Proceedings of the SEM Annual Conference
June 7-10, 2010 Indianapolis, Indiana USA
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LINEAR VISCOELASTIC BEHAVIOR OF POLY(ETHYLENE THEREPHTALATE) ABOVE T_g

AMORPHOUS VISCO-ELASTIC PROPERTY V_S CRYSTALLINITY:

EXPERIMENTAL AND MICROMECHANICAL MODELING

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Abstract

Linear viscoelastic behavior of amorphous and semi-crystalline Poly(ethylene teraphtalate), PET, was experimentally investigated. Micromechanics models were used to predict the elastic and plastic behavior of semi-crystalline polymers successfully, however the viscoelastic behavior still difficult to be predicted with such models. Difficulties lie on the used numerical methods and also on the understanding of the properties of the amorphous phase. In this paper we tried to first simplify the Laplace Carson-based method by using a pseudo-elastic method that ovoid the numerical difficulties encountered before. The time-dependant problem is so replaced by a frequency-dependant set of elastic equations. To validate the new approach, Poly(ethylene threphtalate) (PET) with different crystallinity fraction (X_c) were prepared and characterized. Based on our experimental results (properties of the amorphous PET and semi-crystalline polymers) micromechanical model were used to first predict the viscoelastic properties of the semi-crystalline polymers and also to predict the changes on the viscoelastic properties of the amorphous phase when the crystallinity fraction increases. Good agreement between the predicted and experimental results of the low crystallinty fraction sample (X_c=17%). However for high crystallinity (Xc=24% and Xc=35%) prediction based on the identified amorphous phase as an input for the micromechanical properties failed to fit the viscoelastic behavior of the semi-crystalline polymer. Based on the dynamic mechanical analysis (DMA) experimental data, changes on the glass transition temperature of the amorphous phase were observed, which could confirm the change of the viscoelastic properties of the amorphous phase upon crystallization. This result confirms the effect of confinement due to the presence of the crystalline phase on the prediction of the viscolelastic behavior of semi-crystalline polymer using micromechanical models.

Mechanical

Keywords: Semi-crystalline polymer, Amoprhous phase, Confinement, Viscoelasticity, Micromechanical modeling.

Introduction

Micromechanics models were used for composite materials and recently for semi-crystalline polymers. Micromechanics models were thoroughly used to predict the plastic behavior of semi-crystalline polymers [1-6]. Recently the prediction of the elastic behavior was subject to an intense interest either to estimate macroscopic properties[7-10] or try to shed light on some paradoxes behavior of polyolefin

T. Proulx (ed.), *Time Dependent Constitutive Behavior and Fracture/Failure Processes, Volume 3*, Conference Proceedings of the Society for Experimental Mechanics Series 15, DOI 10.1007/978-1-4419-9794-4_5, © The Society for Experimental Mechanics, Inc. 2011

polymers [11]. However difficulties on applying micromechanics to predict viscoelastic behavior of semi-crystalline polymer still not overcome. 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 model. Numerical techniques were introduced to solve this issue. For composite materials Schapery [12] proposes to use the collocation method coupled with Laplace-Carson inversion transformation technique. In a recent study Brener et al. [13] used the collocation method constraints conditions to predict composite material behavior. The same concept on constraints coupled with the collocation method were used for semi-crystalline polymer shows the limit of the micromechanics model to fit the viscoelastic behavior of semi-crystalline polymer[14]. The confinement of the amorphous phase that was not taken on account was suspected to be the origin of the differences between the experimental data and the model prediction.

In this paper based on different approach to represent the viscoelastic properties the effect of the confinement on the mechanical properties of the amorphous phase was studied. Based on the hypothesis of the modeling the results will be correlated with the literature results.

Materials and methods

2 mm thickness PET Extruded plate from ISOSUD was used in this study. Samples were cut and annealed at T=110 ℃ for different period of time. Three crystallinty fractions were prepared (17, 24 and 35%) DSC run were carried out to determine the glass transition temperature and the crystallinity of each sample. DMA tests using a METRAVIB DMA 150 machine were carried out at 90℃. above the glass transition temperature of the amorphous PET is about 80℃. DMA experiments were carried out over four decades; from 0.01 to 100 Hz (Figure 1)

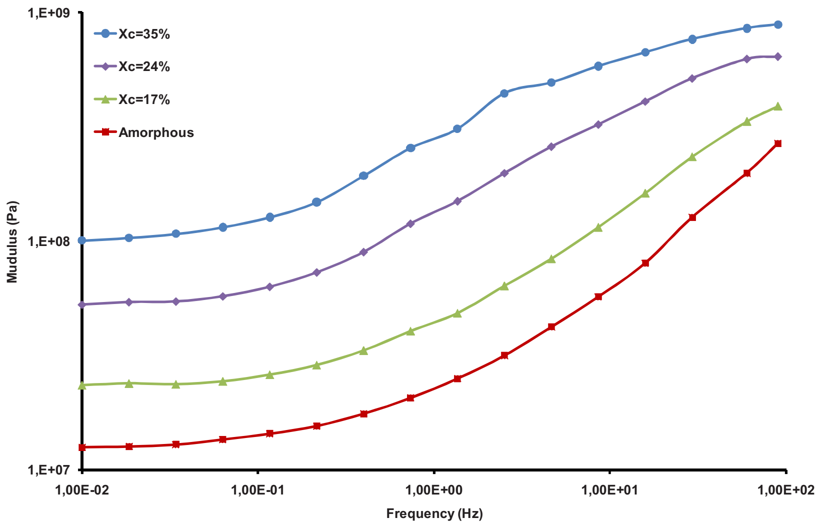

Figure 1: Dynamic modulus for amorphous and semi-crystalline polymers.

Modeling

In a previous papers [8, 11, 14] we used micromechanics models to predict elastic AND viscoelastic properties of semi-crystalline polymers (PP, PE and PET). For elasticity the differential scheme appears the well adapted to predict the elastic properties of such material. However the viscoelsatic properties prediction presents some numerical difficulties due to the collocation method. In order to overcome those difficulties caused by the use using the Laplace-Carson and the collocation method to replace the time dependant problem to pseudo-elastic one, we propose to consider as the viscoelastic properties the complex modulus E* instead of the loss and elastic ones (E' and E" respectively). Coupled with the bulk modulus derived from the PVT diagram, that we suppose constant at a chosen temperature, we replace the time dependant problem by a frequency-dependant elastic one. The new problem consists on a set of elastic equation for each considered frequency (in this study we covered four decades (0.01 to 100 Hz). As we have an elastic problem, the differential scheme will be used to predict the mechanical properties of PET for different crystallinty fractions. The crystalline phase will be considered as the filler with a shape ratio of 2-2-1. These values are the results of previous work [8, 14].

Discussions

The amorphous phase will be considered as isotropic viscoelastic (figure 1) and the crystalline phase as elastic anisotropic[8]. Applying the described procedure for the semi-crystalline polymer, an acceptable agreement between prediction and experimental data was found for the low crystalline fraction (Xc=17%) as presented in figure 2. and based on the experimental data of the amorphous phase (figure 1) and the crystalline phase

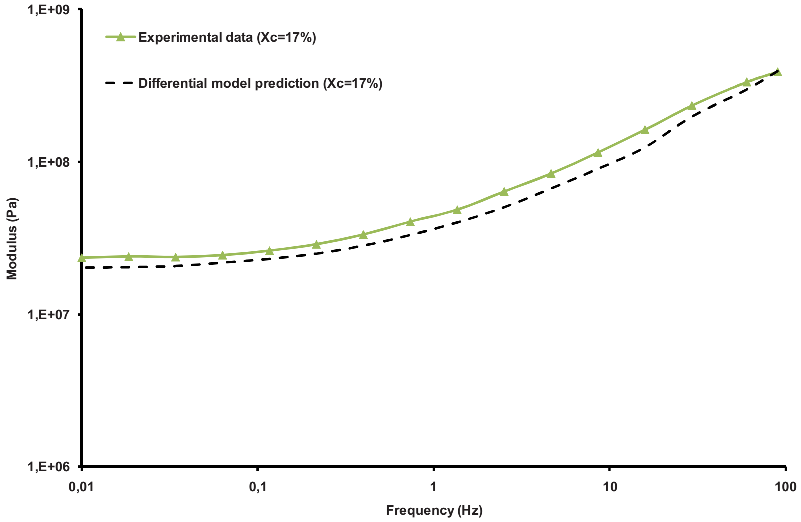

Figure 2: Viscoelastic modulus prediction for Xc=17% using differential model.

Fair predictions however were found for the higher crystalline fraction (Xc=24% and 35%). The same limitations of the modeling were encountered for PET below Tg[14] and also in the case of amorphous PET filled with glass beads. In both cases, even though the length scale is not the same, the confinement of the amorphous phase due to the presence of crystalline lamellae in the case of semi-crystalline polymers and the glass beads in the composite materials, is suspected to be at the origin of the differences between the experimental data and the model prediction. The confinement effect concept and its effect on the mechanical properties of the amorphous phase were introduced to fit the elastic properties of PET using bi-layered representation[10].

A representation of Tan(delta), representative of the glass transition of the amorphous phase, shows clearly that for high crystallinity (24% and 35 % in our case) two peaks could be considered Moreover a shift of the main peak is seen (figure 3).

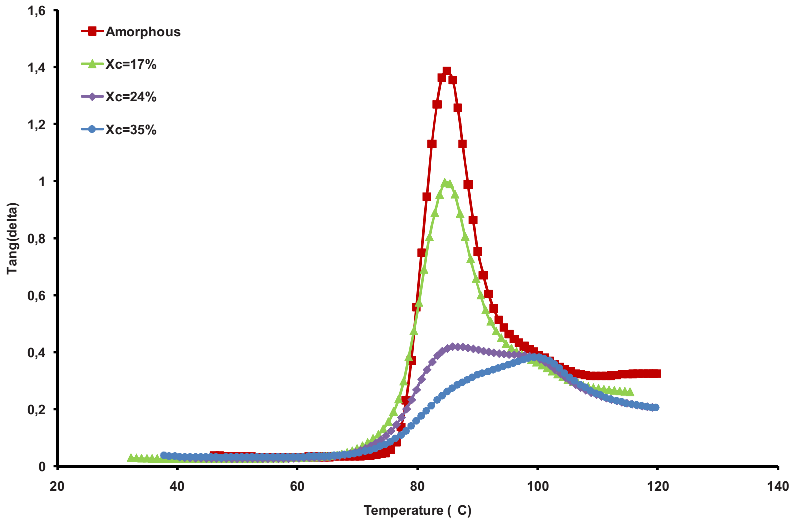

Figure 3: Tan(delta) for amorphous and semi-crystalline polymers.

This two aspects could lead to the conclusion that the glass transition temperature rate increased with increasing cristallinity which is confirmed by Illers and Breuer [15]. Using the Differential scheme, an estimation of what should be the amorphous phase modulus was conducted (Figure 4)

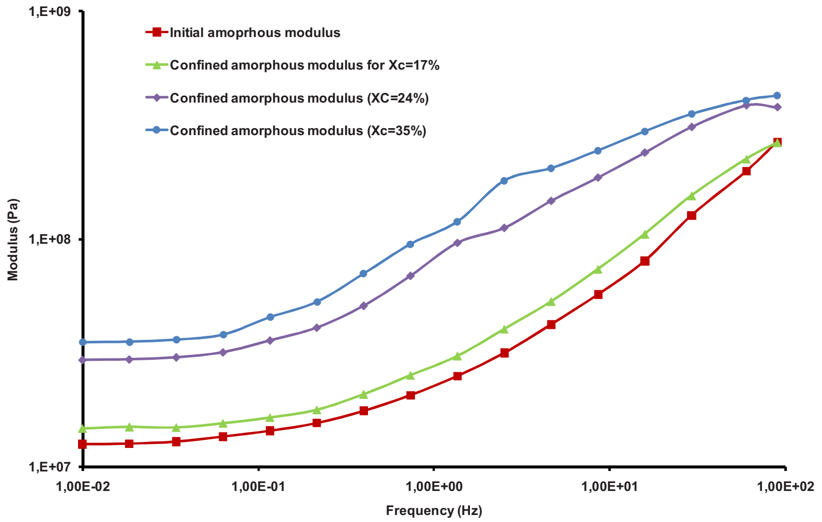

Figure 4: Confined amourphous-phase's moudulus for semi-crystalline polymers compared to the original amorphous polymer.

Conclusion

This study shed some light on the confinement effect which the amorphous phase is subject to due to the increase of the crystallinty fraction. This effect is limited for low crystallinity (Xc=17%) and increased for higher crystallinty (Xc=24 and 35%). This effect was not taken on account in micromechanics models which could be the reason for the fair capability of such models to predict the macroscopic mechanical properties of semi-crystalline polymers such PET. The new approach based on a frequency dependant problem helped overcoming the difficulties encountred in previous work using the Laplace-carson method coupled with collocation method.

Acknowledgment

The author acknowledges the financial support of the Mechanical Engineering Department of the Université de Technologie de Compiègne for this study, under the contract N°M117L.

Conclusion

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