

ON THE ORIGIN OF STRESS PEAK IN UNI-AXIAL STRETCHING OF AMORPHOUS POLYMERS

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ABSTRACT

Rubber of high molar mass, like *cis*-polybutadiene, shows a stress peak on the engineering stress-strain curve during stretching at room temperature. In this work *cis*-polybutadiene samples were swollen in a poor solvent, $\text{CHCl}_3/\text{EtOH}$ (1/1 v/v), for different times. It was found that both the initial modulus and the stress peak on stretching decreased in magnitude with increasing swelling time and the peak disappeared entirely after 1 hour of swelling. On further swelling the initial modulus increased somewhat and a small stress peak re-appeared after swelling for 2 h. The disappearance of the stress peak after swelling is interpreted as the result of disruption of cohesive entanglements present in the initial rubber sample. The re-appearance of a small stress peak and the increase of modulus on further swelling are interpreted as being of the same nature as the phenomenon of anti-plasticization. It is the result of forming some new cohesive entanglements of larger binding energies through longer range chain segmental motions excited after the disruption of the previously existing cohesive entanglements in the rubber. Thus an understanding of the stress peak on stretching a high molar mass rubber and the phenomenon of anti-plasticization on molecular level has been put forward.

INTRODUCTION

The engineering stress-strain curve on stretching an amorphous polymer below its T_g shows a stress peak during yielding, followed by forced rubber elasticity on further stretching. At higher temperatures in the rubbery state the stress-strain relation follows a sigmoid curve close to ideal rubber behavior. In the case of amorphous poly(ethylene terephthalate) it was observed, on following the changes in IR spectrum during stretching, that the transition from *gauche* to *trans* conformation started only after the appearance of the stress peak^[1]. This implies an unlocking mechanism of yielding of amorphous polymers in condensed state. These locking sites were local nematic interaction between segments of the neighboring chains,

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later named as cohesional entanglements^[2] which hinder long range conformational changes. In the case of the rubbery state, when the molar mass is high, however, yielding with a stress peak on stretching has also been observed at room temperature, as in the case of natural rubber^[3], *cis*-1,4-polyisoprene^[4], *cis*-1,4-polybutadiene^[3] and styrene-butadiene copolymer rubbers^[5]. In order to get more clear evidence for the unlocking of cohesional entanglements as a mechanism of yielding of glassy polymers and rubbers of high molar masses at room temperature, the effect of solvent swelling on yielding has been considered. The role of a solvent for a polymer is always to break the interchain and intersegment cohesions. Here, of course, a rather poor solvent has to be chosen so that the polymer is not dissolved into a solution. The introduction of a solvent into a polymer, on the other hand, will decrease the glass transition temperature. Nielsen et al.^[6] observed that when polyvinylchloride (PVC) was plasticized with dibutylsebacate, dioctylphthalate or dibutylphthalate the stress peak on stretching disappeared, while T_g was depressed to near or lower than room temperature, so actually the specimens were stretched in their rubbery state in the presence of a plasticizer. In this work the effect of swelling by a poor solvent on the stress peak of an uncrosslinked *cis*-1,4-polybutadiene rubber sample on stretching has been studied. *Cis*-1,4-polybutadiene was chosen for the investigation because of its very low T_g , ca. -110°C , some 130° below room temperature. At room temperature it is in the rubbery state whether it is swollen with a poor solvent or not, and consequently the change of stretching behavior at room temperature after incorporating a solvent into the rubber could be attributed to the sole effect of solvent swelling.

EXPERIMENTAL

A sample of *cis*-1,4-polybutadiene rubber produced by Jinzhou Petroleum Factory was used, which had a Mooney viscosity of 46 and a $\overline{M}_\eta$ of $6.6 \cdot 10^5$ evaluated from its $[\eta]$ value of 3.87 dL/g determined in toluene at 30.0°C by the relation $[\eta] = 3.24 \cdot 10^{-4} M^{0.70}$ [7]. The molar mass distribution was characterized by $\overline{M}_w/\overline{M}_n = 3.92$ from size exclusion chromatography. The sample was cut in the form of dumbbell shaped sheet specimens around 2 mm thick with a gauge length of 25 mm and a width of 4 mm. The specimens were annealed at 120°C in a vacuum oven for 12 h to remove the thermal history of the sample. The specimens were weighed and their exact dimensions measured using a measuring microscope. The specimens were weighed and their exact dimensions measured using a measuring microscope. The specimens were then immersed in a mixed solvent

of $\text{CHCl}_3/\text{C}_2\text{H}_5\text{OH}$ (1/1 v/v) for swelling times of 0.5, 1, 1.5 and 2 h at room temperature of ca. 25° C. At the end of the swelling period the specimen was taken out of the solvent and the solvent left on the surfaces of the specimen was blotted out. The swollen specimen was immediately mounted on the grips of a tensile testing machine and the load elongation curve was obtained at 25° C under a stretching rate of 25 mm/min. For the changes in weight and volume of the specimen on being swollen, the experiment was carried out at room temperature of ca 14° C. The specimen was measured for its dimensions again and then put into a closed vessel for weighing. Thus the volume change of the specimen and the amount of solvent in the specimen were obtained.

RESULTS AND DISCUSSION

The load elongation curves of the specimens swollen for different times at 25° C are shown in Fig.1. Homogeneous deformation was observed during stretching without necking. Both the initial modulus and the stress peak on yielding decreased with increasing swelling time and the stress peak disappeared after swelling for 1 h. On further swelling the initial modulus increased somewhat and a small stress peak reappeared after swelling for 2 h. The percent weight increase ΔW and percent volume increase ΔV during the course of swelling up to 15.5 h at 14° C are shown in Fig.2.

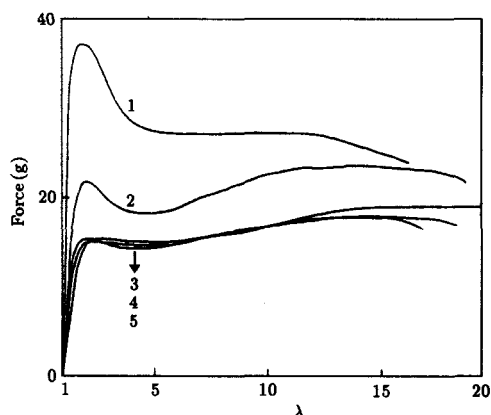


Fig.1 Load elongation curves of the *cis*-polybutadiene sample on stretching after swelling in $\text{CHCl}_3/\text{EtOH}$ (1/1 v/v) for different times at 25° C, λ =stretching ratio, 1, 2, 3, 4, 5- swelling times 0, 0.5, 1, 1.5, 2h, respectively

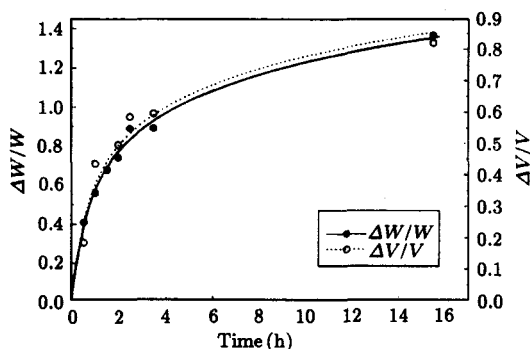


Fig.2 Percent increase in weight ΔW and in volume ΔV of the *cis*-polybutadiene sample during the course of swelling in $\text{CHCl}_3/\text{EtOH}$ at 14° C

The data are averages of 3—7 measurements. The volume measurement was not precise at all but the trend should be of significance. The disappearance of the stress peak after swelling can be understood as the disruption of cohesive entanglements in the rubber as a solvent in a polymer always plays the role of loosening the intersegmental cohesion of the polymer chains. Increase of ΔV of swelling also indicates the decrease of physical crosslink density of the swollen rubber. It is therefore safe to conclude that the origin of the stress peak in the stress-strain behavior is the disruption of cohesive entanglements in the rubber. Of course, the stress peak only appears in the engineering stress-strain curve. When the true stress-strain curve is plotted no peak will appear but a change of slope of the curve

on yielding, which signifies a sudden decrease of incremental modulus, that is, a softening of the specimen. As contrasted to the engineering stress-strain behavior shown in Fig.1 the true stress-strain behavior is shown in Fig.3, calculated from the experimental data assuming no volume change during stretching. The slight increase of the initial modulus and the re-appearance of a small stress peak after swelling for 1.5 and 2 h shown in Fig.1 remind us of the phenomenon of so called "antiplasticization"^[8]. This seems to be the result of forming some new cohesive entanglements of larger binding energies through longer range chain segmental motions excited after disruption of the previously existing cohesive entanglements in the rubber. It is to be emphasized that owing to small binding energy of cohesive entanglements the formation and disruption of cohesive entanglements is a dynamic process going on around room temperature through chain segmental motion. Thus an interpretation of "antiplasticization" on molecular level is offered for the first time.

We have interpreted the origin of the appearance of a stress peak on yielding during uni-axial stretching of an amorphous polymer as coming from the presence

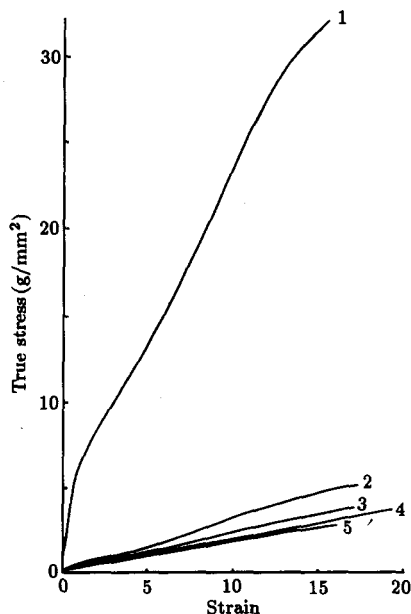


Fig.3 True stress-strain curves of the *cis*-polybutadiene samples of Fig.1 calculated by assuming no volume change on stretching, numbers referring to those in Fig.1

of cohesive entanglements in the polymer. In a previous paper^[2] we interpreted the appearance of an endothermic peak during a heating up run of differential scanning calorimetry (DSC) of an amorphous polymer after sub- T_g annealing also having its origin in cohesive entanglements formed during annealing. Amorphous poly(ethylene terephthalate) after sub- T_g annealing actually showed an enhanced stress peak during stretching at room temperature^[9,10]. The conjuncture by Bauwens-Crowet and Bauwens^[11] that the stress peak on yielding during stretching an amorphous polymer and the endothermic peak on the DSC curve of an amorphous polymer after sub- T_g annealing involve the same elementary process is now clearly interpreted on a molecular level as cohesive entanglements present in amorphous polymers in their glass state. Recent experiments^[12] in this laboratory on the comparison of DSC and stress-strain curves of i) amorphous PET films melt extruded onto a cooled drum and then sub- T_g annealed at 65° C for 40 h, ii) the film (i) after being stretched after yielding, iii) the film (ii) after being sub- T_g annealed at 65° C for 8—24 h. The absence of both the stress peak and the DSC endothermic peak in the case ii) and the presence of a stress peak and a DSC endothermic peak in the case of i) and iii) clearly confirm the conclusion reached above.

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Keywords:

PET; Swelling; Entanglement; Stress peak; Uni-axial stretching

REFERENCES

- [1] Qian, R.; Shen, D. and Li, H., *Chinese. J. Polym. Sci.*, **1989**, 7: 150.
- [2] Qian, R.; Wu, L.; Shen, D.; Napper, D.H.; Mann, R.A. and Sangster, D.F., *Macromolecules*, **1993**, 26: 2950.
- [3] Yu, F.; Yang, Y.; Li, S.; and Qian, B., Collected Papers of Changchun Institute of Applied Chemistry, Academia Sinica, No. 18, **1982**, 1 (in Chinese).
- [4] Qian, B.; Yu, F.; Cheng, R.; Yuan, M.; Zhang, W.; Li, S.; Zhang, Y. and Yang, Y., *Zhongguo Kexue*, **1982**, B969.
- [5] Li, S.; Dong, J.; Yu, F., *Chinese. J. Polym. Sci.*, **1986**, 4: 1.
- [6] Nielsen, L.E.; Buchdahl, R., Leveault, R., *J. Appl. Phys.*, **1950**, 21: 607.
- [7] Qian, B.; Yu, F.; Cheng, R.; Qin, W. and Zhou, E., "Proc. China-US Bilateral Symposium on Polymer Chemistry and Physics, Beijing October, 1979", Science Press, Beijing and Von Nostrand Reinhold Co., New York, **1981**, p.155.
- [8] Bernado, J.J.; Burrell, H., "Polymer Science", A.D. Jenkins, Ed., North-Holland Publishing Co., Amsterdam, **1972**, Vol.1, p.545.

- [9] Tant, M.R.; Wilkes, G., *J. Appl. Polym. Sci.*, **1981**, *26*: 2813.
- [10] Shen, D.; Long, F.; Wen Z. and Qian, R., *Makromol. Chem.*, **1991**, *192*: 301.
- [11] Bauwens-Crowet, C.; Bauwens, J.C., *Polymer*, **1986**, *27*: 709.
- [12] Wang, Y.; Li, F.; Shen, D. and Qian, R., *Acta Polymerica Sinica* (in Chinese), **1996**, (2): 224.

Note added in proof. A paper by Raha, S. and Bowden, P.B. published in *Polymer* **13**, 174 (1972) escaped from our notice, in which they proposed "cohesional points" as a kind of physical crosslinks which should be subject to dissociation by continued straining so that rubber like freedom is introduced at yield. This idea is in complete accord with the concept of "cohesional entanglements" presented in this paper.