Infrared spectroscopic study of the chemical bonds in stressed polymers

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Summary

An attempt was made to evaluate the true stresses on atomic bonds in mechanically stressed polymers. The magnitudes of stresses on bonds were measured by the shift of skeletal vibration frequencies in chain molecules. A considerable frequency shift, revealed in the infrared spectrum, indicated the existence of overstressed bonds in uniaxially extended polymers. The maximum stress on these bonds surpassed at least ten times the average stress in specimens. The stress distribution over bonds was estimated.

The results obtained are quite in agreement with the kinetic conception of the mechanism of fracture.

Introduction

A systematic study of time and temperature effect upon rupture strength has given rise to the kinetic concept of the fracture of solids developed by Zhurkov and collaborators.

According to that concept, the mechanical fracture of a solid can be considered as a process dependent on time, the rupture of chemical bonds under the action of thermofluctuations and the applied stress.

For polymers, the fracture process can be roughly divided into three stages:

1. Excitation of atomic bonds by mechanical stress which reduces the atomic bonding.

2. Breakage of overstressed bonds by thermal fluctuations, and formation of free radicals as recorded by Zhurkov, Tomashevski, and Zakrevski [1, 2].

3. Accumulation of bond ruptures in a stressed polymer, which according to Yastrebinski, Slutsker and Kuksenko [4], results in formation of microcracks and breakdown of specimens.

The basis of the kinetic conception is the supposition that overstressed chemical bonds exist in polymers under stress. The probability of fracture for these bonds is higher than for the bonds stressed to a smaller extent, and the former seem to be initial points of breakdown. Thus the rate of polymer fracture is determined by the magnitude of the true stresses on the bonds being broken. It is therefore essential to demonstrate the existence of overstressed bonds and to confirm in this way the fundamental assumption of the kinetic concept of fracture.

To do this, the authors of the present paper have used the infrared spectroscopy technique. The vibrational frequency of a polymer molecule

is known to depend on the applied force, constants determined by the strength of the atomic binding, and on the valence angles. It is well known that a deformation of interatomic bonds and angles under stress results in a shift of skeletal vibration. Hence the shift of vibrational frequencies allows us to judge the magnitude of true mechanical stresses acting on the polymer chain. We have made use of these data to reveal the overstressed bonds and to estimate the true stresses on them in polymers under stress.

Determination of the true stresses on chemical bonds

The experiments in our study of stresses on bonds were carried out on oriented films and single fibres of polypropylene, polyethyleneterephthalate, and polycapramide (Nylon 6).

The specimens inside the infrared spectrometer were loaded along the axis of orientation which allowed the band shift to be followed.

In Fig. 1 the absorption spectra of a free specimen and those of the same specimen under tensile stress 70 kg/mm² are shown. Band 975 cm^{-1}, according to Mayazawa is due to skeletal vibration [3].

It is seen that the mechanical stress has resulted in a shift of the maximum of the absorption band toward the lower frequencies and in a deformation of the long-wave part of the band.

A similar effect was observed on the other absorption bands of polypropylene connected with skeletal vibrations (842, 908, 940, 998, 1170 cm^{-1}) as well as on skeletal vibration bands of polyethylene terephthalate (437, 975, 1120 cm^{-1}) and polycapromide (930, 980 and 1120 cm^{-1}). In all cases the vibrational frequency of C–C bonds in the chain of macromolecules under stress was found to shift toward lower frequencies, the band shape being distorted.

We have made measurements of the shift of the maximum of the absorption band under various stresses applied to polymer. The results are presented in Fig. 2. It is seen that they can be described well by the equation

$$\nu_\sigma = \nu_0 - a\sigma \qquad (1)$$

where ν_σ and ν_0 are the frequencies of the maximum of absorption bands under stress and without it. The experimental values of the coefficient a for the three polymers investigated are given in Fig. 2.

The shape deformation of the absorption band in its long-wave region indicates a non-uniform stress distribution over the bonds. The majority of skeletal bonds are on the average slightly stressed, their shift being $\sim\Delta\nu_{appl}$. However there are some bonds with considerably stronger stresses and the shift is found to be $\Delta\nu_{max} \gg \Delta\nu_{appl}$. The vibrational

frequencies of such overstressed bonds are shifted toward longer wavelengths, and overlapping produces a deformed band shape.

The linear relation found experimentally between the shift of the maximum of a band and the stress has been predicted theoretically in Gubanov's papers [5, 6] which show that this relation is valid for skeletal vibrations over a broad range of stresses up to the breaking stress. Therefore the linear relationship (equation 1) can be extrapolated to frequencies which correspond to strongly overstressed bonds. By such extrapolation we were able to determine the true stresses on overstressed bonds which were found to be $[\sigma_{max} = (\Delta\nu_{max}/a)]$: 1070 kg/mm² for polypropylene, 2000 kg/mm² for polycaproamide and 2000 kg/mm² for polyethyleneterephthalate. It is important to note that the values obtained lie close to the theoretical rupture stresses for C–C bonds in these polymers; however, as will be shown later, the former are not equal to the latter, but are smaller.

Since the deformed shape of the absorption band reflects the non-uniform stress distribution over bonds we are able to deduce this distribution. Assuming that the shape of the absorption band for single bonds does not depend on stress, we may decompose any complicated band shape into its components. The maximum of every component will be shifted by a value proportional to the true stress on the bond.

Thus the task of finding the bond distribution by stresses comes to solving the following integral equation.

$$D(\nu_1) = \int_{\nu_1-\nu_2}^{\nu_1+\nu_3} f(\sigma)\phi(\nu-\nu_1)d\nu$$

where ν_1 is the frequency at which the absorption is measured $\phi(\nu-\nu_1)$ – the shape of absorption band for the atomic bond, ν_2 and ν_3 – points where $\phi = 0$, and $f(\sigma)$ – the unknown stress distribution over bonds.

The solution of this equation, i.e. the stress distribution over bonds, is given in Fig. 3 for polypropylene under a load of 70 kg/mm². It is seen that about 50% of bonds are stressed uniformly. The rest of them are subjected to a considerably stronger and non-uniform stress, the maximum stress on bonds being 1000 kg/mm², i.e. over ten times more than the average stress in a specimen.

Similar non-uniform stress distribution over bonds proved to be characteristic of two other polymers, also the shape of absorption bands for polyethyleneterephthalate, and polycaproamide (Nylon 6) demonstrate the same non-uniform stress distribution, and again the value of the stress in some bonds were many times greater than the average stress in a specimen.

The above results on the maximum stresses on bonds and the stress distribution over bonds cannot be claimed to be exact. Nevertheless, they do indicate the existence of strongly overstressed bonds and a significant heterogeneity in the stress distribution over the bonds.

Discussion

Heavily overstressed bonds in a stressed polymer, discovered by infrared spectroscopy, are expected to play an important part in the fracture mechanism of polymers.

Due to non-uniform stress distribution over bonds, their rupture does not occur simultaneously. Heavily overstressed bonds are expected to be ruptured in the first instance. When they break, the stress they were carrying must be borne by neighbouring, unbroken bonds. This provokes a time dependent redistribution of stresses over bonds. The redistribution of stresses, in its turn, will change the shape of the absorption band.

Figure 4 shows an absorption band 975 cm^{-1} in the spectrum of polypropylene immediately upon stressing and again after 1 hour at a stress of 42 kg/mm^2. The shape of the absorption band has significantly changed in the course of time indicating a redistribution of stress over bonds. While the absorption in the zone hatched with horizontal lines, corresponding to slightly stressed bonds at 200-400 kg/mm^2 decreases, that in the zone hatched with vertical lines, corresponding to strongly stressed bonds at 600-1000 kg/mm^2, increases. In other words, the number of heavily stressed bonds grow, with time, at the expense of lightly stressed bonds.

In accordance with the kinetic concept of the fracture of solids, the relationship revealed between the lifetime τ, the tensile stress σ and temperature T, can be written in the form of the following equation:

$$\tau = \tau_0 e^{(u_0 - \gamma\sigma)/kT} \tag{2}$$

where τ_0 is the time corresponding, in order of magnitude, to the period of fluctuation in the atomic binding, u_0 is the binding energy, and k, Boltzman's constant.

The coefficient γ involved in equation (2) depends on polymer structure and determines the polymer strength. This coefficient, as follows from the kinetic mechanism of fracture, is a measure of the overstress on bonds being ruptured. Its value is found to be

$$\gamma = \frac{\sigma_{rup}}{\sigma_{appl}} \tag{3}$$

where σ_{rup} is the stress on bonds being ruptured, σ_{appl} the average stress in a specimen, and γ_0, the elementary volume.

We have compared the coefficient γ, determined from mechanical tests by equation (2), with γ, obtained from spectroscopic measurements of the value σ_{max} by equation (3). The results of this comparison have shown that the values obtained by both methods coincide. This means that the spectroscopic value σ_{max} is equal to the true stress on bonds being ruptured.

If σ_{max} is really equal to the strength of a bond being ruptured, two alternative cases are possible:

1. The bond is ruptured only by the stress σ_{max}. In that case the process will be athermic, and the maximum stress on bonds will not depend on temperature.

2. The bond rupture is dependent on both σ_{max} and the thermal motion energy. In that case, the rupture stress on bonds being dependent on temperature, there will be a thermofluctuation rupture.

To determine which of these is correct, the temperature dependence of the maximum stress on bonds being ruptured was studied. The experiments were carried out on high-strength oriented films of polyethyleneterephthalate. The spectrum of the film was recorded under load, at temperatures from 100°K to 400°K. The maximum stress on the bonds being ruptured was determined by the value $\Delta\nu_{max}$. The results obtained from measurements are shown in Fig. 5. It is seen that the maximum stress on bonds decreases linearly with temperature.

Conclusion

1. The use of the infrared spectroscopy has permitted us to demonstrate the existence of overstressed bonds in stressed polymers.

2. The stresses over bonds are distributed non-uniformly and change with time under load.

3. The magnitude of the maximum stresses on bonds exceeds by more than ten times the average stress in a specimen.

4. The results obtained are quite in agreement with the kinetic conception of the mechanism of fracture.

References

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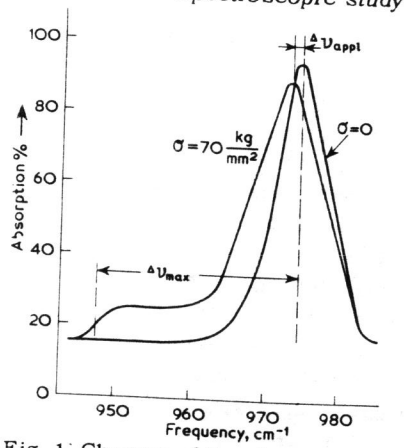

Fig. 1. Changes of the absorption band 975 cm^{-} position and chape in oriented polypropylene under load.

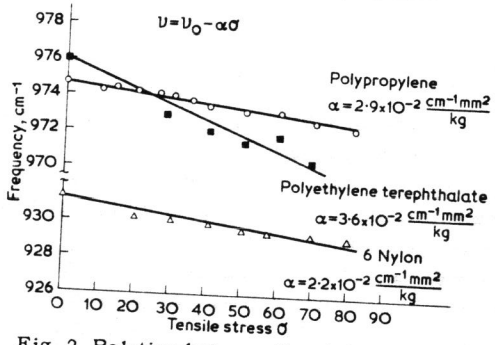

Fig. 2. Relation between the shift of the absorption band maximum and the magnitude of tensile stress.

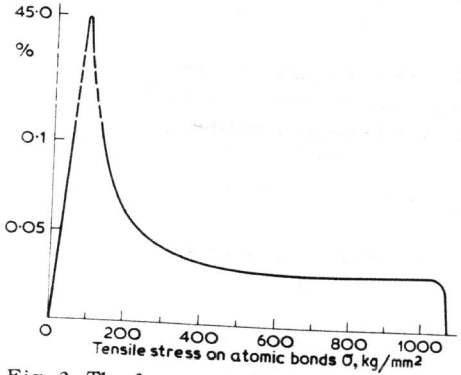

Fig. 3. The function of stress distribution over bonds.

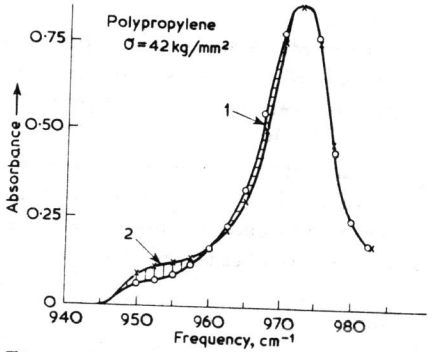

Fig. 4. Time changes of absorption band 975 cm^{-1} in polypropylene: 1. 10 sec. upon loading; 2. 1 hour upon loading.

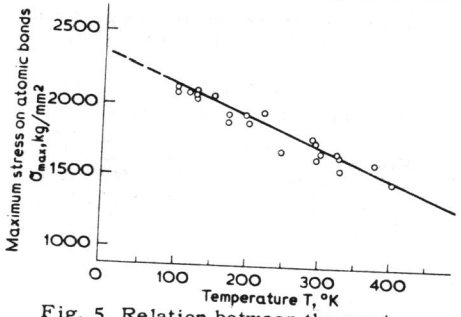

Fig. 5. Relation between the maximum stress on the atomic bonds and temperature.