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Viscoelasticity of biodegradable polymer blends of poly(3-hydroxybutyrate) and poly(ethylene oxide)

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Abstract

The viscoelastic properties, measured via both steady shear and oscillatory experiments, for blends of biodegradable poly(3-hydroxybutyrate) (PHB) and poly(ethylene oxide) (PEO) were examined. We observed that PHB/PEO blends are miscible. The first normal stress difference, the shear stress, and the shear viscosity (obtained from the steady shear experiment) were correlated with the storage modulus, the loss modulus, and the complex viscosity (obtained from the oscillatory experiment) via either the Cox and Merz rule or other empirical equations. For biodegradable PHB/PEO blend systems, we found that both the viscous and the elastic behavior from the steady shear experiment are qualitatively related to those from the oscillatory experiment. © 2001 Published by Elsevier Science Ltd.

Keywords: Biodegradable polymer; PHB; PEO

1. Introduction

Biodegradable plastics are an attractive route to environmental waste management and can replace conventional polymers when recovery for recycling or incineration is difficult and/or not cost-effective. Research has focused on both the addition of biodegradable polymers to common thermoplastics and on purely biodegradable, natural and synthetic polymers [1]. Among these, poly(3-hydroxybutyrate) (PHB), has been developed and investigated as one of the potential candidates for biodegradable plastics to reduce pollution caused by synthetic polymer waste. PHB, a saturated linear polyester behaving like a conventional thermoplastic material, is a polymer of D(−)3-hydroxybutyric acid produced via biosynthesis by a wide variety of bacteria. PHB serves as an intracellular storage material for carbon and energy and is accumulated as granules within the cytoplasm of the bacteria [2].

PHB is relatively abundant in the environment and can be found in various bacteria, such as soil bacteria and estuarine microflora [3]. However, for the industrial production of PHB, the bacterium *Alcaligenes eutrophus* grown on glucose is used. The PHB homopolymer is a biodegradable, biocompatible thermoplastic, implying that it is a resin that becomes highly viscous and moldable at temperatures close to or above its melting point (T_m). Its properties are often compared to those of polypropylene, as both polymers have similar T_ms, degrees of crystallinity, and glass transition temperatures (T_gs). However, PHB is both stiffer and more brittle than polypropylene. The brittleness of PHB is largely due to the presence of large crystallinities in the form of spherulites, which form upon cooling from the melt [4]. PHB can be injection molded or extruded, provided care is taken to lower the T_m and minimize residence time. Injection molded PHB bars often show high crystallinity, especially below the T_g. Thus, it suffers from some disadvantages, including a narrow processibility window and relatively low impact strength [5]. Thereby, to improve the properties of PHB, various PHB-based blends, which also reduce the cost of the final material, have been examined. Note that in order to improve these properties, random copolymers of poly(3-hydrobutyrate-*co*-3-hydroxyvalerate) (P(3HB-*co*-3HV)) have been formulated by replacing the methyl group with an ethyl group in the PHB main chain [6]. On the other hand, blending of PHB may decrease the T_m, which implies the possibility of processing the materials at a lower temperature to avoid or limit degradation [7]. Miscibility between PHB and poly(epichlorohydrin) (PECH) [8], poly(ethylene oxide) (PEO) [9–11], poly(vinyl acetate) (PVAc) [12], poly(vinyl alcohol) [13], ethyl cellulose [14], poly(ε-caprolactone) [15], and poly(ethylene-*co*-vinyl acetate) [16] have been investigated.

Among the above listed blend systems, PEO was selected

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Table 1
Physical properties of the polymers

Polymer	Source	Abbreviation	Molecular weight[a]
Poly(hydroxybutyrate)	ICI (UK)	PHB	$M_n = 192{,}000$[b] $M_w = 472{,}000$
Poly(ethylene oxide)	Scientific Polymer Product Inc.	PEO	$M_n = 80{,}000$[b] $M_w = 90{,}000$

[a] M_n and M_w stand for number average and weight average molecular weights.
[b] Obtained from gel permeation chromatography.

due to its excellent biocompatiblily and misciblility with PHB. In addition, PEO is a hydrophilic, nondegradable thermoplastic commodity and is approved for biomedical applications [17]. The T_g and depression of the T_m provide miscibility criteria for PHB/PEO blends [9,18]. Further, the study of the isothermal crystallization process showed that the presence of PEO causes a depression in the growth rate of PHB spherulites at a given crystallization temperature [9].

Despite many investigations on miscibility, thermal properties, crystallization behavior, and degradability of biodegradable polymers and their blends systems [7], there exist only a few studies that explore the rheological properties of PHB/PEO blends [10,19] or generic biodegradable polymeric systems. Choi et al. [11] reported that for PHB/PEO blends (80/20 by weight), the vacant domains of the PHB were filled with PEO, and this morphology changed the rheological properties. Rheological studies of biodegradable polymers, including poly(caprolacton), poly lactic acid (PLA) [20], poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (P(3HB-*co*-3HV)) [21,22], and starch [23] were reported. Further, miscibility and rheology of synthetic biodegradable aliphatic polyesters blended with PECH [24,25] and PVAc [26] have also been investigated.

In this paper, we will re-examine the effect of PEO in PHB/PEO blends on the rheological properties via both steady shear and oscillatory experiments and will establish the interrelationship among the various rheological properties. These interrelationships will enhance experimental capability for the oscillatory measurements, with small sample amounts and efforts. These correlations are highly empirical, and the validity must be examined for each group of materials, including biodegradable polymers. The rheology of biodegradable polymeric systems is also important in processing and controlling the mechanical properties of the final products.

2. Experimental

PHB samples were acquired from the Imperial Chemical Industries Co., UK. The powder form PEO samples were purchased from Scientific Polymer Product Inc., USA. The physical properties of these polymers are given in Table 1.

Since the T_m of PEO ($T_m \approx 67°C$) is too low for melt blending with PHB ($T_m \approx 180°C$), PHB/PEO blends were produced via a solution blending method, using chloroform ($CHCl_3$) as a co-solvent. The solution was prepared by stirring the PEO mixture for 9 h. However, since PHB is insoluble in chloroform at room temperature, we used an autoclave (Parr Inc.) to stir it for 150 min at 50 psi and 110°C. We examined PHB/PEO blend ratios of 100/0, 80/20, 60/40, 40/60, and 20/80 by weight, which are indexed as PHB100, PHB80, PHB60, PHB40, and PHB20, respectively. After the PHB/PEO solutions were blended by stirring for about 13 h, solutions were cast on a horizontal glass surface, followed by slow evaporation. The films were then dried in a vacuum oven at 70°C until a constant weight was obtained (approximately one week). Both film and disk type samples were obtained.

DSC 910 (DuPont) was used to measure the T_gs of the blend and homopolymer of PHB. The T_g of a blend determines the miscibility of the blend system. In order to measure the T_g of the molten mixture, blend samples were heated to 190°C, they were quenched in liquid nitrogen, followed by heating from −80°C to 190°C at 20°C/min.

We used a rotational rheometer (RMS 800, Rheometrics Inc.) for the steady shear rate measurement. Samples of 2 mm thickness and 2.5 mm radius were analyzed in a parallel plate geometry. The shear viscosity (η), shear stress (τ_s), and first normal stress difference (N_1) were measured in the melt state as a function of shear rate ($\dot{\gamma}$) at 180°C.

Further, the storage modulus (G'), loss modulus (G''), and complex viscosity (η^*) were measured at 180°C as a function of frequency (ω) at a deformation of 15%. To avoid thermal degradation during the measurement, the frequency has been applied from 1 rad s^{-1}, because it takes a longer time for measurements at low frequencies. The polymer above its T_m, degrades and its average molecular weight decreases with time. Therefore, the thermal stability of a sample can be estimated by the extent of degradation. η^* was then obtained as a function of time.

3. Results and discussion

Quenched samples of PHB/PEO blends were analyzed by means of DSC and a single T_g was observed, intermediate

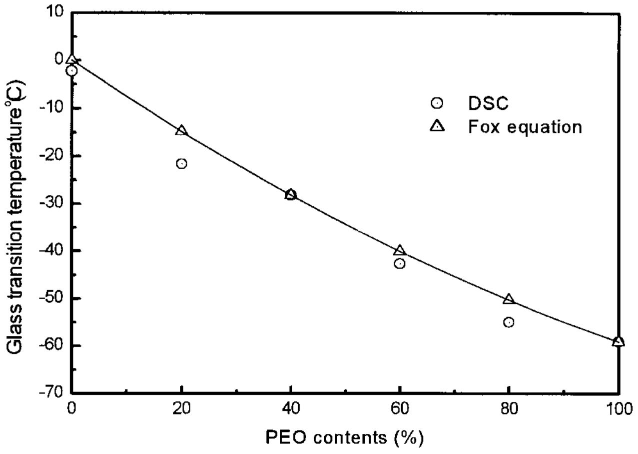

Fig. 1. T_gs of PHB/PEO blends. Solid line indicates T_g predicted using the Fox equation.

between those of PHB and PEO as given in Fig. 1. It shows that the composition dependence of T_g of PHB/PEO blends closely corresponds to the Fox equation shown below, which is usually valid for compatible systems as reported by Avella and Martuscelli [9]:

$$\frac{1}{T_g(\text{blend})} = \frac{W(\text{PHB})}{T_g(\text{PHB})} + \frac{W(\text{PEO})}{T_g(\text{PEO})} \tag{1}$$

Here, W is the weight fraction. T_gs obtained from the Fox equation and by DSC are consistent within an error of measurement, indicating that PHB and PEO are miscible in the whole composition range in the melt state and in the amorphous state.

To examine the relationship between η and $\dot{\gamma}$, we plotted them on a log–log graph (shown in Fig. 2). The Carreau model [27], shown in Eq. (2), is used to fit the data:

$$\eta = \eta_0[1 + (\dot{\gamma}\lambda)^2]^{(n-1)/2} \tag{2}$$

Here, η_0 is the zero shear rate viscosity, λ is the relaxation time, and n is a dimensionless, power-law parameter. The slope in the power-law region is $(n - 1)$. Eq. (2) becomes the Newtonian fluid model with constant viscosity for $n = 1$ or $\dot{\gamma}\lambda \rightarrow 0$, and exhibits shear-thinning behavior for $n < 1$. The calculated values for η_0, n, and λ are given in Table 2. The Carreau model fit the shear viscosities for PHB and its blends at 180°C. Note that shear-thinning region of both BDP/PVAc blends [26] and PEO–clay nanocomposites [28] fit the Carreau model quite well.

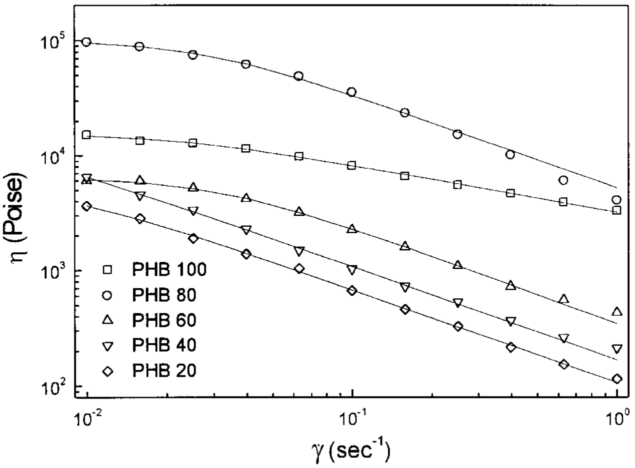

Fig. 2. η vs. $\dot{\gamma}$ (log–log scale) for PHB and its blends at 180°C.

Table 2
Carreau model (Eq. (2)) parameters obtained from PHB blend systems

	η_0 (Pa s) × 10^4	λ (s)	n
PHB100	1.55	47.21	0.59
PHB80	10.0	37.09	0.18
PHB60	0.642	33.34	0.17
PHB40	1.47	260.51	0.20
PHB20	0.570	144.02	0.20

Fig. 3 shows both the shear viscosity of the blend system, obtained via steady shear experiments, and η^*, obtained from G' and G'' data measured from the oscillatory experiments, as functions of $\dot{\gamma}$ and ω, respectively. Cox and Merz [29] observed that plotting $\eta(\dot{\gamma})$ vs. $\dot{\gamma}$ is almost identical to plotting the complex viscosity magnitude $|\eta^*(\omega)|$ vs. ω. This well-known Cox and Merz rule is expressesd as

$$\lim_{\dot{\gamma}\rightarrow\omega} \eta(\dot{\gamma}) = |\eta^*(\omega)| \tag{3}$$

The complex viscosity is obtained from a small amplitude oscillatory shear test:

$$|\eta^*| = \sqrt{(\eta')^2 + (\eta'')^2} \tag{4}$$

From Eq. (4) and the Cox and Merz rule (Eq. (3))

$$\lim_{\dot{\gamma}\rightarrow\omega} \eta(\dot{\gamma}) = \frac{G''}{\omega}\sqrt{1 + (G'/G'')^2} \tag{5}$$

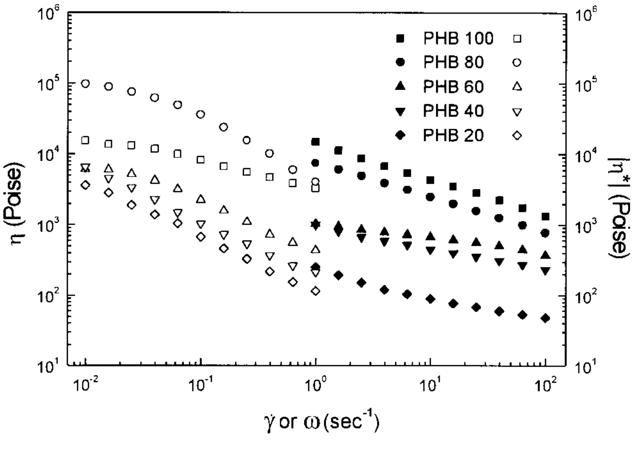

Fig. 3. η (open symbols) vs. $\dot{\gamma}$ and $|\eta^*|$ (filled symbols) vs. ω for PHB and its blends at 180°C.

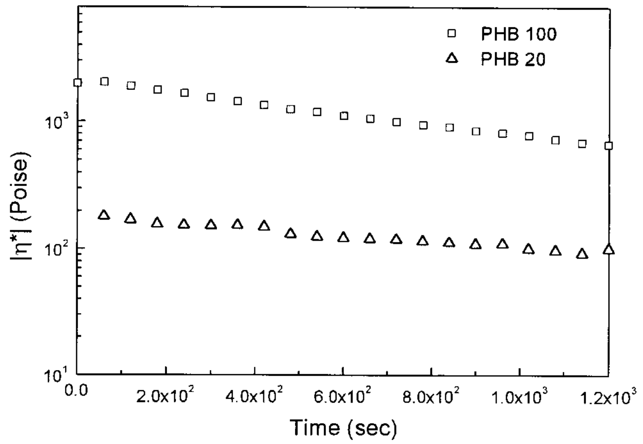

Fig. 4. Complex viscosity vs. elapsed time for PHB at a frequency of 1 rad s^{-1} and 180°C.

This empirical relation is generally valid for a wide class of polymer melts and solutions [27].

From Fig. 3, both η and $|\eta^*|$ of the PHB/PEO blend system decreases with increasing $\dot{\gamma}$ or ω, similar to many other polymeric systems and decrease with increasing PEO content. However, at low shear rates, the shear viscosity of PHB80 is much higher than that of PHB100 (pure PHB). From scanning electron microscopy micrographs, Choi et al. [11] explained this peculiar observation: in the PHB80 blends, PEO fill the vacancies of the PHB, giving PHB80 a larger domain than that of PHB100, despite their miscibility. As it is shown in Fig. 1, the miscibility of the PHB/PEO blends has been well studied. Avella and Martuscelli [9] observed the miscibility of their samples obtained by slowly solution casting from chloroform from a single T_g in the whole composition range. Yoon et al. [10] also observed the miscibility of PHB and PEO using a vapor sorption technique, in which the equilibrium solubility of chloroform vapor in the polymers was measured using a sorption apparatus consisting of a quartz spring to monitor the vapor taken up in the sorption chamber. Polymer–polymer interaction parameters obtained by this technique were found to be negative for PHB/PEO in the whole composition range including PHB/PEO (80/20) blend, indicating their miscibility.

Thereby, there is no doubt that the PHB/PEO (80/20) is miscible. However, analysis of the fractured surface of specimens, performed by using SEM, showed that pure PHB had many vacancies throughout the fracture surface and 20% of PEO might exactly fill the vacancies of the PHB matrix [11]. As also cited by Avella et al. [7], this morphological reason seems to be responsible for the increase of rheological properties including the shear viscosity of the PHB containing 20% of PEO, similar to conventional particle suspended polymeric system [30]. Recently, Choi et al. [30] observed the increase of both shear viscosity and first normal stress difference of kaolinite-suspended polyisobutylene solution, compared to the polymeric system without particle. This PHB/PEO blend composition also has higher values of first normal stress difference and storage modulus than PHB. The shear viscosity of PHB80 decreases more rapidly than PHB100, and they become approximately equal at $\dot{\gamma} = 1\ s^{-1}$. For $\dot{\gamma} > 1\ s^{-1}$, this trend may reverse. This tendency was ascertained from the complex viscosity data at high ω, even though the magnitude of both PHB100 and PHB80 are quite different from those obtained from the shear experiment. As shown in Fig. 3, the complex viscosities deviate from the shear viscosity, becoming more drastic with increasing PHB content. One possible mechanism for this deviation of the complex viscosities from the shear viscosity is due to thermal degradation of microbial PHB at the experimental temperature. Kunioka and Doi [31] observed that all microbial copolyester samples they used such as poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (P(3HB-*co*-3HV); 3HV = 0–71 mol%) and poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate) (P(3HB-*co*-4HB); 4HB = 0–82 mol%) were thermally unstable at temperatures above 170°C, resulting in a rapid decrease in the molecular weights with time. They also examined the thermal degradation of PHB at 180°C.

On the other hand, Arent and Kulicke [32] reported that intermolecular interactions are detectable by comparison of η and $|\eta^*|$, since the derivation from the Cox and Merz rules are due to the energetic interactions such as hydrogen bonds, dipole–dipole forces, and ionomeric clusters [33]. They showed that neither highly concentrated xanthan gum fermentation broths nor a 1 wt% solution of xanthan gum satisfy the Cox and Merz rule. The complex viscosity is higher than the shear viscosity, due to hydrogen bonds between the xanthan gum chains. This explanation is reasonable since aqueous solution of helical polysaccharide schizophyllan exhibit these deviations, while xanthan gum in dimethylsulfoxide, which breaks hydrogen bonds [34], satisfy Cox and Merz rule.

To examine the thermal degradation of PHB, we measured the complex viscosity of both PHB100 and PHB20 as a function of time at 180°C using the same parallel plate geometry. As shown in Fig. 4, the complex viscosity is observed to decrease slightly with time, since the polymer degrades above the T_m. However, the degradation is not as severe as what Kunioka and Doi observed [31].

Despite thermal degradation, Choi et al. [21] found that the elastic behavior, obtained from steady shear experiment is closely related to that obtained from the oscillatory experiments for the biodegradable P(3HB-*co*-3HV) copolymer using a modified Cole–Cole plot.

Note that the Cox and Merz rule is generally applicable for flexible molecules [27]. Exceptions were found for some linear [35] and branched [36] polyethylenes and rigid molecules [37]. Nonetheless, the Cox and Merz rule is a very useful relationship, because it is easier to estimate $|\eta^*(\omega)|$ over a wide range of frequencies than to estimate $\eta(\dot{\gamma})$ over

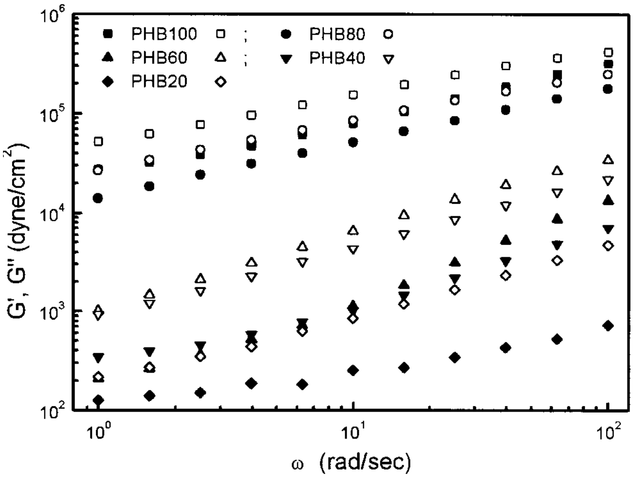

Fig. 5. G' (filed symbols) and G'' (open symbols) vs. ω for PHB and its blends at 180°C.

a wide range of shear rates, using only a rotational rheometer.

G' and G'' for PHB and its blends are presented in Fig. 5. The decrease of G' for PHB with increasing PEO content can be explained by the destruction of the crystalline structure of PHB [11]. The moduli of PHB80 and of PHB100 were similar to each other because PEO fill the vacancies of PHB, as shown in the morphological studies by Choi et al. [11]. G'', which is larger than G', decreases with increasing PEO content, implying that the energy dissipation caused by the viscosity was larger than the elastic energy storage in the case of PHB.

Fig. 6 shows N_1 vs. $\dot{\gamma}$ and $2G'[1 + (G'/G'')^2]^{0.7}$ vs. ω for PHB and its blend systems following Laun's analysis [38]. Laun has developed an empirical equation that relates the first normal stress difference to the dynamic moduli:

$$\lim_{\dot{\gamma}\to\omega} N_1(\dot{\gamma}) = 2G'[1 + (G'/G'')^2]^{0.7} \tag{6}$$

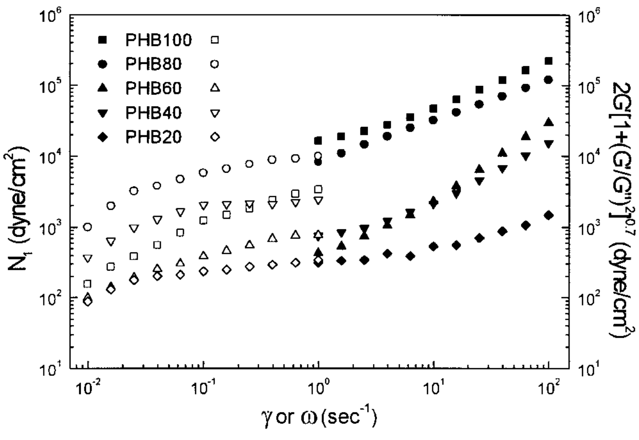

Fig. 6. N_1 (open symbols) vs. $\dot{\gamma}$ and $2G'[1 + (G'/G'')^2]^{0.7}$ (filled symbols) vs. ω for PHB and its blends at 180°C.

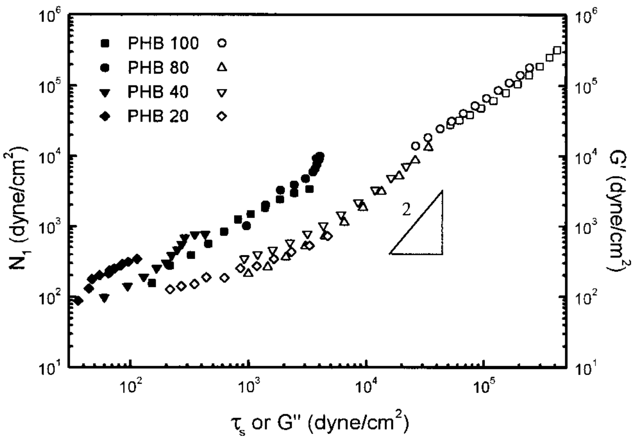

Fig. 7. N_1 (filled symbols) vs. τ_s and G' (open symbols) vs. G'' for PHB and its blends at 180°C.

In the limit of small frequencies or shear rates (i.e. $G'/G'' \ll 1$), we get $N_1(\dot{\gamma}) = 2G'(\omega)$ from Eq. (6).

Fig. 6 also indicates that the N_1 of PHB80 is higher than that of PHB100. This result can also be explained based on the morphological characteristics of PHB80 [11]. N_1 of PHB60 increases rapidly at low shear rates, but it remains almost constant above a shear rate of 0.1 s^{-1}. N_1 values for both PHB40 and PHB20 are lower than that of PHB100. The elastic behavior from the steady shear experiments is closely related to that of the oscillatory experiments at relatively high frequencies.

Fig. 6 gives a better correlation for N_1 vs. $\dot{\gamma}$ and $2G'[1 + (G'/G'')^2]^{0.7}$ vs. ω for PHB and its blend systems, in comparison with the results of Han and Jhon [39] for various commercial grade low-density polyethylenes.

Fig. 7 shows a modified Cole–Cole plot of PHB and its blends, which exhibits little sensitivity to variation in PEO content at a fixed temperature. Further, the slope is slightly less than 2, which is typical for high molecular weight homopolymers. Han and Jhon [39] found that such plots are virtually independent of temperature and molecular weight for the high molecular weight homopolymers. Furthermore, the N_1 vs. τ_s relationship from the steady shear experiment is plotted on a log–log graph in Fig. 7. The curve shows a similar trend as the G' vs. G'' plot, even though there are some scattered data. In simple shear flow, $\dot{\gamma}$ can be considered as an input variable imposed on the fluid, whereas both τ_s and N_1 are output variables, i.e. responses of the fluid under shear. Simply stated, τ_s represents the energy dissipated, and N_1 the energy stored in the fluid. Similarly, in oscillatory shear flow, one may consider ω to be an input variable, whereas both G' (energy stored) and G'' (energy dissipated) are output variables of the fluid under shear. With this interpretation, Han and Jhon [39] suggested that, in comparing the elastic behavior of one fluid against another, N_1 vs. τ_s or G' vs. G'' on log–log graph are useful in studying the rheological compatibility.

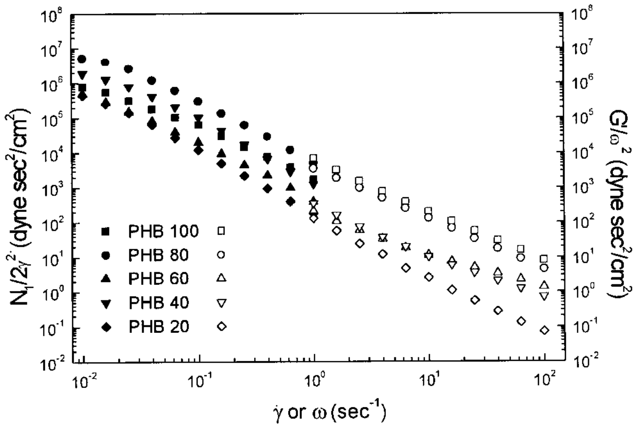

Fig. 8. $N_1/2\dot\gamma^2$ (filled symbols) vs. $\dot\gamma$ and G'/ω^2 (open symbols) vs. ω for PHB and its blends at 180°C.

By studying the elastic behavior of bulk homopolymers, such as polybutadiene, polystyrene, poly(methyl methacrylate), and low-density polyethylene, via N_1 vs. τ_s and of G' vs. G'' plots, Han and Jhon [39] found that these plots are weakly dependent on temperature and the molecular weight for high molecular weight polymers but strongly dependent upon the molecular weight distribution and the degree of side-chain branching.

In Fig. 8, we plot both $N_1/2\dot\gamma^2$ vs. $\dot\gamma$ and G'/ω^2 vs. ω and compare $N_1/2\dot\gamma^2$ and G'/ω^2 at the limiting value of $\dot\gamma$ and ω for PHB100 and its blend systems. For various polymeric liquids, the following relationship is observed:

$$\lim_{\omega\to 0}\frac{G'(\omega)}{\omega^2}=\lim_{\dot\gamma\to 0}\frac{N_1(\dot\gamma)}{2\dot\gamma^2} \tag{7}$$

For PHB and its blends, the values of $N_1/2\dot\gamma^2$ and G'/ω^2 converge at low values of $\dot\gamma$ and ω as shown in Fig. 8.

In conclusion, from the rheological characterization of biodegradable PHB and its blends, we found that the elastic and viscous properties from steady shear experiments are qualitatively related to those measured from the oscillatory experiments despite the thermal degradation of the samples.

Acknowledgements

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