The effect of thermal oxidative degradation of polymers on their viscoelastic response

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Abstract

A model is developed for thermal oxidative degradation of polymer melts and its effect on their viscoelastic response. Based on the theory of temporary heterogeneous networks, stress–strain relations are derived for the time-dependent behavior of a polymer melt at arbitrary three-dimensional deformations with small strains. Within the fragmentation–annihilation concept, kinetic equation is proposed for the distribution of strands with various lengths in a network, and its explicit solution is obtained. Material parameters in the constitutive equations are found by fitting experimental data in shear oscillation tests on a polypropylene melt annealed at elevated temperatures for various times. Good agreement is demonstrated between the observations and the results of numerical simulation.
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1. Introduction

This paper is concerned with the effect of thermal and thermo-oxidative degradation of polymer melts on their linear viscoelastic response at small strains. Thermal oxidative degradation of polymers and polymer nanocomposites has been a focus of attention in the past decade due to the following reasons:

1. An adequate description of the kinetics of thermal oxidative degradation is of primary importance to predict physical properties of reprocessed industrial and post-consumer plastic wastes [1].
2. Degradation of polymers induces noticeable changes in the distribution of their molecular weights [2], which means that observations on the time-dependent response of melts annealed for various times t_a at various temperatures T_a allow correlations to be established between their molecular structure and mechanical properties.

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3. Thermogravimetric analysis reveals a strong decay in the rates of thermal and thermo-oxidative degradation and a substantial improvement of stability of polymers due to their reinforcement with nanofillers [3], which opens novel areas of applications of hybrid nanocomposites as fire-resistant materials.

Although the importance of investigation of thermal and thermo-oxidative degradation of polymers for the fundamental research and applications is obvious, our knowledge of the physics of these processes at the micro-level and ability to predict degradation-induced changes in the mechanical response are rather limited. This may be attributed to the lack of constitutive models to describe changes in the mechanical response caused by evolution of a polymer network (induced by its degradation).

Our experimental investigation of thermo-oxidative degradation follows the conventional approach:

- This study concentrates on the mechanical response of polymer melts subjected to annealing at elevated temperatures. This allows complications to be avoided caused by crystallization of semicrystalline polymers and vitrification of polymer glasses.
- We confine ourselves to the time-dependent behavior at small strains and report observations in standard shear oscillation tests, where the storage G' and loss G'' moduli are measured as functions of frequency of oscillations ω.
- Isotactic polypropylene (iPP) is employed for the analysis, because the kinetics of thermal and thermo-oxidative degradation of polypropylene has recently been studied in a number of publications [4–7].

Our treatment of experimental data, however, differs substantially from the traditional analysis. Within the standard approach, the experimental dependencies $G'(\omega)$ and $G''(\omega)$ are used to find molecular weight of a melt. For this purpose, (i) the storage and loss moduli are replaced with the complex viscosity

$$\eta(\omega) = \frac{1}{\omega}[(G'(\omega))^2 + (G''(\omega))^2]^{1/2}, \tag{1}$$

(ii) the experimental dependence $\eta(\omega)$ is approximated by some phenomenological model which allows the zero-frequency complex viscosity $\eta(0)$ to be predicted, and (iii) the viscosity $\eta(0)$ is linked with mass-average molecular weight M_w by means of the phenomenological relation [8]

$$\eta(0) = KM_w^\alpha, \tag{2}$$

where K and α are adjustable parameters, and the exponent α is assumed to belong to the interval between 3.2 and 3.6.

Two shortcomings of this procedure are to be mentioned:

1. Calculation of the zero-frequency complex viscosity is performed by means of a model that involves several material constants. For example, the Cross equation, widely used in applications,

$$\eta(\omega) = \eta(\infty) + \frac{\eta(0) - \eta(\infty)}{1 + (\tau\omega)^\beta},$$

contains four material constants $\eta(0)$, $\eta(\infty)$, β and τ. This implies that $\eta(0)$ is found with a relatively low accuracy.
2. Applicability of Eq. (2) is rather limited for two reasons: (i) observations on polyolefins with known molecular weight distributions [9–11] demonstrate large deviations of the exponent α from its classical value 3.4, and (ii) generalizations of Eq. (2) that account for the effects of polydispersity and chain branching ([12,13] and the references therein) do not permit mass-average molecular weight to be found uniquely from observations.

The most important disadvantage of the conventional technique is that even when the kinetics of degradation is determined by fitting the dependencies of M_w on annealing time t_a [re-calculated by means of Eq. (2)], this approach does not provide a way to describe degradation-induced evolution of the mechanical behavior, because the function $M_w(t_a)$ is insufficient to predict the moduli $G'(\omega)$ and $G''(\omega)$.