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A molecular model for structural changes during shear yielding and crazing in amorphous polymers

D. Maes[1], G. Groeninckx[1], J. Ravenstijn[2], and L. Aerts[2]

[1]Katholieke Universiteit Leuven, Laboratorium voor Macromoleculaire Structuurchemie, Celestijnenlaan, 200 F, B-3030 Heverlee, Belgium

[2]Dow Chemical (Nederland) B.V., Terneuzen, The Netherlands

SUMMARY

Based on macroscopic and microscopic observations, a model is proposed concerning molecular conformation and chemical structure changes occurring during mechanical deformation of amorphous polymers below their Tg. It is assumed that a bulk polymer, with high molecular mass, consists of interpenetrating, coiled chain molecules. The intrinsic flexibility and the thickness of chain molecules depend on their chemical nature. Stresses are transferred from one chain to others by physical entanglements.

Shear yielding, as a solid state deformation mode, is considered as the result of stretching of the coiled chain segments between the entanglements. Crazing, as a cavitation process, is considered to be the consequence of chain scission after some degree of local shear yielding.

INTRODUCTION

A vast amount of literature has been published with respect to mechanical properties and deformation mechanisms of polymers. On the basis of such studies, molecular models have been proposed concerning structural changes occurring during mechanical deformation. Some authors propose chain scission and others disentanglement (SCHIRRER et al. 1984) . Despite this disunity, it is of fundamental interest to have a thorough insight into the nature of the plastic deformation mechanisms on the molecular level in order to be able to improve the tensile and impact properties of glassy polymers. It is well known that the deformation modes - crazing and shear yielding - are responsible for the mechanical energy absorption of polymers. An adequate molecular model for both deformation mechanisms allows one to predict which mechanism will be dominant and whether the response of the material to tensile deformation will be ductile or not.

specimen via shear yielding. This would indicate that the proposed mechanism of chain stretching is representative for shear yielding.

In the literature various mechanisms have been proposed for craze formation. There is some evidence for chain scission during deformation, obtained directly from ESR and indirectly from IR. Although these techniques are very limited for the investigation of chain scission during crazing due to the fast decay of the small amount of radicals formed; transmission electron microscopic observations on solvent casted thin films, treated in a special way, enable us to deduce indirectly the molecular mechanism of craze formation.

EXPERIMENTAL

For the study of shear yielding, polycarbonate of bisphenol-A (PC), polyvinylchloride (PVC), styrene-acrylonitrile copolymers (SAN), and polystyrene (PS) were used. These were compression moulded into plates of 3 mm thickness. PVC, SAN and PS were preoriented at their Tg by stretching them 1.75 times their original length in order to obtain pure shear yielding during tensile deformation at $T<Tg$ (33% / min). Such pretreatment is not necessary for PC which already exhibits pure shear yielding at this strain rate.

The maximum plastic strain was obtained by comparing the thickness of a totally shear yielded sample with the thickness of the sample in the unoriented state. To avoid the influence of disentanglement during preorientation on the results, the latter measurement of the sample thickness in the unoriented state was carried out after relaxing the strained sample.

For the study of crazing, thin films of SAN and ABS were examined with a transmission electron microscope. The thin films were made by solvent casting and deposited on a copper-grid. After drying for 24 h in a vacuum oven at 100 °C, the films were strained by deforming the copper-grid.

Strained ABS films were first treated for 2.5 h with ozone before staining with osmium tetroxide. For comparison, another strained ABS film was not treated with ozone, but only with osmium tetroxide.

RESULTS

SHEAR YIELDING AS A CONSEQUENCE OF CHAIN STRETCHING

Assuming a random, Gaussian coiled conformation for the chain sequences between entanglements for unstrained samples, one can calculate the maximum extension ratio of a totally stretched chain sequence located between entanglements. The end to end distance of an unstretched chain can be obtained from theta conditions parameters of a dilute polymer solution. In the entanglement model, the end to end distance has to be substituted by the entanglement to entanglement distance; this can easily be done using the critical molecular weight between entanglements in the Mark-Houwink equation.

The maximum theoretical extension ratio (λ_e) is then defined as the ratio of the length of the totally stretched chain segment between entanglements (l_e) to the entanglement to entanglement distance in the unstretched state (d_e):

$$\lambda_e = \frac{l_e}{d_e}$$

The maximum macroscopic strain (experimental extension ratio) was measured for the different polymers mentioned above and plotted as a function of the theoretical extension ratio (λ_e) (figure 1). The 45 degree slope of the straight line indicates total stretching of the coiled chain segments during shear yielding.This linear plot indicates the direct effect of the submicroscopic material parameters on the macroscopic properties. This result is in contrast with literature data obtained on solvent casted films using EM density measurements (KRAMER et al. 1982) . Our measurements favour also the stretching model which describes shear yielding or necking as a result of chain stretching between entanglements.

CRAZING AS A CONSEQUENCE OF CHAIN SCISSION

Figure 2 represents electron micrographs of a strained, solvent casted thin film of SAN. It shows the tip of a craze, and the different stages of craze formation can be distinguished. Firstly, local straining occurs which is observed as thinning of the film (figure 2A); no voids or microfibrils can be seen. At this stage, only some stretching of the molecular coils between the entanglements, as in shear yielding, is supposed to occur. In the next stage, voids are generated in the strained zone (figure 2B); between the voids, some strained material still remains. From now on the typical structure of a craze, voids alternating with microfibrils, is obtained. In the final stage, craze thickening occurs by two mechanisms: further stretching of the original microfibrils, and void formation above and below the primary craze by the same two steps as given above namely stretching and voiding.

In order to confirm that chain scission occurs during voiding,the samples were treated with ozone before staining with osmium tetroxide (figure 3). Our hypothesis is that the staining of crazes is due to staining of the double bonds generated after chain scission. Chain scission leads to reactive radicals which can react with oxygen or convert to a double bond which is stabilized by conjugation with the phenyl or nitrile groups in SAN. Ozone can oxidize these unsaturations to form polar groups like carbonyl and carboxyl functions which should give rise to a higher adsorption of the inorganic oxyde, but this does not happen.

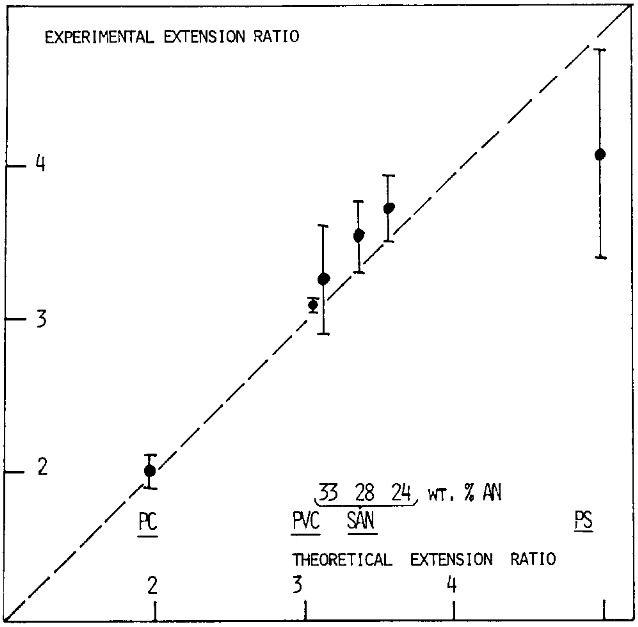

FIGURE 1 : THE COMPARISON BETWEEN THE EXPERIMEMTAL AND THEORETICAL EXTENSION RATIO.

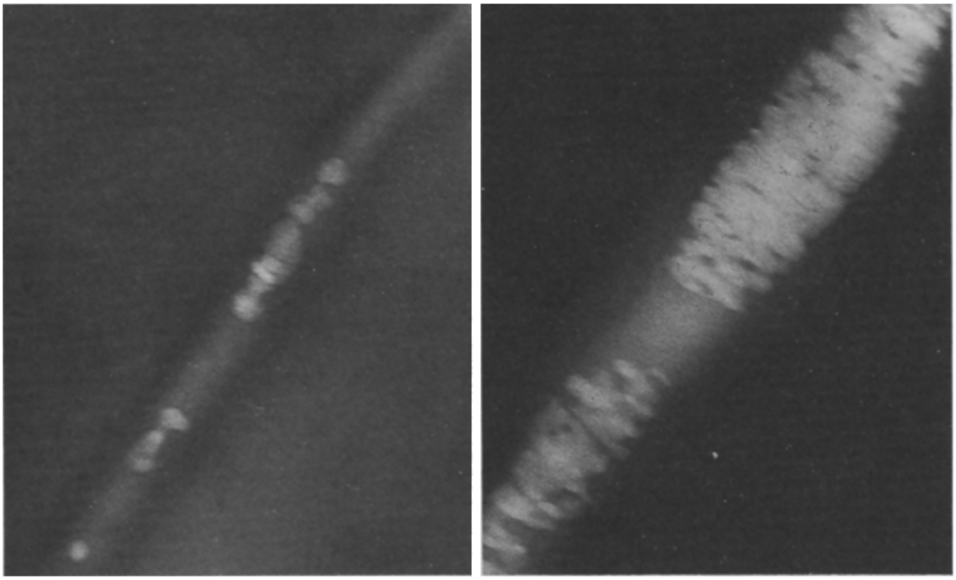

FIGURE 2 : TEM OF A STRAINED SOLVENT CASTED THIN FILM OF SAN. CRAZE TIP. ⊢—⊣ .5 μm

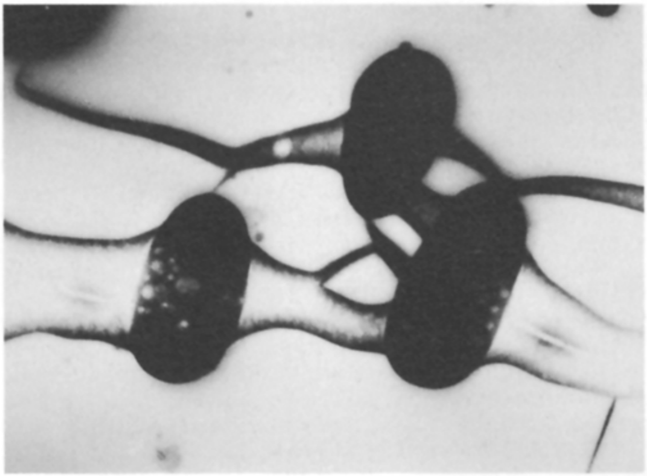

FIGURE 3A : TEM OF A SOLVENT CASTED ABS FILM, STRAINED AND STAINED WITH OSMIUM TETROXIDE. THE RUBBER PARTICLES AND CRAZES ARE STAINED. ├──┤ .5 μm

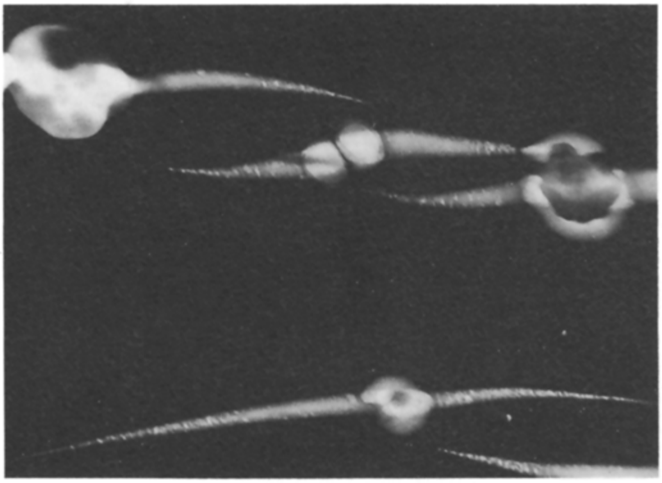

FIGURE 3B : TEM OF A SOLVENT CASTED ABS FILM, TREATED FOR 2 1/2 H WITH OZONE AFTER STRAINING AND BEFORE STAINING WITH OSMIUM TETROXIDE. THE CRAZES ARE NOT STAINED. THE SAN MATRIX IS DARK DUE TO LONGER EXPOSURE TIMES. ├──┤ .5 μm

In this work a solid polymer is considered as a physical network of randomly coiled chains which, under certain conditions, can be stretched and scissioned. The idea of a coiled network is inspired by the model of Flory concerning the conformation behaviour of a polymer chain in a solvent. Under theta conditions, one may assume the same conformations for the chain in solution as in the bulk state. This is confirmed by neutron scattering experiments (WIGNALL et al. 1976; KIRSTE et al. 1975; BALLARD et al. 1973) where the same end to end distances of the coils in a bulk polymer were obtained as for coils in solution under theta conditions. If the chain length exceeds a critical value, entanglements are introduced by which the molecular coils are mechanically connected to each other; this critical chain length between entanglements is related to the chemical nature of the polymer chain. The existence of physical entanglements has been confirmed by different experiments (GREASSLEY et al. 1974; GENT et al. 1972; PORTER et al. 1966).

The conformation of a random coil of a polymer chain depends on its intrinsic flexibility which determines the end to end distance of the coiled chain. Depending on the thermodynamic properties of the solvent and the temperature, the end to end distance can vary, but under well defined conditions, called theta conditions, the coil behaves as if it is influenced by the internal flexibility only. Under these conditions, which are identical to the bulk state circumstances, the end to end distance can be calculated using the Mark-Houwink parameter (K_θ) and the molecular mass of the coil. If one substitutes the molecular mass of the chain by the critical molecular mass between entanglements in the Mark-Houwink equation, one obtains the distance from entanglement to entanglement. It is assumed that the chain sequences between entanglements obey Gaussian statistics. The entanglement to entanglement distance (d_e) can be calculated using the following equation which is deduced from the end to end distance equation in dilute solutions:

$$d_e = \left(\frac{K_\theta}{\bar{\Phi}} \right)^{1/3} x \quad M_e^{1/2}$$

where M_e represents the critical molecular weight between entanglements, K_θ the Mark-Houwink parameter under theta conditions, and $\bar{\Phi}$ is an approximately constant factor (2.5 x 10exp23).

From the critical length of the chain sequences between entanglements and the actual distance between them, a threshold strain can be defined corresponding to the degree of stretching of the coiled chain. In order to confirm this model, macroscopic strain measurements were carried out from which a critical strain can be determined by deforming a

Hence, it can be concluded that osmium tetroxide stains the double bonds generated as a result of chain scission during voiding and does not adsorb at the surface of the microfibrils.

DISCUSSION

The experiments clearly show that the macroscopic strain is related to the submicroscopic extension ratio of a chain segment between entanglements. This observation supports the validity of the entanglement-network model.

On the basis of the electron microscopic investigations and the ozone treatments on strained samples, it can be derived that there is no substantial difference between shear yielding and crazing. With regard to the first stage of deformation, crazing in the sense of voiding, has to be considered as a second step after shear yielding, and it depends on the local stress conditions whether chain scission will take place or not.

Some qualitative predictions can now be made about the effect of some fundamental material parameters (chain flexibility, chain length between entanglements, chain interactions, and the chain cross-sectional area or amount of chains crossing a unit surface) on the deformation modes. This requires the knowledge of the stress for crazing and the stress for shear yielding which are closely related to the material parameters and the deformation conditions (temperature, strain rate and stress state).

The stress for shear yielding is assumed to be affected by intermolecular interactions because shear yielding involves slipping of chain segments along each other. Thus, one can reasonably expect an influence of friction and activated processes, described by the Eyring equation, on the yielding stress.

The stress at which crazing occurs (the stress for chain scission) will be influenced by the stress bearing capacity of a material which depends on the number of chains per unit surface, as determined by the bulkiness of the chain (VINCENT 1972) and the thermal history of the sample (VERHUELPEN-HEYMANS 1976). Annealing decreases the free volume and as a consequence increases the chain density and so the amount of load bearing elements per unit surface.

Indirectly, the entanglement density affects the deformation (DONALD et al. 1982). A low entanglement density leads to a high maximum extension ratio. During loading the material can deform locally by shear yielding to this high strain which gives rise to an increase of the local stress. A similar effect is observed by Khun and Grun (1942) for network structures and is used in rubber elasticity studies. When the local stress exceeds the critical stress for chain scission, voiding will occur. When the entanglement density is high, the shear zone stops before reaching this critical chain scission stress at its tip. This explains partially the ductile nature of materials with flexible chains which lead to high entanglement densities (PC, PPO, PPS, nylons, etc.) and vice versa (PS, SAN, etc.).

An effect of the molecular mass of the polymer (above the critical molecular mass) on the stress for crazing is to be expected due to the influence of chain ends which cannot transfer stresses.

It can thus be concluded that the chain stretching and scission model proposed in this paper can be used to predict deformation modes on the basis of fundamental material parameters.

CONCLUSIONS

An attempt was made to confirm experimentally models of chain stretching during shear yielding and of chain scission during craze formation. These models can also be applied in the case of the deformation of rubber modified and filled glassy polymers. Only the local stress and local strain rate conditions which can be influenced by the second component, have to be considered. Quantitative relations between fundamental parameters like chain flexibility, chain cross-sectional area, chain interactions and the critical stress for chain stretching and scission still have to be developed. If the local stress remains below the stress for chain scission under conditions where chain stretching occurs, the polymer will deform by shear yielding and not by crazing.

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