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Viscoelastic characterization of biodegradable poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate)[1]

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Abstract

The viscoelastic properties of microbial biodegradable copolymers containing 3-hydroxybutylate (3HB) and 3-hydroxyvalerate (3HV) were investigated as well as the reference homopolymer, poly(3-hydroxybutylate) (PHB), by plotting the first normal stress difference (N_1) versus shear stress (τ_s) and the storage modulus (G') versus the loss modulus (G''). At low shear rates, the N_1s of the copolymers were higher than that of PHB, and at high frequencies, the G's of the copolymers were lower than that of PHB. To examine the rheological properties of biodegradable copolymers, we used a modified Cole–Cole plot (N_1 versus τ_s and G' versus G''). From these plots, we found that the elastic behavior from steady shear experiment is closely related to that of the dynamic oscillatory experiments for the biodegradable copolymer.

Keywords: P(3HB/3HV); PHB; First normal stress difference

1. Introduction

During the past decade, there has been a great interest in the development of biodegradable polymers as possible candidates to reduce pollution caused by synthetic plastic waste [1]. Poly(3-hydroxybutyrate) (PHB), a biosynthetic aliphatic polyester obtained by bacterial fermentation, has been developed and investigated for this purpose [2]. PHB is a thermoplastic biodegradable and biocompatible polymer and is known to be the most effective pollution control material [3]. PHB also has excellent applicability because of its transparency, solvent resistance, high melting temperature ($T_m \approx 180°C$), and high glass transition temperature ($T_g \approx 4°C$) [2]. The film-type PHB shows gas-barrier properties comparable to those of poly(vinyl chloride) and poly(ethylene terephthalate). As a result, PHB can compete with commodity polymers in the packaging industry, especially in areas where nonbiodegradable plastic items are not permitted. However, some of the undesirable properties of PHB, such as the brittleness of the melt-processed material and/or the thermal degradability of the polymer at processing temperatures, prevents its wide use as a commodity material.

In order to improve these properties, poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (P(3HB/3HV)) random copolymers were formulated by replacing the methyl group with an ethyl group in the PHB main chain. This microbial copolymer has been produced by *Alcaligenes eutrophus* from propionic acid [4] or pentanoic acid [5]. The mechanical properties of the synthesized copolymers are greatly improved over those of the homopolymer PHB. The copolymers also show a wide range of property changes depending on HV content, resulting in the reduction of the melting temperature [6] to between 50 and 180°C.

Furthermore, PHB and P(3HB/3HV) copolymers have also proved to be useful as model materials for investigating physical properties [7]. For example, PHB is an excellent material for investigating polymer nucleation, due to its lack of catalyst residues and perfect tacticity resulting from its biological origin [8]. Despite various investigations on morphology, thermal properties, miscibility and degradability of PHB and its copolymers [9], few studies have been performed based on their rheological or viscoelastic properties. Choi et al. [10] studied the rheological properties of PHB blended with poly(ethylene oxide) (PEO) and found that an 80/20 PHB/PEO blending ratio by weight exhibits higher values of shear viscosity, first normal stress difference, and storage modulus as a function of temperature than

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[1] Dedicated to Professor Icksam Noh on the occasion of his retirement.

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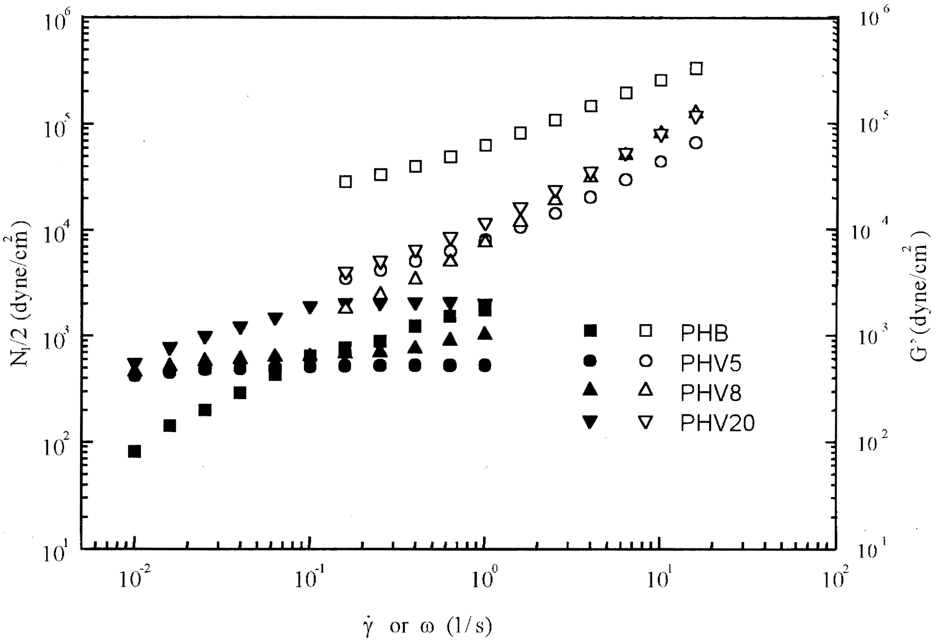

Fig. 1. $N_1/2$ versus $\dot{\gamma}$ (closed symbols) and G' versus ω (open symbols) for PHB and its copolymers at 180°C.

those of pure PHB. In a subsequent paper [11], Choi et al. further examined the rheological properties of PHB and its copolymer using both a rotational and a capillary rheometer. They also examined the viscoelastic properties as functions of time and temperature using Rheovibron.

Our goal in this paper is to re-examine the effect of the HV copolymer content on elastic behavior from logarithmic plots of the first normal stress difference (N_1) versus shear stress (τ_s) and storage modulus (G') versus loss modulus (G''). In simple shear flow, shear rate ($\dot{\gamma}$) can be considered 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 the oscillatory frequency (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 Lem [12] suggested that, in comparing the elastic behavior of one fluid against another, logarithmic plots of N_1 versus τ_s and of G' versus G'' are useful.

By studying the elastic behavior of bulk homopolymers such as polybutadiene, polystyrene, poly(methyl methacrylate) and low-density polyethylene using logarithmic plots of N_1 against τ_s and of G' against G'', Han and Jhon [13] found that these plots are very weakly dependent on temperature and the molecular weight of high molecular weight polymers, but strongly dependent upon the molecular weight distribution and the degree of side-chain branching.

2. Experimental results and discussion

PHB and its copolymer samples (BIOPOL) used in this paper were obtained from ICI (UK). The samples were semicrystalline powder that had been isolated from *A. eutrophus* cultures and precipitated from chloroform solution by the addition of methanol [14]. Compositions of 3HV in the copolymer were 5, 8 and 20 mol%, labeled PHV5, PHV8, and PHV20 respectively. The molecular characteristics of these polymers obtained from gel permeation chromatography (GPC) are identical to those of reference [11]. Disk-type samples, having 2 mm thickness and 2.5 mm radius, were prepared using a hot press and analysed in a parallel plate geometry using an RMS 800 (Rheometric Inc., USA) at a constant temperature of 180°C. From the steady shear experiment, N_1 was obtained as a function of both $\dot{\gamma}$ and τ_s.

The dynamic experiment was also performed for the same geometry. G' and G'' were measured at 180°C as a function of ω with the 15% deformation. Note that N_1 in steady shear flow and G' in oscillatory shear flow are considered as the amount of energy stored in a viscoelastic fluid, and τ_s in steady shear flow and G' in oscillatory shear flow are considered as the amount of energy dissipated. Therefore, the ratios N_1–τ_s and G'–G'' may be interpreted as the ratio of the energy stored to the energy dissipated [13].

Fig. 1 shows $N_1/2$ as a function of $\dot{\gamma}$, and G' as a function of ω for PHB and its copolymers. At low shear rates, the $N_1/2$s of all three copolymers are higher than that of PHB. This is due to the fact that those copolymers possess an ethyl branch, which enhances repulsion and contributes to $N_1/2$

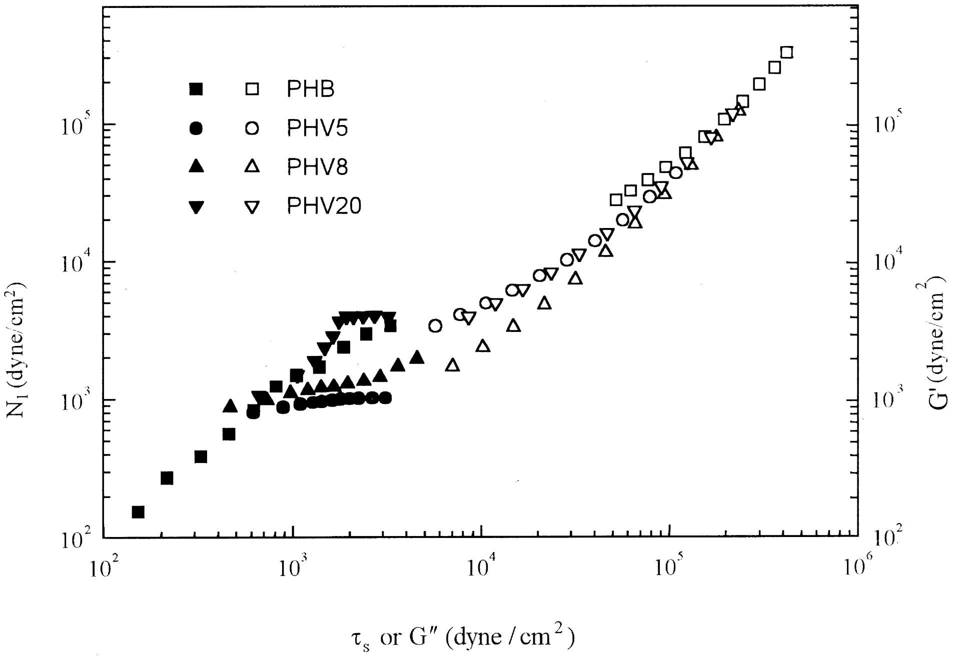

Fig. 2. N_1 versus τ_s (closed symbols) and G' versus G'' (open symbols) for PHB and its copolymers at 180°C.

at low shear rate. However, $N_1/2$ of the homopolymer (PHB) becomes greater than those of the copolymers above 1 s^{-1} shear rate. The elastic behavior from the steady shear experiment are very well related to those from the dynamic oscillatory experiment at relatively high frequencies. G' of the copolymers are lower than that of PHB due to the slow relaxation of the long branch chain of the polymer. From the steady shear and the oscillation experiments, the elasticity of the copolymer increases slightly as the PHV content increases. Compared to the results, which Han and Jhon [13] obtained for various commercial grade low-density polyethylenes, Fig. 1 shows a better correlation between $N_1/2$ versus $\dot{\gamma}$ and G' versus ω for the biodegradable PHB and its copolymers.

Fig. 2 shows a modified Cole–Cole plot for PHB and its copolymers. The G'–G'' plot shows little sensitivity to copolymer ratios. In the region of G'' from 10^4 dyne/cm^2 to 10^6 dyne/cm^2, the G'–G'' plot gives a correlation only

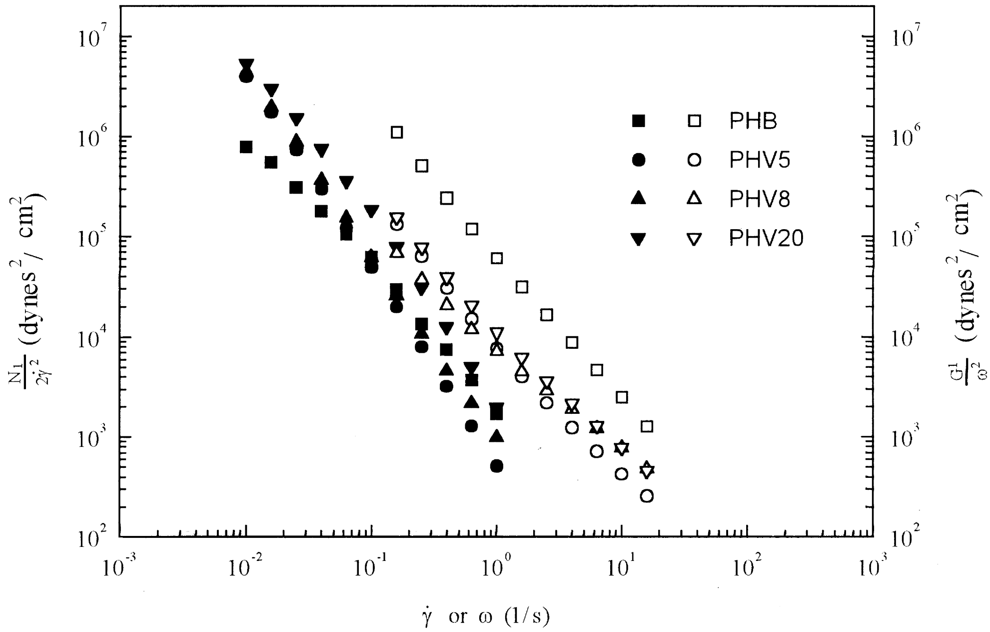

Fig. 3. $\frac{N_1}{2\dot{\gamma}^2}$ versus $\dot{\gamma}$ (closed symbols) and $\frac{G'}{\omega^2}$ versus ω (open symbols) for the PHB and its copolymers at 180°C, satisfying the limiting behavior as $\omega, \dot{\gamma} \rightarrow 0$.

slightly sensitive to the molecular weight distribution of the polymer samples tested [13]. It has been observed that G'–G'' plots are virtually independent of the molecular weight of the polymer sample tested [13]. However, the slight increase in log G' shown in Fig. 2 is attributable in part to the increase in the polydispersity index (PDI), i.e. the broadening of the molecular weight distribution. PDIs for the copolymers were 3.64, 2.54, and 2.65 for PHV5, PHV8, and PHV20 respectively. The effect of PDI on G'–G'' plots for various polymers such as polystyrenes and polybutadienes can be found in reference [13]. However, at high frequencies, this sensitivity to copolymer PDI decreases. In addition, the N_1–τ_s plot obtained from the steady shear experiment, overlapped on Fig. 2, shows a similar trend to the G'–G'' plot, though some scattered data are observed.

It is noted that the ratio of N_1 to τ_s in steady simple shear flow may be defined as the dimensionless Weissenberg number, characterizing the ratio of elastic to viscous forces for the polymer system or the degree of stretching of the macromolecule in a flow field [15, 16]. For most polymer solutions or melts in general, this ratio is approximately unity [17].

In addition, in Fig. 3 we plot both $N_1/2\dot{\gamma}^2$ versus $\dot{\gamma}$ and G'/ω^2 versus ω and compare $N_1/2\dot{\gamma}^2$ and G'/ω^2 for PHB and its copolymers. For various polymeric liquids [16, 18–20], it is found that the following continuum mechanics requirement is observed:

$$\lim_{\omega \to 0} \frac{G'(\omega)}{\omega^2} = \lim_{\dot{\gamma} \to 0} \frac{N_1(\dot{\gamma})}{2\dot{\gamma}^2}. \tag{1}$$

As shown in Fig. 3, for all three copolymers except the homopolymer, the values of $N_1/2\dot{\gamma}^2$ and G'/ω^2 coincide at low values of $\dot{\gamma}$ and ω.

In conclusion, from this rheological characterization of biodegradable P(3HB/3HV), we found that the elastic behavior from steady shear experiments is closely related to that of the dynamic oscillatory experiments, when we analyzed logarithmic plots of N_1 versus τ_s and G' versus G''.

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