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Linear viscoelastic behavior of poly(ethylene terephtalate) above T_g amorphous viscoelastic properties Vs crystallinity: Experimental and micromechanical modeling

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ABSTRACT

Linear viscoelastic behavior of amorphous and semicrystalline poly(ethylene terephtalate), (PET), was experimentally investigated. PET's samples with different crystallinities (Xc) were prepared and viscoelastically characterized. Based on our experimental results (properties of the amorphous PET and semicrystalline polymers), micromechanical model was used to, first predict the viscoelastic properties of the semicrystalline polymers and second predict the changes on the viscoelastic properties of the amorphous phase when the crystallinity increases. For the micromechanical modeling of semicrystalline material's viscoelastic properties, difficulties lie on the used numerical methods (Laplace-Carson transformation) and also on the actual physical and mechanical properties of the amorphous phase. In this paper we tried to simplify the Laplace-Carson-based method by using a pseudo-elastic one that avoids the numerical difficulties encountered before. The time-dependant problem is so replaced by a frequency-dependant set of elastic equations. Good agreement with low crystallinity fraction was found however large discrepancies appear for medium and high crystallinity. The poor agreement raises the issue of which amorphous mechanical properties should be taken as input in the micromechanical model? According to the dynamic mechanical analysis (DMA) experimental data, multiple amorphous phases with different glass transition temperatures were observed for each tested semicrystalline sample. For each sample, new glass transition temperature related to an equivalent amorphous phase was determined. DMA tests done at 1 Hz help estimating the mechanical properties of the new amorphous phase based on its new glass transition temperature. Using the new micromechanical approach developed in this paper, the changes occurring on the viscoelastic behavior of the amorphous phase upon crystallization were estimated. Good agreement was found after comparing the micromechanically estimated amorphous behavior with the experimentally estimated one leading to believe that the physical and mechanical properties of the amorphous phase change upon crystallization and taking on account this phenomenon is a key to a good prediction of the semicrystalline behavior using micromechanical models.

1. Introduction

Polymer materials are increasingly used in industrial parts. It is true for both, semicrystalline and amorphous polymers which are widely used as structural materials in critical functions. These new applications make, technologically and academically, mandatory to understand their behavior under complex conditions (chemical environment, stress field… etc.). Monitoring the behavior of these materials *in-situ* and *ex-situ*, to investigate the different mechanisms at different length scales should help building robust behavior laws that could be used in dimensioning new structures using polymer materials. A multiscale description of the structure, i.e., a representation of the structure and morphology at several length scales (from micro-scale down to nano-scale), is the currently favored approach. However, valid prediction of the materials properties by any of the current models requires precise description of the relevant structural parameters. Focus should be beyond standard microstructural characterization in term of phase fraction, mechanical measurements and computational modeling. More interest should be attached on the interconnection of the constituent phases and how that could affect their respective physical and/or mechanical properties.

Micromechanical models were thoroughly used to predict mechanical properties of semicrystalline polymers (plastic behavior) [1–9]. Recently the prediction of the elastic behavior was subject to

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an intense interest either to estimate macroscopic properties [9–14] or try to shed some light on some paradoxes behavior in polyolefin polymers (polyethylene and polypropylene) [15]. However difficulties on applying micromechanics to predict viscoelastic behavior of semicrystalline polymer still not overcome. In previous work both amorphous and semicrystalline PET were characterized [12,16]. X-ray data allowed the determination of the shape ratio of crystalline phase. Different micromechanical models were used to estimate the viscoelastic behavior of the semicrystalline polymer [16]. For low crystallinity, good agreement was found however large discrepancy was found for higher crystalline fraction. The discrepancy modeling/experiment was attributed to the possible effect of confinement of the amorphous phase due to the presence of the crystalline phase. In a recent paper dealing with elastic behavior of PET, an inter-phase with different mechanical properties was introduced to help predict the macroscopic mechanical properties of the semicrystalline polymers. This new inter-phase was justified based on previous work [17] assuming a possible change that could affect the mechanical properties of the PET's amorphous phase upon crystallization. However no experimental techniques had mechanically quantified that effect.

In this paper combining viscoelastic DMA characterization and simplified viscoelastic micromechanical modeling, we tried to shed light on the effect of crystallization on the mechanical properties of the amorphous phase.

Unlike elasticity, viscoelastic behavior assumes an evolution of the mechanical properties (Young's modulus e.g.) Vs. time. This dependence could not be taken on account using standard micromechanical models. Numerical techniques were introduced to help solving this issue. For composite materials Schapery [18] proposed to use the collocation method coupled with Laplace-Carson transformation and inversion tool. In a recent study Rekik and Brenner [19] introduces a constraints collocation method to predict composite materials behavior. The same concept, based on constraints coupled with the collocation method were used for semicrystalline polymer, shows the limit of the micromechanics model to fit the viscoelastic behavior of semicrystalline polymers [16]. The numerical difficulties due to the Laplace-Carson inversion and numerical inversion coupled with suspicion of the changes that occurs on the mechanical properties of the amorphous phase makes difficult the interpretation of the results.

In this paper we, *first* focus on simplifying the numerical method by replacing the Laplace-Carson transformed problem by a frequency-dependant one based on the use of the complex modulus instead of the storage and loss ones. In other word the time-dependant problem will be replaced by a frequency one leading to easier problem where any elastic micromechanical model could be used. According to previous results [12] the differential scheme is well suited to predict the macroscopic properties of such materials. More details about the micromechanical model could be found in previous work [12,15]

Second, based on the DMA results, the changes, in term of mechanical behavior, occurring in the both amorphous and semicrystalline polymers behavior will be correlated to the prediction given by the micromechanical model. It appears that the glass transition of the amorphous phase changes upon the increase of the crystallization leading to a shift in the actual behavior of the amorphous phase (T_g and Tan(δ)). The increase of the T_g could be explained as the signature of the confinement effect. That effect was not taken on account in mechanical properties of the amorphous phase and lead to the discrepancies model-experiment in previous work [16].

2. Experiment and results

2 mm thick PET Extruded plate from ISO-SUD was used in this study. Samples were cut as rectangular stripes (easy to be used for DMA experiments) and annealed at T = 110 °C for different period of time. Three crystallinities were prepared (17, 24 and 35%). DSC run were carried out to determine the crystallinity of each sample. From the total area of the exothermic and the endothermic peaks crystallization and fusion enthalpy were determined. For crystallinity calculation purposes melting enthalpy of fully crystalline PET is $\Delta H^*_{mc} = 117.6\ J/g$ [20] along with densities of pure amorphous and crystals ($\rho_c = 1.445\ g\,cm^{-3}, \rho_c = 1.335\ g\,cm^{-3}$) [21] were used. DMA tests using a METRAVIB DMA 150 machine were conducted over four decades (0.01–100 Hz) at 90 °C to ensure being above the glass transition temperature of the amorphous phase of PET (replacing semicrystalline polymer) ($T_g \approx 80$ °C). Fig. 1 presents the DMA results for the four samples (amorphous and crystalline). Amorphous and low crystallinity sample (17%) polymers undergo a parabolic dependence of the complex modulus vs. the frequency. However for frequencies between 0.1 Hz and 10 Hz, the medium and high crystallinity samples (24 and 35%) show steep modulus shape.

To investigate this effect, temperature sweep at 1 Hz dynamic excitation experiments were conducted on the four different samples. The tan(δ) Vs. temperature presented in Fig. 2 confirms a different viscoelastic behavior between in one hand amorphous and low crystallinity (Xc = 17%) samples and on the other the hand medium and high crystallinity ones (24 and 35%).

For amorphous as for the 17% crystallinity a major peak appear around 84 °C that could be considered as the T_g temperature and a minor peak at higher temperature. For Xc = 24% and Xc = 35% the tan(δ) graph shows clearly two different peaks. Origin software [22] was used to deconvolute the peaks. Peaks are considered Gaussian. In order to perform the deconvolution operation we are supposed to introduce the baseline parameters. In our case, for all the samples, a fourth order polynomial function was used as baseline (see Fig. 3).

It appears for amorphous and low crystallinity the major peak is around 84 °C (T_g of the pure amorphous polymer) and a minor peak at 92 °C. For Xc = 24% the two peaks, almost with equal weight, are at 84 °C and 96.6 °C respectively. For the highest crystallinity, (35%) the first peak, the minor one in this case, is around 86 °C and the second one appears around 99.5 °C.

The presence of two peaks in the Tan(δ) Vs. temperature graphs could be explained as a coexistence of two amorphous phases with different glass transition temperatures [23]. In semicrystalline polymer speculation about two different amorphous phases (free and constrained) were discussed in previous papers [14,17,24]. Upon annealing above T_g, crystalline lamellae

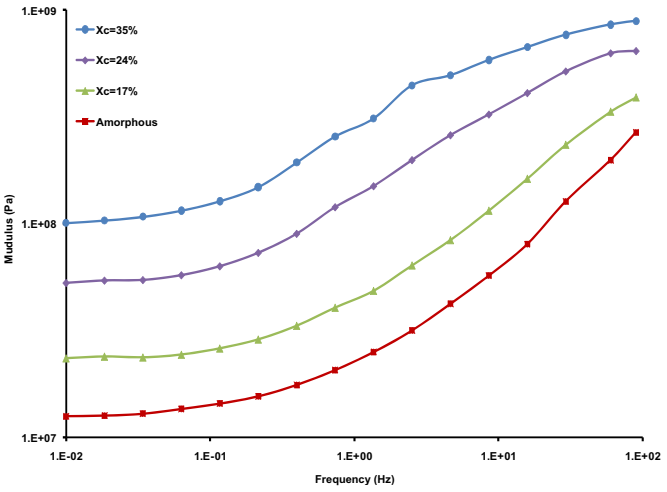

Fig. 1. DMA data for amorphous and semicrystalline polymers.