

Effect of additives on the melt rheology and thermal degradation of poly[(R)-3-hydroxybutyric acid]

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ABSTRACT: Thermal degradation of poly[(R)-3-hydroxybutyric acid] (PHB) during melt mixing results in random chain scission that produces shorter polymer chains containing crotonic and carboxyl end groups. One way of preventing this serious reduction of molar mass is to add agents that react with at least two of the newly generated end groups. Different types of commercially available additives known to react with carboxyl group, namely bis(3,4-epoxycyclohexylmethyl) adipate (BECMA), 2,2'-bis(2-oxazoline) (BOX), trimethylolpropane tris(2-methyl-1-aziridinepropionate) (PETAP), triphenyl phosphate (TPP), tris(nonylphenyl) phosphate (TNPP), polycarbodiimide (PCDI), and poly(methyl methacrylate-co-glycidyl methacrylate) (GMA.MMA) were mixed with PHB by cocasting from solution in chloroform. Dynamic rheology as well as measurements of molar masses before and after dynamic analysis was used to evaluate the effect of the additives on the melt stability of PHB. Measurements of the dynamic shear modulus and the molar mass of molten PHB with the additives PCDI and GMA.MMA showed a minor improvement on the thermal stability. Furthermore, TPP and TNPP did not affect the thermal stability of PHB, whereas the presence of BECMA, BOX, and PETAP gave a strong decrease of the dynamic modulus compared with neat PHB. © 2014 The Authors Journal of Applied Polymer Science Published by Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41836.

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INTRODUCTION

Polyhydroxyalkanoates (PHAs) are biobased, biodegradable, and sustainable polyesters that are accumulated as intracellular carbon energy storage material by a wide range of bacteria. In addition, PHAs can be processed as conventional petrochemical-based plastics. The most common PHA is poly(3-hydroxybutyrate) (PHB) which was also the first type of PHA to be studied, characterized and commercialized.¹ PHB shows mechanical properties similar to those of well established polymers, such as polypropylene, and has a glass transition temperature around 4°C, 60% crystallinity and a melting temperature around 175°C.² However, PHB is brittle at room temperature and has a fairly narrow processing window due to thermal degradation at higher temperatures. By chain scission

through β -elimination, PHB-chains break randomly into smaller sub-chains. As a result, the molar mass decreases and the mechanical properties of the biopolymer are altered. To overcome this issue, several kinds of PHAs have been biosynthesized by incorporating additional units into the PHB backbone, thus forming copolymers with lower melting temperature such as poly(3-hydroxybutyrate-co-3-hydroxyvalerate), poly(3-hydroxybutyrate-co-3-hydroxyhexanoate), and poly(3-hydroxybutyrate-co-4-hydroxybutyrate), which broadens the processing window in relation to PHB.^{3,4} Moreover, blends of PHB with poly(ethylene oxide), poly(methyl acrylate), poly(vinyl acetate), poly(vinyl alcohol), epoxidized natural rubber, poly(vinylidene fluoride), poly(epichlorhydrine), poly(butylenes adipate), ethylene-propylene rubber, modified EPR rubbers, grafted with succinic anhydride (EPR-g-SA) and dibutyl maleate (EPR-g-DBM), or

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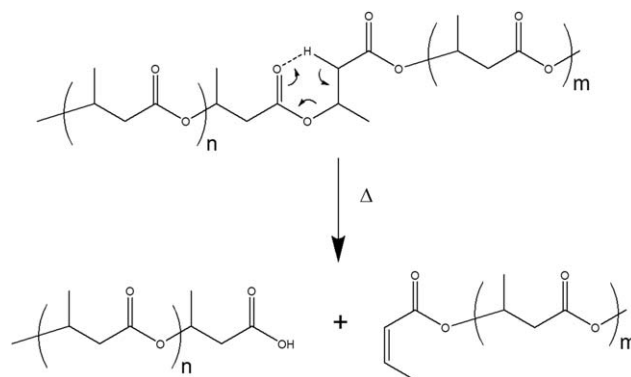
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poly(vinyl phenol) have been studied as a way of improving the mechanical properties of PHB.^{5–18} The use of additives such as inorganic oxides, quaternary ammonium salts, salts of organic and mineral acids, and metal compounds have also been studied, having in most cases a pronounced detrimental effect on the thermal stability of the PHB.^{19–23} Recently, Persico *et al.* claimed an enhancement of the thermal stability of PHB by adding pomace extract.²⁴ Pomace extract contains, however, a large variety of chemical components which specific activities are unknown. Crotonic and carboxylic acid end groups are generated as a consequence of the β -elimination reaction. Polymerization of the crotonyl moieties have been attempted by employing different combinations of free radical initiators along with multifunctional unsaturated compounds.²⁵ However, not only the formation of crosslinks but also an acceleration of the thermal degradation of PHB was observed. The carboxylic acid end group, on the other hand, has been targeted in two different studies by a poly(methyl methacrylate-co-glycidyl methacrylate) (PGMA) which contains pendant epoxide groups, and a polymeric carbodiimide agent (PCDI).^{26,27} In the former, the authors claimed an improvement of the thermal stability of PHB due to a crosslinking reaction between the PHB carboxyl end groups and the epoxide groups, as observed by thermogravimetric analysis (TGA). In the later, TGA and size exclusion chromatography (SEC) studies showed an increase in the molar mass of PHB although a decrease of its thermal stability by the addition of PCDI. In these studies as well as in many others involving the thermal stability of PHB, the starting material is usually employed as-received. As-received PHB contains metal ions and other impurities which are known to accelerate the polymer degradation process.²⁸ The presence of such impurities may then impede a more fundamental understanding of the thermal degradation and chain-extension chemistry of PHB.²⁹ In this study, a purified and high molar mass PHB has been used in conjunction with additives known to react with carboxylic acid groups. Here we report, a systematic analysis of the modification of the thermal stability of PHB in the melt by the incorporation of such additives.

EXPERIMENTAL

Materials

PHB with $M_w = 620 \text{ kg mol}^{-1}$ was supplied by BIOMER and treated with acidic water according to a previously disclosed procedure to increase the decomposition temperature.²⁹ Poly(methyl methacrylate-co-glycidyl methacrylate) (GMA.MMA) was prepared as previously reported.³⁰ Polycarbodiimide (PCDI, Stabaxol P) was received from Rhein Chemie. 2,2'-Bis(2-oxazoline) (>97%) (BOX) was purchased from TCI. Triphenyl phosphite (97%) (TPP), tris(nonylphenyl) phosphite (TNPP), and trimethylolpropane tris(2-methyl-1-aziridinepropionate) (technical, $\geq 90\%$) (PETAP) were purchased from Sigma-Aldrich. Bis(3,4-epoxycyclohexylmethyl) adipate (BECMA) was purchased from Univar AB (Sweden). Hydrochloric acid and chloroform HPLC grade were purchased from Fisher. With the exception of PHB, all chemicals were used without further purification. The molar mass of the additives is shown in Supporting Information Table S1.



Scheme 1. Mechanism of β -elimination and scission.

Preparation of the Samples

Thin films were prepared by casting from solutions of the mixed components, followed by evaporation of the solvent at room temperature. First, PHB (ca. 700 mg) was dissolved in chloroform (80 mL) at 100°C in a sealed vessel during 5 min. Once at room temperature, the PHB solution was transferred and diluted in a 100-mL volumetric flask. To 25-mL aliquot of the solution, different amounts of a solution of the additive in chloroform (ca. 1 mg/mL) were added to achieve the desired concentrations. After casting, the films were dried under vacuum at 60°C for 24 h. Finally, the films were pressed at 180°C for 2 min to produce discs with a diameter of 15 mm and a thickness of ~ 0.85 mm.

Rheology

Dynamic mechanical analysis of the melt was carried out with an Advanced Rheometer AR2000 ETC from TA Instruments. Parallel plates with a diameter of 15 mm were used for the measurements. Time sweep experiments in shear were performed at 180°C , at an angular frequency of 62.83 rad s^{-1} (10 Hz) and a strain amplitude of 2%, under nitrogen atmosphere. Each test was started 2.5 min after the insertion of the disc into the rheometer at 180°C . This allowed for the attainment of thermal equilibrium. The phase angle δ and the dynamic shear modulus $|G^*|$, expressed as:

$$|G^*| = \frac{\tau_{\text{ampl}}}{\gamma_{\text{ampl}}} \text{ [Pa]} \quad (1)$$

where τ_{ampl} and γ_{ampl} are the maximum stress amplitude and maximum strain amplitude, respectively, were measured.

Size Exclusion Chromatography (SEC)

Molar masses and molar mass distributions were determined by SEC using three Shodex columns in serie (KF-805, -804, and -802.5) and a refractive index (RI) detector (Viscotek Model 250). All samples were measured at room temperature in chloroform at a concentration of 3 mg mL^{-1} , and at an elution rate of 1 mL min^{-1} . Calibration was obtained by four polystyrene standard samples ($M_n = 650 \text{ kg mol}^{-1}$ from Water Associates, 96 and 30.3 kg mol^{-1} from Polymer Laboratories, and 3180 g mol^{-1} from Agilent Technologies).

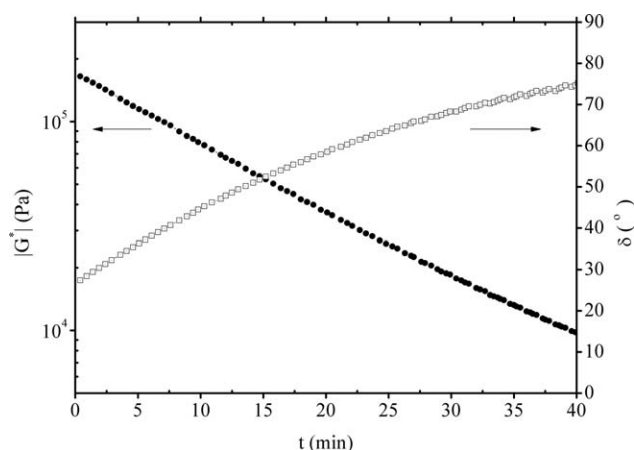


Figure 1. Dynamic shear modulus and phase angle delta of PHB as a function of time at 180°C and $\omega = 62.8 \text{ rad s}^{-1}$.

RESULTS AND DISCUSSION

There is a general agreement in the literature that the thermal degradation of PHB proceeds mainly via the mechanism of β -elimination and scission, where smaller polymer segments containing carboxylic acid and crotonic end-groups are randomly generated (Scheme 1).^{31–33}

However, other mechanisms including E1cB via carboxylate-induced α -deprotonation, and the occurrence of auto-acceleration during thermal degradation have been suggested as well.^{34,35} Nonetheless, the thermal degradation in the melt state can easily be monitored using dynamic mechanical analysis by means of a rheometer in the transition from the rubber plateau to the Newtonian flow region due to the relation between the viscoelastic properties and the molar masses.³⁶ Figure 1 shows the dynamic shear modulus and the phase angle δ for PHB at 180°C as a function of time at a frequency of 62.8 rad s⁻¹. At this temperature, the dynamic shear modulus drops by about 94% during 40 min which implies a decrease in the weight average molar mass of 77% as indicated by SEC measurements

Table I. Dynamical Shear Modulus and Molar Mass of Neat PHB and PHB Containing PCDI and GMA.MMA after 40 min at 180°C

Sample	$ G^* $ (kPa)	M_w (kg mol ⁻¹)
Pristine PHB	164.9	620
PHB	10.6	142
0.5 wt % PCDI	11.6	152
1 wt % PCDI	15.9	174
2 wt % PCDI	14.2	162
3 wt % PCDI	14.4	170
1 wt % GMA.MMA	14.2	157
2 wt % GMA.MMA	16.9	190
3 wt % GMA.MMA	20.9	203
5 wt % GMA.MMA	23.2	228
10 wt % GMA.MMA	31.3	246
20 wt % GMA.MMA	29.9	252
30 wt % GMA.MMA	23.0	224

(Table I). In addition, the phase angle δ increases from 27 to 75°, thus indicating a behavioral change of the viscoelastic properties of the molten polymer, from being predominantly elastic to almost Newtonian.

One way of compensating for the decrease in dynamic modulus caused by random scission during the thermal degradation is to incorporate small amounts of chain-extenders.^{37,38} These compounds contain active groups that may potentially react with the chain-ends of the degraded PHB in the melt, thus increasing the average molar mass of the polymer. In this study, we

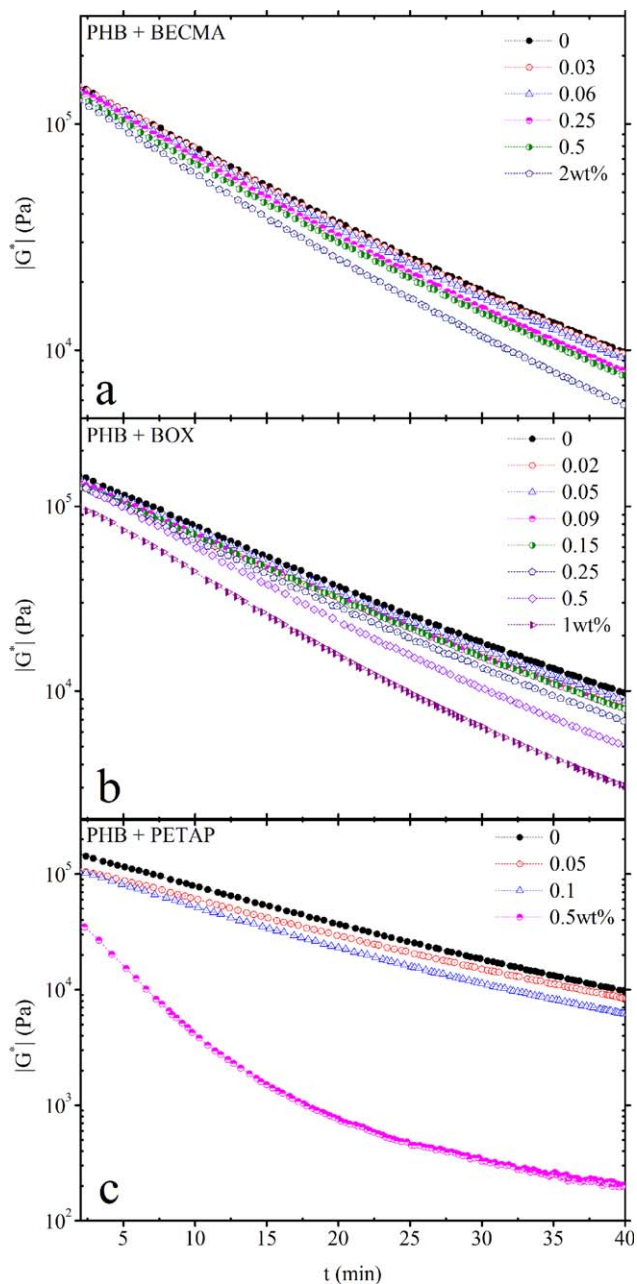
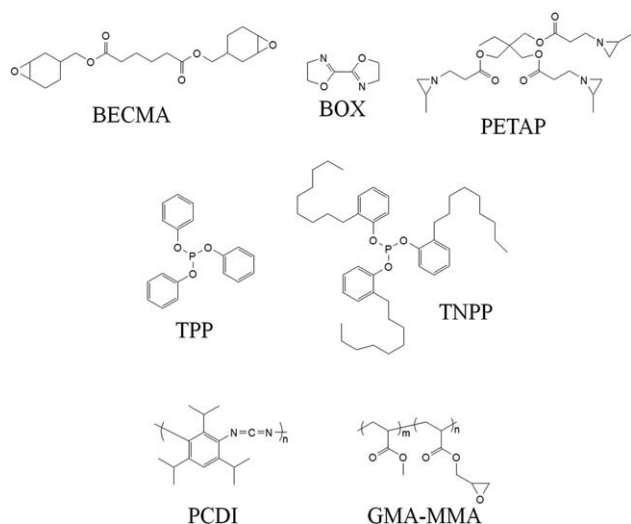


Figure 2. Dynamic shear modulus of neat PHB and PHB containing (a) BECMA, (b) BOX, and (c) PETAP as a function of time, at 180°C and $\omega = 62.8 \text{ rad s}^{-1}$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Scheme 2. Chemical structures of the different additives.

focused on compounds known to react with carboxyl-terminated polyesters. Di-epoxide (BECMA), bisoxazoline (BOX), triaziridine (PETAP), triarylphosphites (TPP and TNPP), polycarbodiimide (PCDI), and multi-functional epoxide (GMA-MMA) were mixed with PHB by solvent-casting, and the effect on the rheology and molar mass of molten PHB was examined, see Scheme 2.

It is important to stress at this point that characterization of possible interactions between the additives and the end groups of thermally degraded PHB were not feasible. Even after 40 min at 180°C the molar mass of PHB lays well above the level for end-group analysis using either proton nuclear magnetic resonance ($^1\text{H-NMR}$) or Fourier transform infrared spectroscopy (FTIR). Figure 2 shows the thermal degradation process of PHB with increasing amounts of bifunctional (BECMA and BOX) and trifunctional (PETAP) chain-extenders, respectively. The content of the additives ranged from 0.03 to 2 wt % for BECMA, 0.02 to 1 wt % for BOX and 0.05 to 0.5 wt % for PETAP. The addition of BECMA shows no increase in the dynamic shear modulus during the 40 min long experiment at 180°C in the rheometer, Figure 2(a). On the contrary, as the amount of di-epoxide compound is increased, the modulus dropped systematically from 9.7 kPa, for pure PHB, to 5.7 kPa for PHB containing 2 wt % BECMA, after 40 min. In the case of PHB containing BOX, Figure 2(b), a similar tendency is observed. The dynamic modulus, after 40 min at 180°C, falls even further to 3.1 kPa for PHB containing 1 wt % bisoxazoline. The effect of PETAP on the thermal stability of PHB is even more negative, Figure 2(c). At a concentration of 0.5 wt % of triaziridine, the shear modulus decreased already after 20 min by 99.5% compared with 78% for the pure PHB.

Bakar *et al.* studied the melt reaction in blends comprising PHB and epoxidized natural rubber (ENR), and showed that the rate constant for PHB decay was always higher than the rate constant for the carboxylic acid consumption reaction, for all different temperatures studied.¹¹ Furthermore, it was shown that ENR did not only react with PHB but that it also raised the decay constant for PHB as the concentration increased. Conse-

quently, the effect of BECMA on thermal stability of PHB in the melt in this work is consistent with the results from the aforementioned study.

The addition of triarylphosphites to molten polyesters has been shown to stabilize their thermal stability in several studies.^{39–41} The mechanism involves selective reactions between polymer chain ends and the phosphate, thus avoiding transesterification reactions and hydrolytic degradation. In this work, the addition of either TPP (from 0.05 to 1 wt %) or TNPP (from 0.05 to 2 wt %) showed no effect on the thermal stability of PHB at 180°C during 40 min in the rheometer. Figure 3 shows the rheology results for the PHB/TPP and the PHB/TNPP, respectively. Regardless of the concentration of the phosphites, the dynamic shear modulus remains at the same level as that of the pure PHB during the entire experiment.

Polycarbodiimides have been used since the early 60s to cross-link polymers with carboxylic acid functional groups.⁴² The use of polycarbodiimide has also been reported to stabilize PLA during processing and even PHB.⁴³ In our study, the dynamic shear modulus was measured for the system PHB/PCDI from 0.05 to 3 wt %, Figure 4(a). The effect of the additive after 40 min shows an increase of the moduli in comparison to pure PHB. At a concentration of 1 wt % of PCDI, the modulus

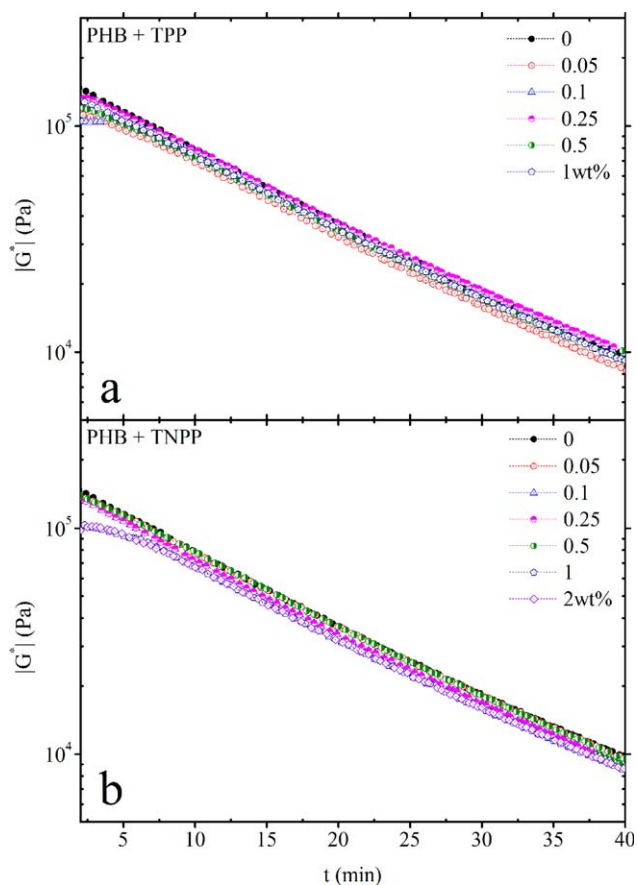


Figure 3. Dynamic shear modulus of neat PHB and PHB containing (a) TPP and (b) TNPP as a function of time, at 180°C and at $\omega = 62.8 \text{ rad s}^{-1}$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reached a peak value of 15.9 kPa. The SEC measurements of the modified samples at 180°C after 40 min confirmed the enhanced molar mass, see Table I.

Since the system PHB/BECMA degraded the least amongst the systems PHB/bifunctional additive, after 40 min at 180°C, we also attempted the approach of using a multifunctional epoxide chain-extender to compensate for the reduction of molar mass of PHB. A copolymer of glycidyl methacrylate and methyl methacrylate (GMA.MMA) was mixed with PHB by the solvent casting method, ranging from 0.1 to 30 wt %. Figure 4(b) shows a systematic enhancement of the dynamic shear modulus as the concentration of GMA.MMA increased, reaching a peak value at a concentration of 10 wt %, after 40 min at 180°C. At concentrations higher than 5 wt %, the rheological behavior of the system PHB/GMA.MMA started to show a plasticizing effect caused by the additive. The shear modulus was indeed lower than that of PHB containing less than 5 wt %, already at the beginning of the experiment. This was confirmed by SEC measurements prior to the rheological experiments, where the molar masses of PHB containing 5 wt % of GMA.MMA and higher, were the same as that found for the pure PHB (data not shown). Figure 5 and Supporting Information Table S2 show the dynamic shear modulus and the phase angle δ after 30 min

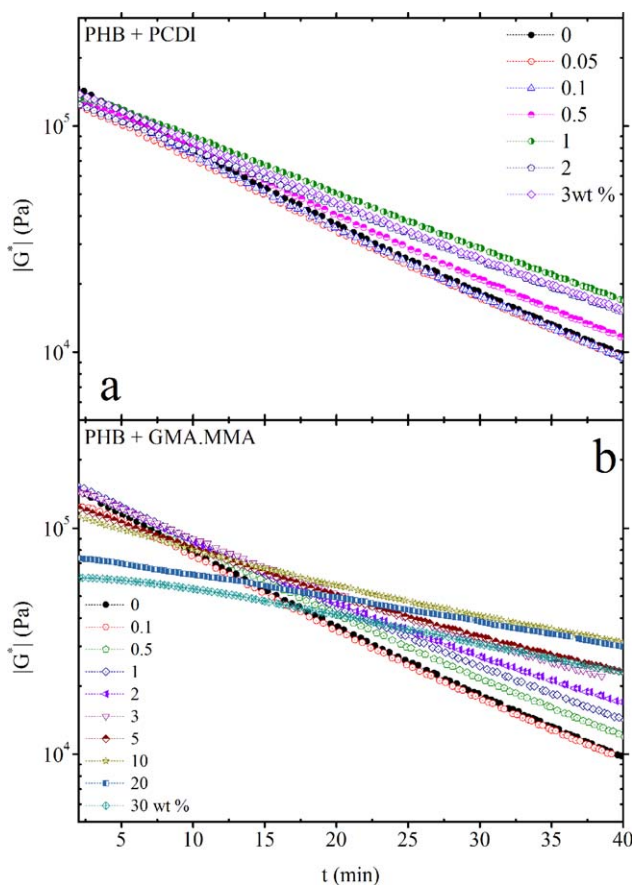


Figure 4. Dynamic shear modulus of neat PHB and PHB containing (a) PCDI and (b) GMA.MMA as a function of time, at 180°C and at $\omega = 62.8 \text{ rad s}^{-1}$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

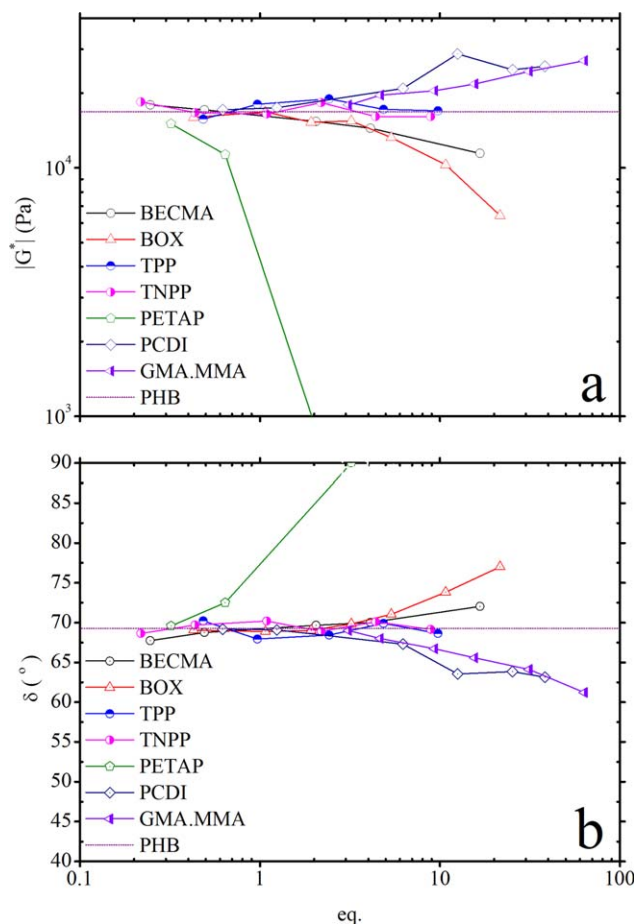


Figure 5. Dynamic shear modulus (a) and phase angle delta (b) of PHB with and without additives after 30 min at 180°C as a function of the equivalent ratio between functional group equivalents of the additives and carboxylic acid equivalents of PHB with a number average molar mass of about 300 kg mol^{-1} . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

at 180°C as a function of the equivalent of additive added, considering a number average molar mass for PHB of about 300 kg mol^{-1} . Only in the case of adding multi-functional additives (PCDI and GMA.MMA), the shear modulus is somewhat increased compared with pure PHB. Consistently, the phase angle for mentioned systems decreases when the shear modulus increases, and thus indicates the increase in the molar mass of PHB. In addition, when comparing the effect of bifunctional chain-extenders, it was observed that bisoxazoline (BOX) had a more negative effect on the thermal stability of molten PHB than di-epoxide (BECMA). Triarylphosphites (TPP and TNPP) did not lower the shear modulus nor increase the phase angle of PHB after 40 min at 180°C, whereas trifunctional aziridine (PETAP) had a strong negative effect on the thermal stability of molten PHB as clearly observed from Figure 5.

CONCLUSIONS

The effect on the melt stability of a purified PHB by using commercially available additives was investigated through rheometry and size exclusion chromatography measurements. Despite a

careful purification of the PHB used, bifunctional epoxide (BECMA), bifunctional oxazoline (BOX), and trifunctional aziridine (PETAP) had a clear, unexpected negative effect on the thermal stability of PHB as the amount of additive increased. Neither triaryl phosphite (TPP and TNPP) caused any significant effect on the thermal stability of PHB. Finally, minor improvements on the melt stability were achieved by using the multifunctional epoxide (GMM.MMA) and the multifunctional carbodiimide (PCDI). The disparity among the results obtained is considered to be due to the existence of two competing factors affecting the melt stability of PHB. One is the increase of rate of chain scission, which, besides the temperature, is influenced by interaction with the additive, and the other is a possible chain extension. Further research is needed to gain a deeper understanding of the role of both effects.

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