



MODIFICATION OF MOLECULAR STRESS FUNCTION (MSF) THEORY TO PREDICT THE EXTENSIONAL VISCOSITY OF AUTOCLAVE LDPEs

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Doi-Edwards (DE) theory based on the tube concept is a successful model to describe viscoelastic properties of monodisperse linear polymers. The original DE constitutive equation assumes no chain stretch therefore no strain hardening is predicted in extensional flows. To overcome this problem Wagner et. al [J. Rheol. 45 (2001) 1387-1412] assumed that the tube diameter is not constant and the tube segments stretch during the deformation. They introduce the molecular stress function (MSF) f , into the DE constitutive equation, where f is calculated from an evolution equation with respect to the strain energy function and virtual work concepts. The last version of MSF theory [J. Rheol. 47 (2003) 779-793] for long chain branched polymers is based on specific strain energy function which considers both backbone stretching and side chain compression. This theory has two non-linear parameters β and f_{max} in irrotational flows where β represents the ratio of molar mass of the branched polymer chain to the molar mass of the backbone and f_{max} is related to the maximum stretch of polymer chain. Our studies shows that this model cannot predict quantitatively extensional viscosity of some more complex structures of LDPEs in extensional flows; therefore we modified the strain energy function based on different backbone and side chain stretching and make more agreements between experimental extensional viscosity data and model predictions. A correlation between molecular structures and β parameter of two laboratory-scaled autoclave LDPEs, published by Stadler et al. [Rheol. Acta 48 (2009) 479-490], was investigated. A combined Comb-like and Caley tree structures are proposed for these complex LDPEs.