Polymer Testing 66 (2018) 189–194

Contents lists available at ScienceDirect

Polymer Testing

journal homepage: www.elsevier.com/locate/polytest

Property Modelling

Prediction of complex modulus in phase-separated poly (lactic acid)/poly (ethylene oxide)/carbon nanotubes nanocomposites

Yasser Zare[a], Hamid Garmabi[a], Kyong Yop Rhee[b,*]

[a] Department of Polymer Engineering and Color Technology, Amirkabir University of Technology, Tehran, Iran
[b] Department of Mechanical Engineering, College of Engineering, Kyung Hee University, Yongin 446-701, Republic of Korea

ARTICLE INFO

Keywords:
PLA/PEO/CNT nanocomposites
Rheology
Phase separation
Complex modulus
Palierne model

ABSTRACT

This study focuses on the modeling of complex modulus in phase-separated poly (lactic acid) (PLA)/poly (ethylene oxide) (PEO)/carbon nanotubes (CNT) nanocomposites. Palierne model for complex modulus of immiscible blends is developed assuming the significances of CNT and interphase regions. The predictions of developed model are compared to the experimental data from rheological experiment and the predictability of the developed model is studied. Furthermore, the roles of main parameters in the complex modulus of nanocomposites are explained to validate the developed model. The calculations show proper agreements with the experimental data confirming the predictability of the developed model. A higher concentration of continuous matrix and a smaller content of PEO droplets cause thicker and stronger interphase in nanocomposites. High CNT concentration and thin CNT mainly improve the complex modulus. Additionally, both thickness and complex modulus of interphase regions directly control the complex modulus of nanocomposites. This study can afford an insight for researchers to control and optimize the complex modulus in immiscible nanocomposites.

1. Introduction

The biomedical and agricultural requests of biodegradable polymers such as poly (lactic acid) (PLA) have inspired much study, due to their degradation in various media [1–6]. Although PLA displays high rigidity and good biocompatibility, the slow degradation of PLA has restricted the biomedical applications. To solve this problem, PLA can be mixed with polymers or nanoparticles to hasten the degradation rate [5,7]. Poly (ethylene oxide) as a biocompatible, tough, hydrophilic and biodegradable polymer [8] can combine with PLA producing a biodegradable and biocompatible blend. It was reported that this blend is immiscible or partially miscible at different compositions [9,10]. So, the study on the miscibility of this advantageous blend deserves a profound investigation.

Carbon nanotubes (CNT) favorably affect the general behavior of polymers such as crystallinity, free volume, mobility and dynamics [11–14]. The literature is full of reports, which investigated the characteristics of polymer CNT nanocomposites from experimental and theoretical approaches [15–17]. Gong et al. [18] reported a selective distribution of multi-walled CNT (MWCNT) and controlling the migration process of MWCNT in the composites resulting in the outstanding performance of samples. Additionally, controlling the dispersion of MWCNT through ethylene-α-octene block copolymer produced a low percolation threshold, ultrahigh dielectric permittivity and toughness [19]. In addition, CNT commonly accelerate the degradation of polymers, because they play a catalytic role in the degradation [20,21]. Moreover, the excellent modulus and high conductivity of CNT grow the mechanical properties and conductivity of nanocomposites [22,23]. These findings justify the addition of CNT to PLA/PEO blend, which promotes the applications in electronics, sensors and actuators. Pu et al. [24] designed a good strain sensor by the novel end-to-end contact conductive networks of MWCNT in ethylene-α-octene block copolymer matrix, which exhibits very good stretch-ability up to 300% and high cycling durability. Therefore, CNT advantageously affect the mechanical and sensing performances of polymer nanocomposites.

Rheology can present the viscoelastic properties of miscible or immiscible samples at different temperatures and frequencies. Actually, rheology is the most promising and sensitive instrument to characterize the phase separation in polymer blends among the public methods such as optical microscopy and light scattering [25–27]. The growth of elasticity due to the concentration fluctuation and the change of interfacial tension between polymers is an indication of phase separation during rheological surveys [28]. The former studies used time-temperature superposition approach, Cole-Cole plots and Han curves to decide whether the blend is uniform or not [29,30]. Despite the experimental studies, the modeling methods predicting the viscoelastic

* Corresponding author. Giheung, Yongin, Gyeonggi 449-701, Republic of Korea.
E-mail address: rheeky@khu.ac.kr (K.Y. Rhee).

https://doi.org/10.1016/j.polymertesting.2018.01.031
Received 5 December 2017; Received in revised form 27 January 2018; Accepted 28 January 2018

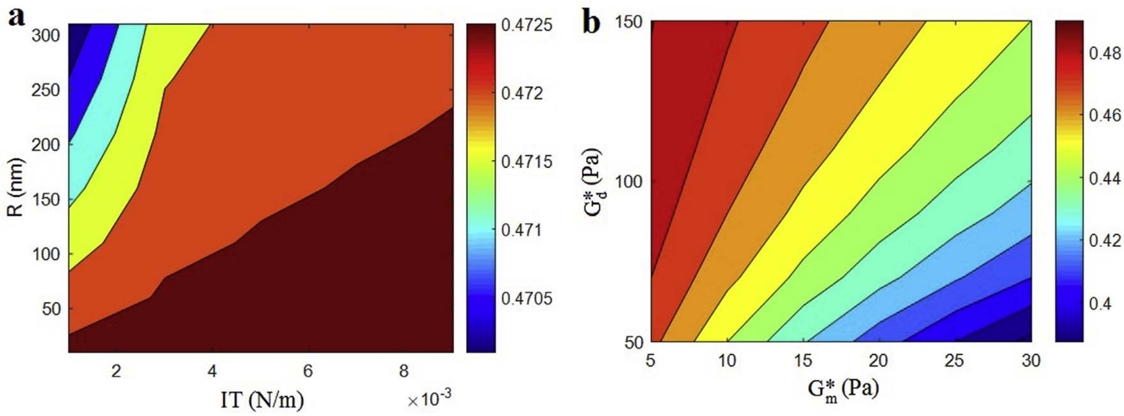

Fig. 1. Contour plots to show the roles of a) IT and R (G_m^* = 10 Pa and G_d^* = 100 Pa) and b) G_m^* and G_d^* (IT = 0.004 N/m and R = 20 nm) parameters in H* term (Eq. (2)).

properties in homogenous and phase-separated nanocomposites are completely limited. Accordingly, the authors should focus on the modeling techniques rather than the experimental works to estimate the viscoelastic behavior of nanocomposites.

Palierne [31] developed a simple model to describe the linear viscoelastic properties of phase-separated blends assuming the interfacial tension between matrix and droplets, droplet size and the concentrations of droplets. This model was originally proposed for wholly immiscible blends. So, this model cannot predict the complex modulus of phase-separated nanocomposites. Also, there is not a simple model estimating the complex modulus in phase-separated nanocomposites, while the modeling techniques help the researchers for optimization of properties. It was reported that the interphase regions due to the outstanding of interfacial area between polymer and nanoparticles manipulate the tensile modulus and strength of nanocomposites [32,33]. So, the interphase characteristics undoubtedly modulate the complex modulus of nanocomposites.

In this article, PLA/PEO/CNT nanocomposites are prepared and the rheological analysis is applied to determine the complex modulus of homogenous and heterogeneous samples. Palierne model for immiscible blends is developed to predict the complex modulus of immiscible nanocomposites assuming the main roles of CNT and interphase regions. In addition, some parameters, which negligibly affect the complex modulus are removed from the model. The predictions of developed model are compared to the experimental data and the predictability of the developed model is analyzed. Furthermore, three-dimensional (3D) and contour plots are applied to investigate the roles of main parameters in the complex modulus of heterogeneous nanocomposites and to confirm the developed model. This study provides an insight for researchers to control and optimize the complex modulus of immiscible polymer nanocomposites by the properties of nanoparticles and interphase zones.

2. Theoretical approach

Palierne model was initially developed for completely immiscible blends, when the polydispersity of droplets is smaller than 2.3.

Palierne model predicts the complex modulus of heterogeneous binary blends as:

$$G^* = G_m^* \frac{1 + 3\varphi_d H^*}{1 - 2\varphi_d H^*} \tag{1}$$

$$H^* = \frac{4(IT/R_d)[2G_m^* + 5G_d^*] + [G_d^* - G_m^*][16G_m^* + 19G_d^*]}{40(IT/R_d)[G_m^* + G_d^*] + [2G_d^* + 3G_m^*][16G_m^* + 19G_d^*]} \tag{2}$$

where G_m^* and G_d^* are the complex modulus of continuous matrix and dispersed phase, respectively. Also, φ_d is the volume fraction of dispersed phase, IT is the interfacial tension between components and R_d is the volume average radius of the dispersed phase. However, this model disregards the roles of CNT and interphase regions in the complex modulus of nanocomposites. Undoubtedly, more significant modulus of CNT and interphase regions compared to polymer matrix and droplets mainly govern the stiffness of nanocomposites.

The reinforcing efficiencies of CNT and interphase regions develop Eq. (1) to:

$$G^* = G_m^* \frac{1 + 3\varphi_d H_d^* + 3\varphi_f H_f^* + 3\varphi_i H_i^*}{1 - 2\varphi_d H_d^* - 2\varphi_f H_f^* - 2\varphi_i H_i^*} \tag{3}$$

$$H_d^* = \frac{4(IT_{PLA-PEO}/R_d)[2G_m^* + 5G_d^*] + [G_d^* - G_m^*][16G_m^* + 19G_d^*]}{40(IT_{PLA-PEO}/R_d)[G_m^* + G_d^*] + [2G_d^* + 3G_m^*][16G_m^* + 19G_d^*]} \tag{4}$$

$$H_f^* = \frac{4(IT_{PLA-CNT}/R)[2G_m^* + 5G_f^*]] + [G_f^* - G_m^*][16G_m^* + 19G_f^*]}{40(IT_{PLA-CNT}/R)[G_m^* + G_f^*] + [2G_f^* + 3G_m^*][16G_m^* + 19G_f^*]} \tag{5}$$

$$H_i^* = \frac{4(IT_{PLA-interphase}/t)[2G_m^* + 5G_i^*] + [G_i^* - G_m^*][16G_m^* + 19G_i^*]}{40(IT_{PLA-interphase}/t)[G_m^* + G_i^*] + [2G_i^* + 3G_m^*][16G_m^* + 19G_i^*]} \tag{6}$$

where the subscripts m, f and i denote the continuous matrix, CNT and interphase regions, respectively. In addition, R and t are CNT radius and interphase thickness, in that order.

The calculations of H* terms from the latter equations indicate that H* negligibly varies at different levels of all parameters. Fig. 1 displays the variations of H* at the long ranges of parameters by contour plots. Fig. 1a demonstrates the effects of IT and R parameters on the H* at average G_m^* = 10 Pa and G_d^* = 100 Pa. High IT and small R increase the H*, whereas low IT and high R cause low H*. However, H* slightly differs around 0.47 at the different extents of IT and R parameters. In other words, the various levels of interfacial tension between components and the radius of dispersed phase trivially manipulate the H* term. Fig. 1b also reveals the impacts of G_m^* and G_d^* parameters on the H* at average IT = 0.004 N/m and R = 20 nm. Although the highest H* is obtained by the smallest G_m^* and the highest G_d^*, H* only changes from about 0.38 to 0.49. In other words, the different levels of G_m^* and G_d^* insignificantly change the H* demonstrating the inefficiency of G_m^* and G_d^* parameters on the H* term. Therefore, H* terms defined in Eqs. (4)–(6) can be considered as a constant parameter as 0.5 in for the current samples simplifying Eq. (3) to:

$$G^* = G_m^* \frac{1 + 1.5(\varphi_d + \varphi_f + \varphi_i)}{1 - \varphi_d - \varphi_f - \varphi_i} \tag{7}$$

This equation underpredicts the complex modulus of nanocomposites, because the small G_m^* and the very low values of φ_d, φ_f and φ_i (below 1) produce very slight levels for complex modulus of nanocomposites, which are far from the experimental data.

It can be suggested that the modulus of components manipulates the reinforcement of nanocomposites and influences the complex modulus