority of the rubber molecules to retain and recover their equilibrium conformation before and during the vulcanization. During the last two decades, however, injection moulding has gained in importance as a production method for rubber goods. Injection moulding entails a stronger influence of orienting flow on the rubber molecules and shorter relaxation times before and during the vulcanization compared to compression moulding, the traditional production method in the rubber industry. Injection moulding may thus produce an anisotropic material; this problem has been discussed by Isayev[4].

As part of an extensive study[5] on the subject of anisotropy in rubber materials, this paper describes X-ray scattering measurements on anisotropic rubber discs. The anisotropies of the discs were determined by mechanical and swelling methods. The anisotropic data presented in this paper refer only to the materials chosen for these introductory X-ray scattering measurements.

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EXPERIMENTAL

The materials used were one carbon-black-filled styrene-butadiene rubber (SBR) vulcanizate and one unfilled ethylene-propylene-diene rubber (EPDM) vulcanizate. The materials were sulphur vulcanized, and the recipes are given in *Table 1*. Some of the polymer data were as follows: Cariflex 1500: M_w (g.p.c.–r.i., PS-equivalence) 456000; M_w/M_n 6.4; 23.5% bound styrene. Vistalon 2504: M_w (g.p.c.–r.i., PE-equivalence) 155000; M_w/M_n 8.0; non-branched; monomers, C_2 48 wt%, C_3 48 wt% and ethylene norbornene 4 wt%.

According to the supplier (Rånäs Bruks AB, Sweden), the zinc oxide used in the compounds was produced by the French process and had the following properties: ZnO $\geqslant$99.0%; surface area $\sim 4\ m^2\ g^{-1}$; particle size $\leqslant 5\ \mu m$ (100%), $\leqslant 1\ \mu m$ (65%). The rubber compounds were injection moulded at 190°C to give centrally gated discs, which were 4 mm thick and had a diameter of 150 mm. The discs were delaminated by water-jet cutting, and the mechanical properties were measured by stress–strain measurements. Swelling was measured to determine the state of cure and the dimensional swelling. These measurements showed that the discs were markedly anisotropic. In summary, in the 'core', i.e. the central volume element of the disc, the modulus was higher and the dimensional swelling smaller in the tangential direction than in the radial direction. This may be ascribed to molecular orientation obtained during the mould-filling process. *Figure 1* shows how the directions are defined. Some of the data of anisotropic properties are given in *Table 1*. A complete description of preparation, measurements and results will be given in forthcoming papers[5]. The samples used in the X-ray scattering measurements were taken 59 $\pm$ 4 mm from the disc centre and with the surface material removed, see *Figure 1*. A Leitz microtome was used to obtain samples

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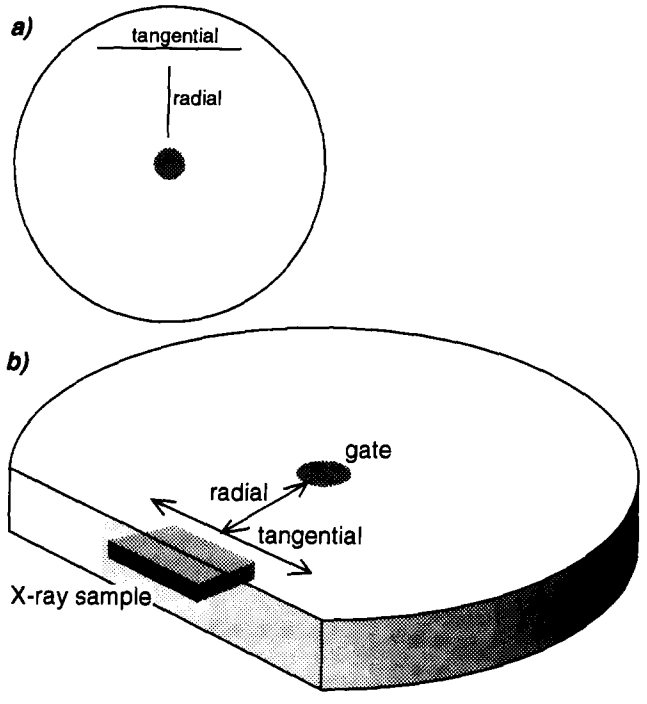

Figure 1 Diagram of disc: (a) definition of radial and tangential directions; (b) location from which samples were taken. (Non-uniform scale: disc diameter 150 mm, thickness 4 mm; X-ray sample thickness 0.2 mm)

Table 1 Recipe (parts per hundred rubber) and mechanical and swelling anisotropy

EPDM		SBR	
Vistalon 2504[a]	100	Cariflex 1500[g]	100
Nypar 40[b]	10	Plasticizer T[h]	10
		N330[i]	50
ZnO	5	ZnO	5
Stearic acid	1	Stearic acid	1
Sulphur-80	2.5	Sulphur-80	2.8
TMTD-80[c]	1	CBS-70[j]	1.7
TDEC-70[d]	1.1	TMTM-80[k]	0.3
DPTT-70[e]	1.1	TMQ[l]	1
MBT-70[f]	2.1	6PPD[m]	1.5

Anisotropy of (tangential/radial property)	EPDM core	SBR core
Young's modulus at 100% elongation	1.6	1.5
dimensional swelling	0.94	0.95

Ingredients:
[a] Ethylene-propylene-diene rubber
[b] Mineral oil
[c] Tetramethylthiuram disulfide
[d] Tellurium dithiocarbamate
[e] Dipentamethylenethiuram tetrasulfide
[f] Mercaptobenzothiazole
[g] Styrene-butadiene rubber
[h] Mineral oil
[i] Carbon black
[j] *N*-cyclohexyl-2-benzothiazole-2-sulfenamide
[k] Tetramethylthiuram monosulfide
[l] Polymerized 1,2-dihydro-2,2,4-trimethylquinoline
[m] *N*-phenyl-*N*'(1,3-dimethylbutyl)*p*-phenylendiamine

thin enough ($\leqslant 0.2$ mm) for the X-ray scattering measurements.

X-ray scattering was carried out to reveal chain orientation in the rubber samples. A STOE STADI/P powder diffractometer was used with CuKα_1 radiation ($\lambda = 1.5405981$ Å) and a curved position sensitive detector (PSD) covering the scattering angle range $10° < 2\theta < 45°$. For each sample, 10 different diffractograms were recorded. The scattering was measured at a series of azimuthal angles: $\phi = 0, 10, 20 \ldots 90°$, where $\phi = 0°$ represents a measurement with the longer edge of the rectangular cross-section of the incident X-ray beam parallel to the tangential direction of the disc, i.e. the sample reference direction as shown in *Figure 2*. During each scattering experiment the angle between the normal of the sample surface and the incident X-ray beam, ω, was scanned from 5° to 22.5° in order to register all scattering angles, 2θ, on the PSD in a uniform way.

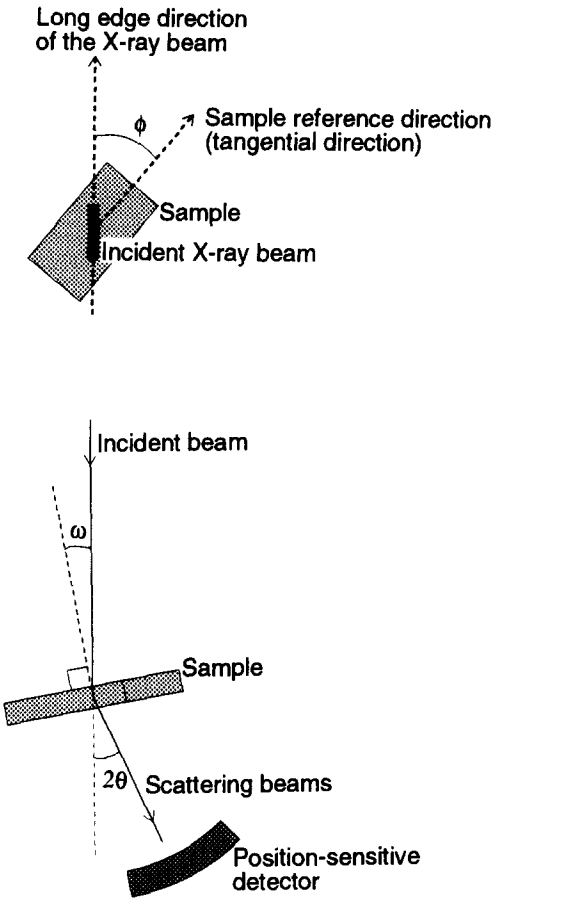

Figure 2 Diagrams showing the position of sample during the scattering measurements

RESULTS AND DISCUSSION

Figure 3 shows the diffraction patterns of the EPDM sample at $\phi = 0°$ and $\phi = 90°$. The broad peak at $d \approx 4.85$ Å, both at $\phi = 0$ and $\phi = 90°$ in *Figure 3*, can be interpreted as caused by interchain distances, as discussed by Mitchell[3]. The higher intensity of the peak at $\phi = 0°$ indicates that this was the preferred direction of the molecule chains (i.e. the normal to the scattering plane was perpendicular to the most frequently occurring chain direction). This result is in accordance with the mechanical and swelling anisotropies, which indicated a molecular orientation in the tangential direction, i.e. $\phi = 0°$. The position of the broad peak at $d \approx 4.85$ Å indicates an average distance between the aligned rubber molecules of approximately 4.85 Å.

The peaks at $d = 2.83, 2.62$ and 2.49 Å can be identified as the three strongest Bragg reflections from hexagonal zinc oxide crystallites; unit cell dimensions $a = b = 3.2498$ Å and $c = 5.2066$ Å (Powder Diffraction File,

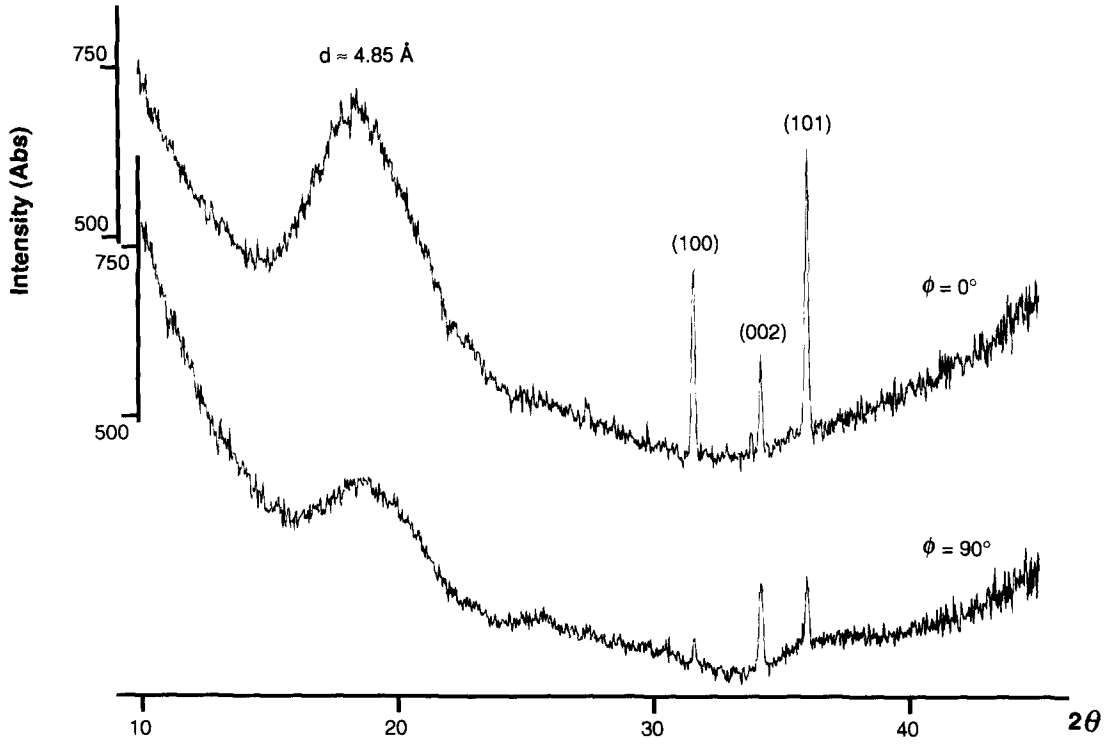

Figure 3 X-ray diffractograms of the EPDM sample at the azimuthal angles $\phi = 0$ and $\phi = 90°$

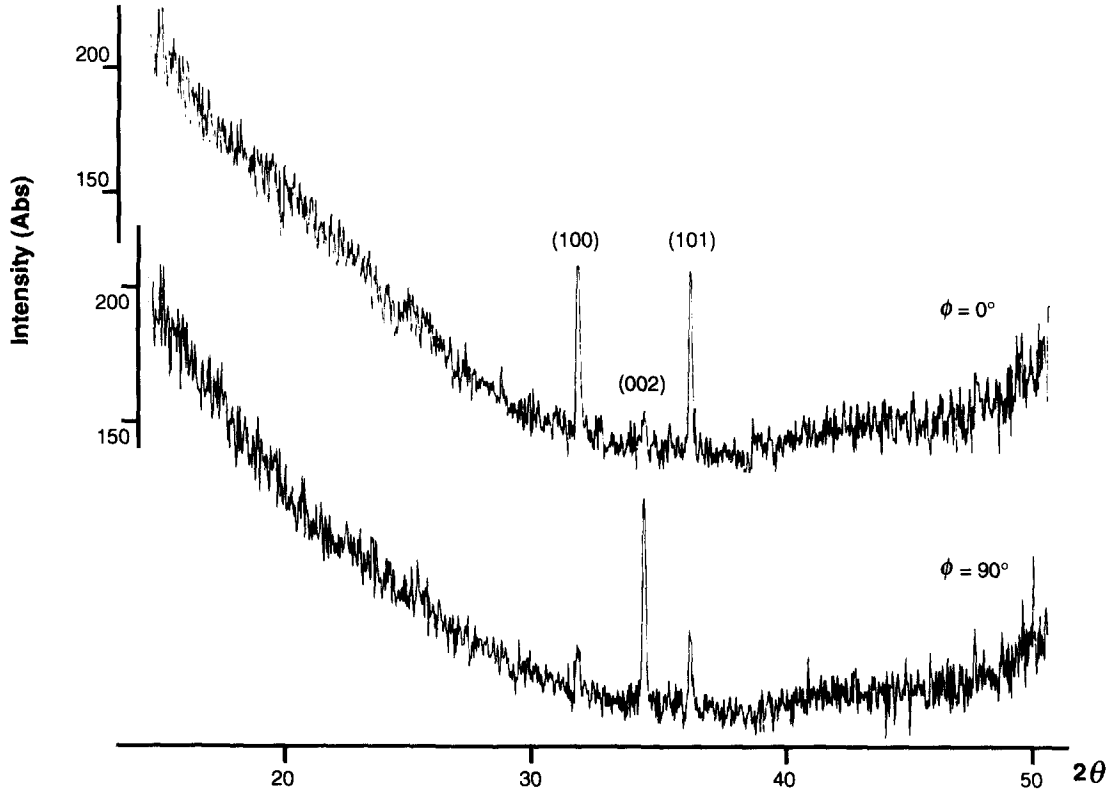

Figure 4 X-ray diffractograms of the SBR sample at the azimuthal angles $\phi = 0$ and $\phi = 90°$

PDF-2, number 36-1451). As can be seen from *Figure 3*, the (1 0 0) and (1 0 1) reflections were strong at $\phi = 0°$, but almost disappeared at $\phi = 90°$, which indicates orientation of the zinc oxide crystallites. The (0 0 2) reflection, however, was of approximately equal size for all ϕ values. Thus, the microcrystalline zinc oxide incorporated in the rubber mix before vulcanization was still present in the discs. Zinc oxide is incorporated in rubber materials as an activator with sulphur vulcanization systems[6] and is consumed in the vulcanization reaction.

The X-ray diffraction patterns of the SBR sample shown in *Figure 4* have no broad peak which could represent a main chain direction in the material. Bragg reflections from zinc oxide are clearly seen in the patterns, however. In this material the (0 0 2) reflection gradually increased in intensity from $\phi = 0°$ to a maximum at

$\phi = 90°$. As the (0 0 2) reflection represents a unique direction in a hexagonal structure, it is possible to derive Herman's orientation function[7], originally formulated to quantify the degree of axial orientation in crystalline fibres and defined as in equation (1), for the diffraction plane perpendicular to the *c*-axis of a zinc oxide crystallite, with the tangential direction of the disc taken as the reference direction.

$$f = \frac{1}{2}(3\langle\cos^2\phi\rangle - 1) \quad (1)$$

For the (0 0 2) reflection $\langle\cos^2\phi\rangle = 0.54$ and $f = -0.31$. The result may be compared with the theoretical values of $\langle\cos^2\phi\rangle$ and f for different states of orientation (*Table 2*) and gives the information that the average orientation of the diffraction planes was nearly perpendicular to the reference direction, i.e. the average orientation of the *c*-axes of the zinc oxide crystallites was nearly parallel to the reference direction. The orientation of the zinc oxide crystallites in the EPDM sample was not possible to quantify according to Herman's orientation function since only (0 0 *l*) reflections represent a unique direction in zinc oxide, and the (0 0 2) reflection remained constant for all ϕ values.

Louër[8] has determined the mean shape of zinc oxide crystallites via X-ray measurements. In that study, the zinc oxide was produced by thermal decomposition of zinc hydroxonitrate $Zn_3(OH)_4(NO_3)_2$ and the crystals had a cylindrical or a hexagonal prismatic form, which was revealed by studies of diffraction line broadening. Their mean length (*c*-axis direction) was 229–252 Å and the mean diameter was 102–117 Å. The structure of the zinc oxide used in the present study is shown in *Figure 5*, where it can be seen that the grains had both cylindrical and irregular shapes. The orientation effect of the zinc oxide crystallites, revealed by the X-ray measurement, was probably caused by the rubber-melt flow orienting the cylinder-shaped crystallites. Thus, there appears to be a correlation between the orientation of the main chain direction in the rubber phase and that of the microcrystalline zinc oxide.

Table 2 Theoretical values of $\langle\cos^2\phi\rangle$

	Orientation with respect to reference direction		
Parameter	Parallel	Random	Perpendicular
$\langle\cos^2\phi\rangle$	1	1/3	0
f	1	0	−1/2

CONCLUSION

From the X-ray scattering measurements it may be concluded that the zinc oxide can be used to give indirect information about anisotropic macromolecular structure in rubber samples, even when the rubber molecules themselves do not yield any anisotropic X-ray diffraction effects. Forthcoming, more complete studies of the entire discs, in which the processing conditions will also be varied, may be expected to give better knowledge of the correlation orientation between zinc oxide crystals and rubber molecules.

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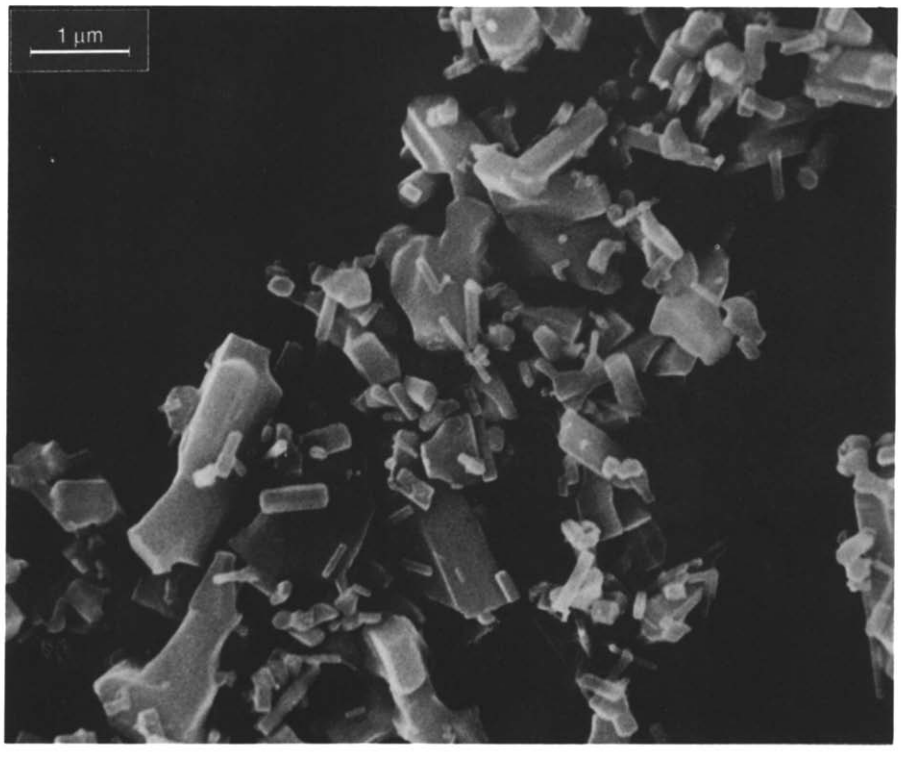

Figure 5 Scanning electron micrograph of the zinc oxide

help with processing and Kimtech AB for lending the water-jet cutting system.

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