DETERMINATION OF ATOMIC STRESS DISTRI-
BUTION IN ORIENTED POLYPROPYLENE
BY INFRARED SPECTROSCOPY

One of the most difficult problems in the formulation of a valid atomistic theory of the strength of solids is the description of the manner in which an externally applied load is distributed among the solid's internal chemical bonds. The assumption of uniformily distributed atomic stresses leads to predicted strengths approximately two orders of magnitude larger than actual strengths (1) and is clearly unrealistic in view of the complex morphology of real materials. This letter reports preliminary results which indicate that the actual distribution of stresses among the backbone bonds of an oriented polymer can be inferred from changes which occur in the polymer's infrared C–C stretching bands due to an applied load.

It is generally held (2) that an increase in the length of a covalent chemical bond, say due to stress, will decrease the bond's atomic force constant and lead to a corresponding decrease in the bond's infrared absorption frequency for stretching vibrations. The amount by which the absorption band is shifted to lower frequencies would be related to the magnitude of the atomic stress experienced by the chemical bonds; as such the ir shift acts as an "atomic strain gage" which can be "calibrated" with respect to the externally applied stress. For such a technique to be successful, the stress-induced shifts must obviously be large enough to measure with available ir spectrometers. For most bulk polymers this will not be the case since application of load to these materials generally causes failure at some region of stress concentration while the vast majority of chemical bonds experience only very low atomic stresses (3). Infrared shifts will be strongest in those polymers which are able to distribute their atomic stresses most nearly uniformly, i.e., in crystalline, highly oriented fibers or films.

We have subjected a highly oriented drawn polypropylene film to various constant loads while holding the film in the beam of a Beckman IR-11 infrared spectrophotometer. The tests were done at room temperature with no humidity control and with no consideration of time effects. The spectrum was generally recorded within approximately thirty seconds after a stepwise increase of the applied load. Although several absorption bands in polypropylene are attributable at least to some degree to C–C stretching (4), the observations reported here are confined to the strong band at 975 cm^{-1}.

Figure 1 shows the ir spectra in the 975 cm^{-1} region at zero stress and at 30 ksi (30,000 pounds per square inch). After numerical subtraction of the surrounding absorption bands, the stress-induced changes in the 975 cm^{-1} band are clearly seen in Figure 2. The position of the band's peak intensity is shifted to lower frequency by application of the stress and, in addition,
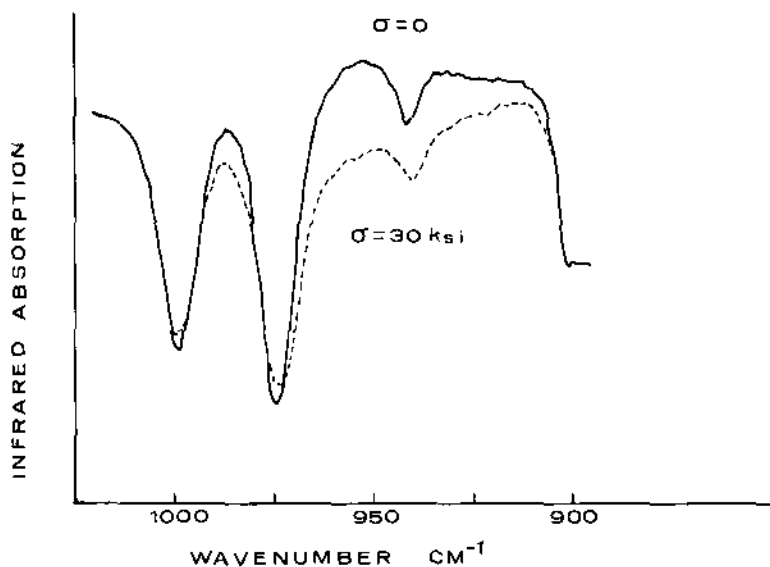
Fig. 1. Change in infrared absorption (relative units)
of oriented polypropylene with stress.

the band has developed a low-frequency "tail" extending to approximately
905 cm^{-1}. This broadened band can be interpreted by considering a large
fraction of the backbone bond population to experience atomic stresses near
the nominal 30 ksi value and to contribute to absorption at a frequency
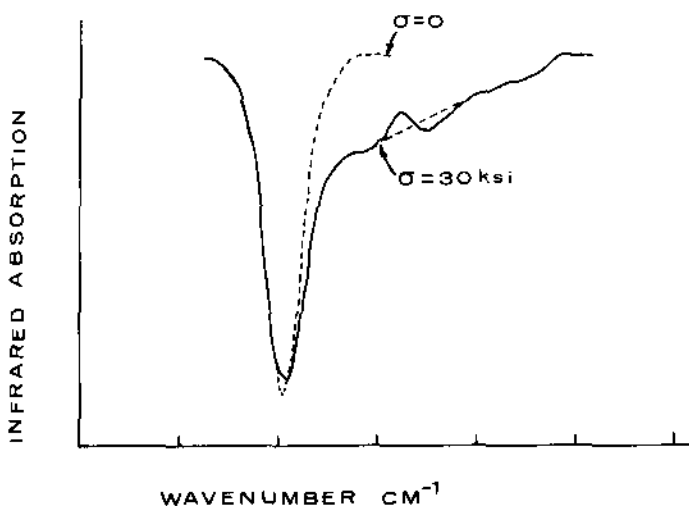slightly lower than the unstressed value while smaller but still appreciable

Fig. 2. Change in shape of infrared 974.5 cm^{-1} band due to stress.

fractions of the bond population experience atomic stresses much larger than the nominal stress and contribute to absorption at various frequencies in the "tail" depending on the magnitude of the atomic stress. The broadened 30 ksi band can than be taken as the convolution product of the undistorted (zero stress) band shape and the population distribution function over the range of frequencies.

The frequency axis can be converted to a stress axis—the "calibration" referred to above—by considering the variation of the shift of the band's peak with stress. These variables are plotted in Figure 3 and it is seen they obey
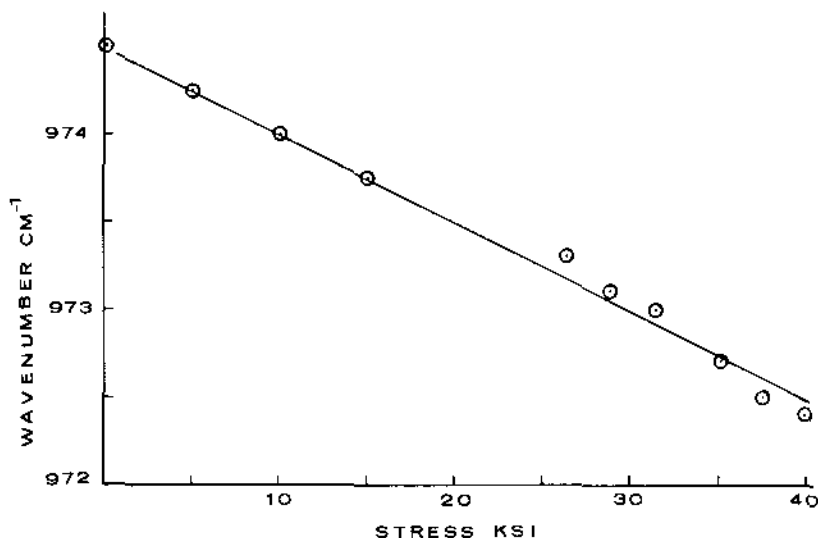

Fig. 3. Shift in the position of 974.5 cm^{-1} band of oriented polypropylene film due to stress.

a linear relationship with a proportionality constant of $\alpha = 0.05$ cm^{-1}/ksi. Extrapolating this relationship to cover the entire range of frequencies, the stress σ corresponding to a frequency ν is found by $\sigma = (\nu_0 - \nu)/\alpha$ where $\nu_0 = 974.5$ cm^{-1}. The validity of this extrapolation can be justified at least in part by the theoretical observation that absorption frequency and atomic stress vary linearly for values of stress up to the theoretical bond strength (5). The bond population distribution function for 30 ksi was numerically "unfolded" from the broadened band of Figure 2 using Ergun's method of direct convolutions (6) on a small (4K) digital computer. The normalized result, plotted against stress, is shown in Figure 4. (In this plot the percentage of backbone bonds experiencing a stress in the interval $a \leq \alpha \leq b$ is just the integral of the curve from a to b.)
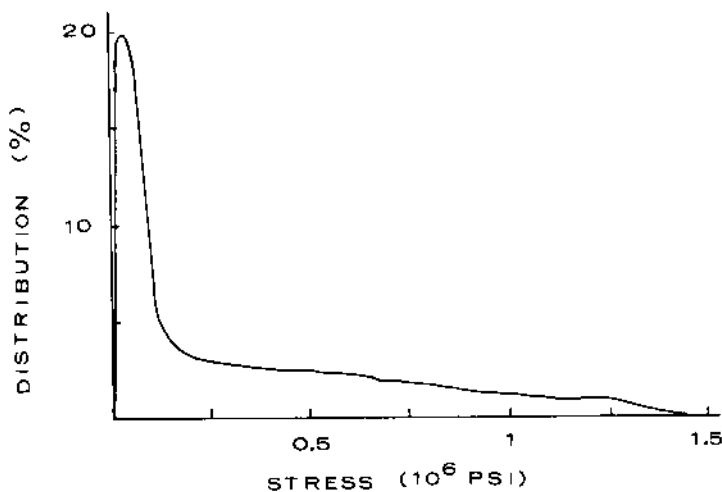
Fig. 4. Distribution function versus "bond stress"
for oriented polypropylene film.

Although the calibration procedure above is not truly rigorous and the stress axis may be telescoped one way or the other, the numerical values obtained suggest that the solution is fundamentally valid: the maximum bond stress at 1.4 million psi is very near the theoretical atomic strength of polypropylene (1); the maximum bond stress concentration factor $\sigma_{max}/\sigma_{nominal}$ is near fifty which is in the 10 to 100 range predicted by Peterlin (7) on the basis of morphology and mechanical studies. This same stress concentration factor is also found in electron paramagnetic resonance studies of bond rupture in oriented polymers (8).

We feel that many of the unique mechanical properties of this particular polypropylene film (to be reported separately) may be due to this material having a morphology which produces an unusually broad distribution of stresses over the bond population. By comparison, a stress distribution obtained by Zhurkov (9) for polypropylene averaged only 0.03 per cent in the high-stress wing. The stress distribution function may well be a fundamental measure of the relation between the morphology and the mechanical response of a polymer. It should be informative to monitor the distribution as a function of various processing, structural, and property parameters as well as the temperature and time history of the loading. But perhaps most important, the stress distribution provides a valuable input to new atomistic models of polymer fracture which are presently under development (8,10,11).

References

(1) K. E. Perepelkin, Mekh. Polim., $\underline{2}$, 845 (1966).

(2) H. J. Bernstein, Spectroclinnica Acta., $\underline{18}$, 161 (1962).

(3) D. K. Roylance, unpublished Ph. D. dissertation, University of Utah, Salt Lake City, Utah, 1968.

(4) Miyazawa, J. Poly. Sci., C, 7, 59 (1964).

(5) A. Gubanov, Mekh. Polim., $\underline{3}$, 771 (1967).

(6) S. Engun, J. Appl. Crystal., $\underline{1}$, 19 (1968).

(7) A. Peterlin, J. Polymer Sci., A-2, $\underline{7}$, 1160 (1969).

(8) B. A. Lloyd, unpublished Ph. D. dissertation, University of Utah, Salt Lake City, Utah, 1971.

(9) S. N. Zhurkov, et al., Fracture 1969, 531 (1969).

(10) K. L. DeVries and R. J. Farris, Internat. J. Fracture Mechanics,

(11) H. H. Kausch-Blecken von Schmeling, J. Macromol. Sci.—Revs. Macromol. Chem., $\underline{C}$4, 243 (1970).

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