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Dynamic Birefringence of Amorphous Polymers

Kunihiro Osaki, Hiroshi Watanabe, Tadashi Inoue, Hirotaka Okamoto

The birefringence in oscillatory deformation is related to the viscoelasticity through the stress-optical rule (SOR) in the rubbery and the terminal flow zones. The deviation from the SOR in the glassy and the glass-to-rubber transition zones can be described with a modified SOR, based on the assumption that the stress is a sum of two components associated with respective stress-optical coefficients.

Keywords: Dynamic birefringence/ Glass-to-rubber transition/ Stress-optical rule/ Polymer rheology

When a strain is applied to a polymeric material, the refractive index becomes anisotropic, i.e., the material becomes birefringent. The birefringence is deeply related with the stress and can be used in the studies of relaxation process of polymeric materials. Although its strong relation to the stress may mean that it does not give much additional information, the relation reveals specific features which cannot be studied by other methods such as the dielectric relaxation.

In the rubbery plateau zone or in the terminal flow zone of polymers, the deviatoric component of the refractive index tensor is proportional to that of the stress tensor. This relation, called the stress-optical rule (SOR), has extensively been employed in rheological studies of polymeric liquids in steady flow as well as in non-steady flow. The ratio of the birefringence to the stress is called the stress-optical coefficient. This is essentially determined by the polymer structure and is rather insensitive to the temperature, the solvent species, or the polymer concentration. The stress-optical rule is interpreted in terms of the deformation of Gauss segments for flexible polymers.

For polymers in the glassy zone or for crystalline polymers, the birefringence is proportional to the applied stress when the stress is varied. This relation is known as the photoelasticity (PE). The photoelastic coefficient is usually different from the stress-optical coefficient defined in the rubbery and terminal flow zones. It follows that the birefringence is not proportional to the stress in the process of the stress relaxation over the glassy and glass-to-rubber transition zones. Thus, the relaxation of birefringence at low temperatures or at the short times can be an interesting subject similar to the stress relaxation or the linear viscoelasticity.

In order to study the relaxation of the birefringence around the glass transition zone, an apparatus was built to measure the birefringence under oscillatory deformation as a function of frequency of deformation and temperature [1]. This apparatus can measure the dynamic viscoelasticity simultaneously.

The dynamic birefringence, frequency dependence of the birefringence, and the viscoelasticity around the glass transition zone have been measured for a number of polymers by our group [1-8]. These results show that...
the behavior of birefringence and stress of amorphous polymers can be separated into three groups [9].

Type I: Polystyrene [1], bisphenol A polycarbonate [2], some engineering plastics [3], amorphous polyolefin [5] and polyisoprene [7] form a group (Type I). In this group, a modified stress-optical rule (MSOR) holds well between birefringence and stress: The relaxation spectra of the two quantities can be decomposed into two component functions (R and G). The SOR holds well for each component individually. The two components can be determined by a simultaneous measurement of stress and birefringence. In the rubbery plateau and terminal flow zones, the G component has relaxed, and therefore the stress is supported by the R component. Molecular origin of the R component can be interpreted as the orientation of the statistical segments of the chain. In the glassy zone, the stress is mainly originated by the G component. The G components of various polymers have many similarities with each other and with other glass-forming materials like o-terphenyl and dibutyl phthalate.

Type II and III: It is expected that the MSOR fails for polymers that exhibit \(T\)-relaxation of viscoelasticity due to the side chain motion in the frequency range close to the main chain dispersion. This is the case with polymethacrylates. The birefringence as well as viscoelasticity is complicated in the glassy zone. On the other hand, the MSOR was found to fail for a few polymers for which no extra viscoelastic relaxation has been reported in the range close to the main chain dispersion. Examples are poly(2-vinyl naphthalene) (PVN) [6] and polyisobutylene (PIB) [8]. For the case of PVN (we call type II polymer), the behavior is markedly different from that of type I polymers only in the glassy zone; in the transition zone the behavior is similar to that of type I. For PIB which we call type III the difference is not limited to the glassy zone. A power law dependence of the loss modulus was observed over about three decades of frequency range just below the maximum of the loss modulus. A tendency similar to that of PIB, the failure of MSOR and a power law dependence of modulus in the transition zone, was observed for an ethylene-propylene rubber.

The obtained experimental results can be interpreted by using a simple molecular model [8, 9]. The polymer is supposed to be composed of identical units that do not change the shape over the time scale to be investigated. The polymer can change its shape by rotating the unit about the connecting bond with fixed angle (freely rotating chain). The birefringence due to the deformation can be written as a sum of two contributions, which can be derived from respective orientation functions describing the orientation of the unit along and about the connecting bond. The stress also can be described in the form similar to the birefringence by using the above two orientation functions and the time-averaged local stress tensor for each unit. However, in the expression for the stress, one additional term exists. This term is due to the fluctuation of local stress tensor which disappears in short time region. For such a case the MSOR holds well because both the stress and birefringence can be written as a linear combination of the two orientation functions. The failure of MSOR found in type II polymers can be attributed to the larger fluctuation term in the stress expression probably due to the large side chains. Anomalous frequency dependence found in type III polymer suggests the stronger intra-chain correlation in the rotation of the unit about the main chain [8].

Around the glass transition temperature, amorphous polymers show remarkable nonlinear viscoelasticity. The MSOR was applied for this subject and it is shown that these nonlinear viscoelasticity can be attributed to the nonlinearity of the G component [10]. Other interesting features of the glassy polymers like physical ageing are under progress.

References