Correlation between interfacial interactions and internal stresses in filled high density polyethylene

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Abstract: The stress relaxation and the creep behaviour of high density polyethylene (HDPE) filled with glass fibres, clay (plate-like particles) or CaCO₃ (particles with irregular shape) were measured in uniaxial extension at room temperature. It was observed that the addition of filler increased the internal stress level, as evaluated from stress relaxation data. This increase was larger than the corresponding increase in the (short-term) elastic modulus. This behaviour may be attributed to a reduced macromolecular mobility in the matrix material close to the filler surface, i.e. to formation of an interphase region in the HDPE-matrix. From the internal stress values, the thickness of this interphase region around each filler particle was estimated, assuming a uniform coverage of the particles. It was suggested that the amount of matrix material with reduced mobility (or the thickness of the interphase region) reflected the degree of adhesion between the filler and HDPE. The change in the internal stress level due to the incorporation of different fillers, which were surface treated in some cases, was also consistent with the observed creep behaviour.

Key words: Interface, polyethylene, inorganic filler, stress relaxation, creep

1. Introduction

The time-dependent mechanical properties, such as stress relaxation and creep, of filled and reinforced polymers have, due to the technical importance of these materials, attracted increasing interest during recent years [1–5]. Despite the apparent physical differences between the stress relaxation and creep processes an important feature is that the behaviour of both processes depends on the internal stress level $\sigma_i$ of the material, which can be evaluated from stress relaxation data.

A stress relaxation curve usually has a sigmoid shape and in most cases, for both polymers and metals at room temperature, the stress at longer times often approaches asymptotically a certain non-zero value, i.e. the internal stress level $\sigma_i$. For many materials the internal stress increases with initial strain $\varepsilon_0$ (or initial stress $\sigma_{0i}$) of the experiment [6–8]; it may be identified with the load bearing capability of a material at longer times. The creep behaviour of a material is related to the internal stress, since the strain rate depends on the effective stress $\sigma^* = \sigma - \sigma_i$, i.e. the difference between the applied stress and the internal stress [9–10]. An increasing internal stress is in fact responsible for the diminishing creep rate as a creep experiment proceeds.

When studying the mechanical behaviour of filled polymers, it is recognized that the nature of the interface between polymer and filler could be of primary importance. Chemical and physical interactions at the interface can be responsible for the occurrence of an interphase region close to the filler surface [11–16]. Having different properties from the remaining matrix, the interphase region can clearly affect the mechanical properties of the composite.

In an earlier work [17] dealing with the viscoelastic properties of HDPE-CaCO₃ composites there were indications that the internal stress was influenced not only by the properties of the matrix and the filler content but also by interactions at the interface. The importance of these interactions, with regard to the properties of the composite, constitute an important area of current research. It was furthermore concluded in the above work that the effect of these interactions became more pronounced at longer loading times, at higher strain levels and at higher filler concentrations [17]. If the contributions to the internal stress level from the matrix and the filler can be
determined, then that part of the internal stress associated with the situation at the interface can be evaluated and could possibly be used for characterizing interfacial interactions with regard to long-term mechanical properties. It is this concept that underlies the work presented in this paper. From previous dynamic-mechanical analyses of certain filled polymers it was concluded that close to the filler surface an interphase region does exist [14, 17, 18]. It is of interest to investigate whether the internal stress concept can be used to estimate the extension of this interphase region, which in some cases can be associated with the degree of adhesion between the two phases.

A primary aim of this paper is to investigate the influence of different rigid inorganic fillers on the internal stress level, determined from stress relaxation experiments in high density polyethylene (HDPE). Fillers tested were glass fibres, clay and CaCO₃; i.e. 1-3 dimensional fillers, respectively. The results show that of these, glass fibres, clay and CaCO₃ improve both the short- and long term mechanical behaviour most efficiently although clay in HDPE also gives an improved long term behaviour (almost as good as for the glass fibre composite). It was observed that the filler addition increased the internal stress to a greater level than that predicted from the increase in elastic modulus. The additional increase depended on the composition of the composite and is suggested to be associated with a decrease in the mobility of the macromolecules close to the filler surface [17]. By accounting for the variation of the internal stress level with strain and filler content a good prediction of the creep behaviour of the filled HDPE was obtained.

Another aim of this work was to investigate the effects of surface treated filler particles on the creep and stress relaxation behaviour. The glass fibres and the clay platelets were treated with silanes and the CaCO₃-particles with maleated polypropylene wax. A considerable problem when evaluating surface modifying agents is to quantify how they affect the corresponding interfacial interactions. As mentioned above, the internal stress concept appears to provide this tool. The surface treatments of CaCO₃ and the glass fibres did increase the internal stress level and reduced correspondingly the creep rate of the composites. These improvements are, however, less pronounced than those reported in [19] where covalent bonding between HDPE and glass spheres was accomplished by means of an azide functional alkoxysilane. This would indicate that the improvements reported here are mainly due to an increase in interaction forces of the van der Waals type. From the increase in the internal stresses, a measure of the extension of the interphase region could be calculated, and in some cases this extension may be correlated with the degree of adhesion between the filler and the matrix.

2. Short theoretical Background

For solid polymers, it is often possible to describe the uniaxial viscoelastic behaviour with a power-type law (Hooke-Norton) [20]

\[ \dot{\varepsilon} = \dot{\varepsilon}_0 + A(\sigma - \sigma_f)^n. \]  

(1)

Here \( \varepsilon \) is the strain, \( E \) the elastic modulus, and \( A \) and \( n \) are constants. For stress relaxation eq. (1) becomes

\[ \dot{\varepsilon} = -B(\sigma - \sigma_f)^n. \]  

(2)

where \( B = A E \) is constant. It has been shown earlier [21] that the power-law eq. (2) provides a reasonable description of the relaxation behaviour of HDPE at room temperature. It should be mentioned that a combination of an exponential law at shorter times and the power law at longer times provides a better description [6]. The counterpart of eq. (1) in the creep case is [20]

\[ \dot{\varepsilon} = A(\sigma - \sigma_f)^n. \]  

(3)

From eqs. (2) and (3) it is evident that \( \sigma_f \) is an important factor when describing flow in solids. A \( \sigma_f \)-level increasing with strain [6-8] gives, for stress relaxation, a higher load bearing capability and a lower stress rate in experiments with higher strain (or stress) levels, cf. eq. (2). For creep, eq. (3), the variation of \( \sigma_f \) with strain can be responsible for both the primary and secondary creep stages, and a stress lower than or equal to the internal stress level will result in a ceasing creep process. It is possible to predict the creep behaviour from stress relaxation data using the internal stress concept. The influence of the internal stress on primary and secondary creep and the interconversion from stress relaxation to creep is discussed in more detail in [21].

3. Experimental

3.1 Materials

The high density polyethylene used in this study was Lupolen 6031 M (BASF) with a density of 0.962-0.966 g/cm³ and melt flow index 8 g/10 min (MFI190/2.16).

The fillers and fibres used were:

- CaCO₃, Omyalite 90 (Plüss-Staufer) with a density of 2.7 g/cm³, and an average particle size of 1 µm. 90% of the particles were smaller than 2 µm. The BET surface area (from \( N_2 \) adsorption) was 10 m²/g.
- Polestar 200 R calcined clay and Polarite 103 A vinyl silane coated calcined clay (ECC-International) with a density of 2.6 g/cm³ and a BET surface area of 8.5 m²/g. 55-60% of the particles were smaller than 2 µm.
- Glass fibre, FR 1395 (Scandinavian Glassfibre), with a fibre length of 3 mm, a diameter of 10 µm, and a density of 2.55 g/cm³.

All filler and fibre contents given below are volume percentages.