

molding. At molding pressures above 1000 atm, the number of defects increases again, owing to the formation of high-energy domains consisting of chain conformations which were thermodynamically favorable under the vitrification conditions but are unstable at room conditions. Some of these high-energy structures relax rapidly upon release of the molding pressure to form regions of high local void volume. However, some high-energy structures are constrained by the surrounding compacted polymer matrix and undergo a much slower subsequent relaxation. The decay of such high-energy structural domains is markedly accelerated by heating, straining, or plasticizing the glassy polymer, which results in the faster or greater relaxation phenomena observed in the various methods of testing; i.e., the accelerated decay constitutes an additional relaxation mechanism.

The results suggest that an optimum molding pressure may exist for polystyrene around 1000 atm or somewhat lower. This is not far above the pressures a modern commercial extruder is capable of developing. Below this limit, the effect of higher molding pressure is to reduce the number of microvoid defects and to produce a more compact polymer with stronger interchain cohesion. This is reflected in a higher modulus, higher yield strength, and lower gas permeability.

CONCLUSIONS

Polystyrene samples molded at pressures in the kilobar range have been found to show (1) a lower mechanical damping factor, due to a loss of independent segmental mobility; (2) higher elastic modulus in simple compression, due to more extensive interchain cohesion; (3) a maximum in compressive yield stress at a molding pressure around 1000 atm; (4) lower strain at yield, which was found to be almost entirely in the "plastic strain" component, and faster relaxation at yield; (5) an exothermic relaxation accompanied by volume dilation, which starts at some temperature below T_g and continues through the glass transition; and (6) faster relaxation in methyl ethyl ketone vapor, leading to more rapid rates of sorption of vapor.

These results indicate that moderately high molding pressures cause a rearrangement of segmental structure involving compaction of the polymer matrix. This produces samples with higher strength, higher modulus, and lower gas permeability. At higher molding pressures, microstructural defects are generated by the relaxation of high-energy conformations which are unstable at room conditions. The predominance of these defects and high-energy conformations results in a loss of strength and faster relaxation in the presence of solvent, heat, or strain. The existence of an optimum molding pressure for polystyrene is thus indicated to be somewhat below 1000 atm.

The marked improvement in polymer properties resulting from sample preparation using molding pressures greater than those achieved by more conventional molding processes suggest that these higher-pressure molding

procedures may be useful for obtaining polymer materials with modified properties required for more exacting applications. It is anticipated that polymers other than polystyrene, which are more sensitive to pressure compaction,^{2,3} may show even greater changes in properties when molded under suitably high pressures.

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