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REGULAR ARTICLE

Prediction of Normal Stress Difference and Relaxation Modulus of Polylactic Acid/Calcium Phosphate Nanocomposites

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New research is being conducted to better understand the relationship between mechanical characteristics and strain rate in polymeric materials. In this study, calcium phosphate nanoparticles were incorporated into polylactic acid using ultrasonic vibration-assisted melt mixing, and the samples were cast under vacuum. The normal stress difference and relaxation modulus for the Polylactic acid/Calcium phosphate nanocomposites were calculated using the experimentally measured value of viscoelastic properties. The dependency of normal stress difference and relaxation modulus on different parameters was also shown for the validation of the expressions. The first normal stress difference and relaxation modulus were predicted based on the frequency dependence viscoelastic characteristics of polylactic acid/calcium phosphate nanocomposites. The first normal stress difference increases with shear rate and reaches a plateau at lower shear rates. The value of the first normal stress differential increases with calcium phosphate nanoparticle concentration, demonstrating that calcium phosphate promotes elasticity. The relaxation modulus falls as shear rates increase while increasing with calcium phosphate nanoparticle concentration. However, the incorporation of the calcium phosphate nanoparticle to polylactic acid increases the relaxation modulus because of polymer-filler interaction.

Keywords: Polylactic acid, Calcium phosphate, Normal stress difference, Viscoelastic properties, Relaxation modulus.

1. INTRODUCTION

The shearing of viscoelastic polymeric materials between two flat surfaces at significant shear rates causes the formation of normal stress differences (N_1 and N_2) and viscous shear stress. The value of first normal stress difference (N_1) is larger among both the normal stress difference and its values are either positive or zero, whereas the second normal stress difference (N_2) is always negative. It is quite difficult to measure the normal stress difference and cannot be exactly measured because errors maybe associated as a result of variations in temperature, consistency of the instruments. Also, the wall slip affects the normal stress difference measurement [1]. However, the elasticity of the polymer melt was not estimated in comparison to shear measurement because of difficulties in measurement [2]. Generally, the elasticity is examined by the force measurements, capillary flow, and die swell test [1]. Only a few works have been reported in the literature for the investigation of N_1 for polymer melts. Lin Y et al. [3] studied the effect of particles on the N_1 of the polymers experimentally.

The frequency-dependent viscoelastic properties of the materials such as complex viscosity (η), storage modulus

(E'), loss modulus (E''), and damping factor (tan δ), are measured by dynamic oscillatory shear rheology [4]. For the thermosetting plastics, Dynamic mechanical analysis is mainly used to know the maximum working temperature, glass transition temperature (T_g), which helps to decide the feasibility of the material for the specific condition and environment [5]. However, thermoplastics such as Polylactic acid (PLA) are used above (T_g), for which mechanical response is time-dependent; hence frequency-dependent data is less beneficial. The limited work has been found for the prediction of N_1, and $E(t)$ was in the literature. Zeltmann et al. [6] developed a relationship between the relaxation modulus $E(t)$ and the dynamic mechanical analysis (DMA) data for the high-density polyethylene. Zare et al. [7] correlated the N_1 and $E(t)$ with the viscoelastic data of the carbon nanotubes (CNT) incorporated blends of polylactic acid (PLA) and poly (ethylene oxide) (PEO). Though, various theoretical methods are available, which are helpful for understanding the origins of these parameters.

In this work, N_1 and Relaxation Modulus $E(t)$ for the polylactic acid/calcium phosphate (PLA/CaP) nanocomposites have been estimated using the frequency-dependent viscoelastic properties, which is very difficult to measure

experimentally due to many constraints as discussed previously. The reason behind selecting PLA for the study in the present work is its predominant use in various biomedical and packaging industries for new items [8-10]. However, the use of PLA in orthopedics is limited because of its poor mechanical properties. Also, the degradation of pure PLA produces acidic products, which cause inflammatory reactions during resorption. Many biodegradable composites have been prepared to overcome this issue. Incorporation of calcium phosphate (CaP) fillers into the pure PLA found a great approach to enhance its mechanical properties. Also, the addition of CaP prevents the formation of acidic environments, which promotes bone healing [8, 9]. However, the corre-lation described in this work is likely to be also appro-priate to many other polymers.

2. MATERIALS AND EXPERIMENTAL

2.1 Sample preperation

Pure PLA and PLA/CaP nanocomposite samples were prepared by the melt mixing assisted with ultra-sonic techniques inside the vacuum chamber according to our previous work [8, 9]. The CaP nanoparticle were added from 5 % to 20 % by weight with respect to the PLA matrix at discreet concentration.

2.2 Dynamic Oscillatory Rheology

The Viscoelastic behavior of all the samples were performed by MCR 102, with varying angular frequency from 0.1 rad/sec to 400 rad/sec according to our previous research [9].

3. THEORETICAL BACKGROUND

The value of the N_1 can be calculated from Eq. (1) [11]

$$N_1 = 2E' \left[1 + \left(\frac{E'}{E''}\right)^2\right]^{0.7} \tag{1}$$

where E' and E'' are measured with variation in angular frequencies (ω).

$\omega = \gamma'$ (shear rate) allows to express N_1 in terms of shear rate for further calculations.

The shear stress (τ_{12}) and N_1 can be interrelated according to Eq. (2) given by Lodge-Meissner relationship [12],

$$N_1 = \tau_{12}\gamma = \gamma^2 E(t) \tag{2}$$

where $E(t)$ and γ are relaxation modulus and strain, respectively. This expression shows the dependency of N_1 on the relaxation modulus and strain. This expression can also be rearranged in the form of relaxation modulus according to Eq. (3)

$$E(t) = \frac{N_1}{\gamma^2} \tag{3}$$

When the value of N_1 in Eq. (3) is replaced from Eq. (1), $E(t)$ is related as

$$E(t) = \frac{2E'\left[1 + \left(\frac{E'}{E''}\right)^2\right]^{0.7}}{\gamma^2} \tag{4}$$

Eq. (4) correlates the relaxation modulus $E(t)$ to storage and loss moduli and strain. The relaxation modulus $E(t)$ can also be reconstructed in terms of the shear rate as:

$$E(t) = \frac{2E'\left[1 + \left(\frac{E'}{E''}\right)^2\right]^{0.7}}{(t\gamma')^2} \tag{5}$$

The above equations are used to predict $E(t)$ and N_1 for PLA/CaP nanocomposite at various shear rates and show the dependency of $E(t)$ and N_1 on basic parameters.

4. RESULTS AND DISCUSSIONS

4.1 Dynamic Oscillatory Rheology

Viscoelastic properties such as storage modulus, loss modulus and loss factor of the PLA/CaP nanocom-posites concerning the angular frequency were measured experimentally and reported in detail in our previous article [9]. The outcome of previous work reveals that the storage and loss moduli of the PLA/CaP nanocomposites increased with the addition of the CaP nanoparticles and also with frequency. The value of storage and loss moduli were used in this work for the prediction of normal stress difference and relaxation modulus.

4.2 First Normal Stress Difference (N_1)

The N_1 at various shear rates is shown in Fig. 1. N_1 for all the nanocomposite samples is evaluated from the value of storage and loss moduli acquired from the frequency sweep test. The Figure shows that N_1 increases with an increase in the shear rate and confirms a small plateau region at a lower shear rate. Furthermore, N_1 also increases with the concentration of CaP nanoparticles, confirming that the addition of the CaP into the PLA matrix improves its elasticity due to the formation of polymer-filler networks. The enhancement in N_1 with the incorporation of CaP is credited to the alignment of nanoparticles in the streaming direction and also with filler-filler and polymer-filler interactions [1]. Additionally, the degree of filler distribution in PLA/CaP nanocomposites influences the N_1, and variation in the value of N_1 at lower filler concentration specified the weakening of the PLA matrix. Similar behavior was also observed for PLA/graphite nanocomposites [1].

The value of N_1 found constant or less dependency on shear rates at the region of lower shear rates, caused by large networks formation. The formation of big networks of CaP nanoparticles denying the dependency of N_1 on shear rates because the nanocomposites behave like a solid at low-frequency regions. Though, N_1 of the nanocomposites increased with CaP concentration at lower frequency region because of the change in the elasticity of the PLA matrix [13].
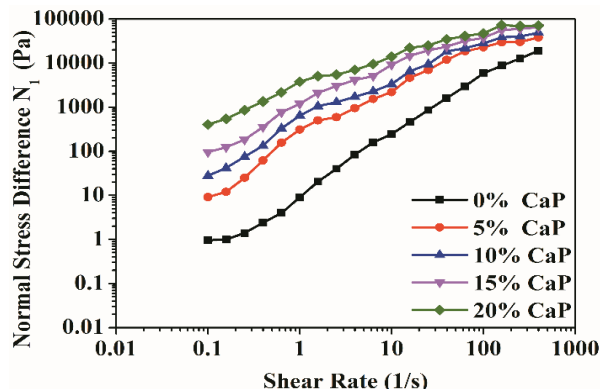
Fig. 1 – Normal stress difference N_1 as a function of shear rate for the PLA and PLA/CaP nanocomposite samples

N_1 shows similar values at higher frequencies region because, at a shorter deformation range, the elastic response of all the samples is common. It implies that the relaxations of PLA chains at short-range deformation are less dependent upon the CaP concentration. Additionally, denying the dependency of N_1 on higher shear rates region may be related to the orientation capability of CaP in the streaming direction [14]. The lower value of elasticity is achieved by zero normal stress for the isometric filler composites [15] but an anisotropic filler improves the elasticity because of the improvement of N_1.

Fig. 2 shows the variations of N_1 with the storage modulus and loss modulus of the PLA/CaP nanocomposites according to Eq. (1) by 3-Dimentional surface. From the figure, it is observed that N_1 increases to 75 KPa at $E' = 3$ KPa and $E'' = 0.5$ KPa whereas the E' less than 0.3 KPa decreases the N_1 to 0.5 KPa. Subsequently, the N_1 of the samples increases with the high storage modulus with the low loss modulus, only the lower storage modulus decreases N_1. This tendency is reasonable since N_1 is elastic commencement [16].
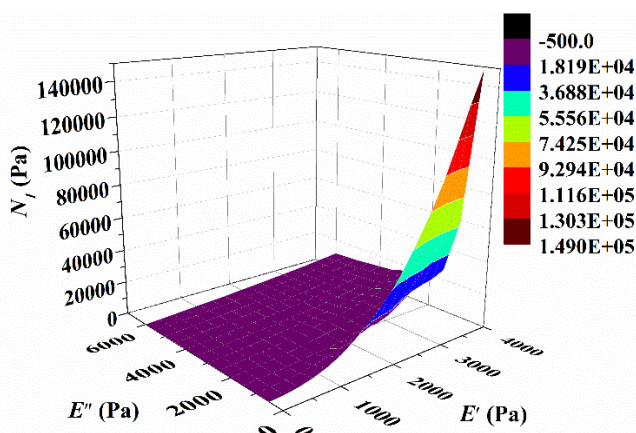

Fig. 2 – Normal stress difference N_1 with storage and loss moduli

Definitively, Eq. (1) appropriately calculate the effects of storage modulus and loss modulus on the N_1 for PLA nanocomposite. Fig. 3 shows the effects of $E(t)$ and strain

on the N_1 based on Eq. (2). The maximum value of $N_1 = 20$ KPa is found for 4 strain value and the 1.25 KPa $E(t)$ value. However, $E(t) = 0.25$ KPa and strain < 0.5 mainly decrease the value of N_1 to about 0. Hence, $E(t)$ and strain directly affect the N_1 for the nanocomposite sample. The higher value of both the $E(t)$ and strain enhances the N_1, and their lower values result weakening of the N_1. It might be said that the $E(t)$ and the strain influence the elasticity of the nanocomposites sample altering the N_1.
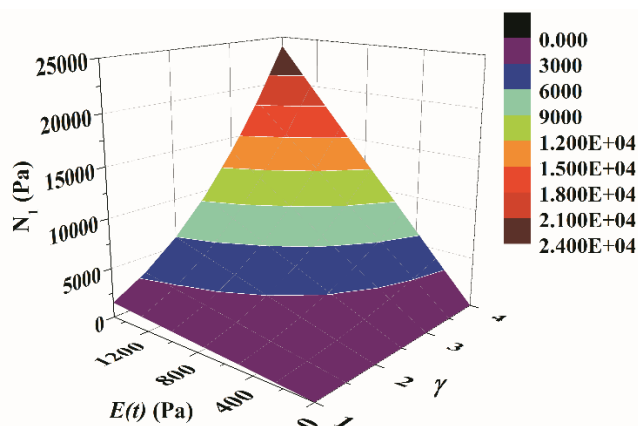

Fig. 3 – Normal stress difference N_1 with Relaxation Modulus $E(t)$ and strain

4.3 Relaxation Modulus

The relaxation modulus $E(t)$ of the PLA nanocomposites at various shear rates can be predicted by Eq. (4) using the viscoelastic properties obtained from the frequency sweep test. Fig. 4 shows the variation of $E(t)$ with the shear rate of the PLA nanocomposite. $E(t)$ of all the nanocomposite samples decreases with an increase in the shear rates. Since a sufficiently long testing time results in the relaxation of the PLA chains decreases the $E(t)$. Also, the incorporation of the CaP nanoparticles to the PLA improves the $E(t)$, because of the interaction of the polymer chain with the solid nanoparticles, restricting the relaxation [17]. $E(t)$ for all the nanocomposites samples decreases at lower frequency region due to quick response of elastic as well as loss component of the energy at low strain. Additionally, the $E(t)$ of the nanocomposites are almost similar for all the CaP concentrations since a higher shear rate regulates the short-range relaxation of the polymeric matrix, which is unaffected by the amount of nanoparticle inclusion. In other words, the incorporation of CaP nanoparticles doesn't alter the shorter-range response of the PLA sections; hence all the nanocomposite sample shows an almost similar value of $E(t)$ at higher shear rates.

Fig. 5 shows the impact of E' and E'' on the relaxation modulus $E(t)$ for the PLA nanocomposite at $\gamma = 2$ based on Eq. (4).
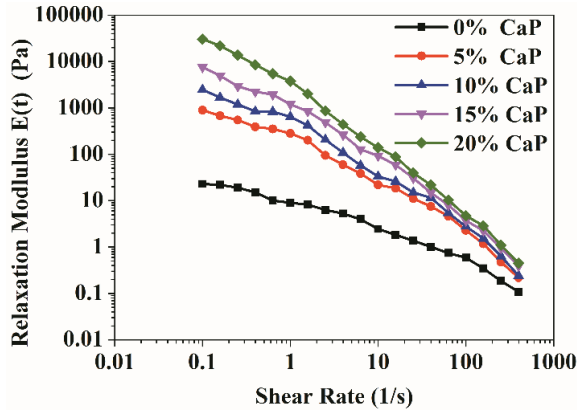
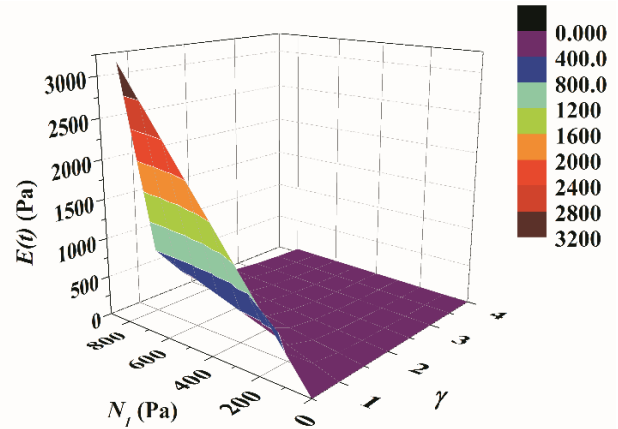**Fig. 4** – Relaxation modulus $E(t)$ as a function of shear rate for the PLA and PLA/CaP nanocomposite samples
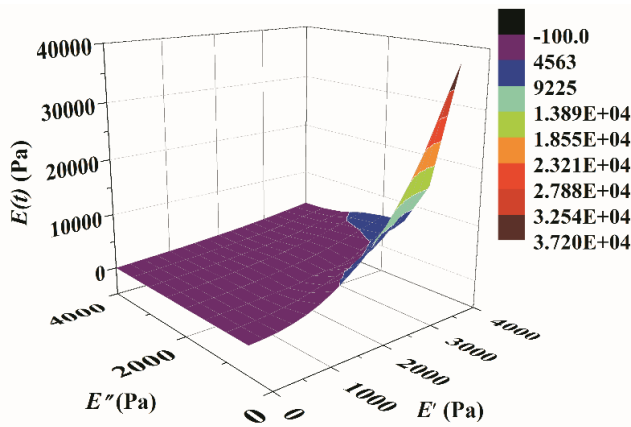

Fig. 5 – Relaxation Modulus $E(t)$ with storage and loss moduli

The $E(t)$ increases to 18.785 KPa at $E' = 3$ KPa and $E'' = 0.5$ KPa, whereas the least $E(t)$ of about 0.146 KPa is observed at $E' < 0.25$ KPa. Hence, a maximum value of $E(t)$ was observed for the higher storage, and lower loss modulus value, and $E(t)$ reduces with lower storage modulus only. These results reveal that $E(t)$ is mainly affected by storage modulus only, whereas less affected by loss modulus. As a result, the presented equations confirmed the effect of strain and N_1 on $E(t)$ for PLA nanocomposites.

Fig. 6 describes the dependence of relaxation modulus $E(t)$ on the γ and N_1 as given in Eq. (3).

From the figure, it is observed that for $\gamma > 1.5$ or $N_1 = 0.05$ KPa reduces the $E(t)$ to around 0, whereas the maximum $E(t)$ value 12 KPa is attained for $\gamma = 0.5$ and $N_1 = 3$ KPa. Hence, $E(t)$ greatly improves with small strain and high N_1, whereas decreases with large strain and low N_1 decrease the value of $E(t)$. Specifically, smaller γ and higher N_1 are needed to enhance polymeric nanocomposite's $E(t)$. These outcomes are usual since a smaller γ and higher N_1 are caused by higher storage modulus value, which is responsible for altering the $E(t)$.

Fig. 6 – Relaxation Modulus $E(t)$ with normal stress difference N_1 and strain

5. CONCLUSION

The N_1 and $E(t)$ for the PLA/CaP nanocomposites were calculated using the experimentally measured value of viscoelastic properties. Likewise, the dependency of N_1 and $E(t)$ on different parameters was also shown for the validation of the expressions. N_1 exhibits a plateau region at a lower shear rate for all the PLA nanocomposites sample and increases with further increasing the shear rate. The incorporation of CaP nanoparticles into the PLA increases the N_1. It shows constant or less dependent at lower shear rates because of large networks formation, which deals with the elasticity of the composite samples. The higher value storage modulus and lower loss modulus greatly improve the N_1 of PLA nanocomposites and decrease with low loss modulus. Also, the higher value of strain and $E(t)$ increases N_1, whereas their small values decrease the N_1. $E(t)$ of all the samples decreases with an increase in the shear rates due to long-time facilitates the relaxation of the PLA chain.

Additionally, the incorporation of the CaP nanoparticle to PLA increases the $E(t)$ because of polymer-filler interaction. A higher value E' and lower E'' enhance the $E(t)$, whereas a lower storage modulus only decreases the $E(t)$. Also, a high strain and poor N_1 weakens the $E(t)$. These results reveal that the more viscous part of energy decreases the value of N_1 and $E(t)$, indicating that both N_1 and $E(t)$ have elastic origins. N_1 and strain show more impact on the value of $E(t)$. The significance of this work is to explore method of obtaining normal stress difference and relaxation modulus from the frequency dependence viscoelastic data, which is very difficult to measure experimentally.

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Прогнозування нормальної різниці напруги та модуля релаксації нанокомпозитів полімолочна кислота/фосфат кальцію

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Були проведені нові дослідження, щоб краще зрозуміти взаємозв'язок між механічними характеристиками та швидкістю деформації полімерних матеріалів. Наночастинки фосфату кальцію були включені в полімолочну кислоту за допомогою змішування розплаву за допомогою ультразвукової вібрації, а зразки були отримані у вакуумі. Нормальна різниця напружень і модуль релаксації для нанокомпозитів полімолочна кислота/фосфат кальцію були розраховані з використанням експериментально виміряного значення в'язкопружних властивостей. Для підтвердження виразів також було показано залежність різниці нормальних напружень і модуля релаксації від різних параметрів. Перша нормальна різниця напружень і модуль релаксації були передбачені на основі частотної залежності в'язкопружних характеристик нанокомпозитів полімолочна кислота/фосфат кальцію. Нормальна різниця напруг зростає зі швидкістю зсуву і досягає плато при нижчих швидкостях зсуву. Значення першого нормального диференціалу напруги зростає з концентрацією наночастинок фосфату кальцію, демонструючи, що фосфат кальцію сприяє еластичності. Модуль релаксації падає зі збільшенням швидкості зсуву, одночасно збільшуючи концентрацію наночастинок фосфату кальцію. Однак включення наночастинок фосфату кальцію в полімолочну кислоту збільшує модуль релаксації через взаємодію полімер-наповнювача.

Ключові слова: Полімолочна кислота, Фосфат кальцію, Різниця нормальних напружень, В'язкопружні властивості, Модуль релаксації.