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CHAIN EXTENDED POLY(3-HYDROXYBUTYRATE) WITH IMPROVED RHEOLOGICAL PROPERTIES AND THERMAL STABILITY, THROUGH REACTIVE MODIFICATION IN THE MELT STATE

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Chain extended poly(3-hydroxybutyrate) with improved rheological properties and thermal stability, through reactive modification in the melt state^a

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Abstract

Branching and crosslinking of polyhydroxybutyrate (PHB) is accomplished for the first time through reactive modification in the melt state, using dicumyl peroxide (DCP) as the free-radical initiator and a tri-functional coagent, triallyl trimesate (TAM). The dynamic oscillatory rheological properties, as well as extensional viscosities provide strong evidence of branching and crosslinking, depending on the amounts of DCP and TAM. In addition to the significant increases in viscosity due to branching/crosslinking, coagent modified samples exhibit a significant increase in the crystallization temperature, indicative of a nucleating effect, accompanied by a decrease of crystal spherulite sizes. In addition, the solid-state storage modulus in DMTA experiments is 65% higher in formulations that contain high gel contents, whereas the glass transition temperature of the cured formulations is slightly lower. Coagent modified PHB exhibit a substantial improvement in the thermal stability, both in isothermal dynamic oscillatory temperature sweeps, as well as non-isothermal TGA experiments.

Keywords: polyhydroxybutyrate; reactive extrusion; crosslinking; branching; dicumyl peroxide; triallyl trimesate

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1. Introduction

Poly(3-hydroxyalkanoates) (PHAs) are microbially produced, biodegradable polymers derived from renewable resources [1]. PHAs can degrade to water and carbon dioxide in the presence of microorganisms in different environments, such as seawater, soil and sludge. Depending on their structure they are considered to be suitable alternatives to conventional thermoplastics, such as polyethylene, polypropylene and some synthetic elastomers, since they possess similar material properties [2, 3]. Recently, there has been significant expansion in the number of studies using short and medium-chain length PHAs (polyhydroxybutyrate (PHB), polyhydroxyoctanoate (PHO), polyhydroxynonanoate (PHN) and etc.) for biomedical applications [4-10].

Poly(3-hydroxybutyrate) [P(3HB)] is the most commonly used and best characterized member of the PHA family. It is a biopolymer with exceptional stereochemical purity. The chiral centers in the linear chains all possess the R-stereochemical configuration. Therefore, the polymer is highly crystalline [11], with properties similar to high-density polyethylene and polypropylene. However, PHB is very brittle and prone to thermal degradation at temperatures above the melting point. This limits seriously its potential applications [12-16]. The processability and mechanical properties of PHB can be improved through copolymerization or blending [17-22]. For instance, poly[(3-hydroxybutyrate)-co-(3-hydroxyvalerate)] (PHBV), a copolymer comprising 3-hydroxybutyrate (HB) and 20 wt% 3-hydroxyvalerate (HV) is a tough material, with significantly improved thermal stability [23]. Numerous blends of PHB with other PHAs, such as poly(3-hydroxyoctanoate) (PHO) [19, 24], PHBV [25] as well as with other polymers, and plasticizers, such as polycaprolactone (PCL), polyvinyl butyral (PVB), poly(methyl methacrylate) (PMMA), polylactic acid (PLA), starch etc., have been studied [25-33].

Chemical modification techniques, such as chain extension, crosslinking, grafting and functionalization are frequently used to increase the utility of commodity polyolefins and polyesters, [34-38], as well as biopolymers, such as thermoplastic starch and various biopolyesters [39-41]. These modifications can be carried out in solution, or by using solvent-free modifications in the melt state. The latter, which are generally considered more environmentally friendly and suitable for larger scale production, are carried out using conventional polymer processing operations, such as twin-screw extruders [42-46].

Biopolyesters, such as PHB and PLA generally suffer from low melt strength and slow crystallization kinetics, which limit their use in many polymer processing applications. In PLA, chain extension techniques to improve the melt strength and processability using multi-functional chain extenders such as tris (nonylphenyl) phosphite, polycarbodiimide and epoxy-functionalized oligomeric acrylic copolymer

(trade name Joncryl[®] from BASF) have been particularly successful [47-49]. However these techniques have not been proven effective in PHB.

Free-radical mediated, reactive modification approaches that are initiated by peroxides, as well as irradiation techniques, can also be used to modify the architecture of linear polyolefins and to generate cross-linked structures in solvent-free melt-state processing. This approach has also been considered as a means to cross-link medium-chain length PHAs, such as PHO [24, 50] and PHBV [18, 23]. To the best of our knowledge, chain extension or cross-linking of PHB using free-radical mediated reactions has never been accomplished. In polymers having tertiary carbons in their backbones, such as polypropylene and PHB, processing in the presence of free-radicals causes severe chain scission. To counteract this, free radical- mediated- reactive extrusion in the melt state, assisted by coagents is frequently employed as a means to introduce long-chain branching [42, 51, 52]. We recently implemented peroxide-initiated grafting of a multi-functional coagent, triallyl trimesate (TAM) in the melt state together with dicumyl peroxide (DCP), to obtain PLA with long chain branching having significantly improved melt strength and crystallization kinetics [53]. The same approach successfully increased the viscosity of polyhydroxyalkanoate (PHO), a medium-chain length PHA, and resulted in reactively modified PLA/PHO blends with significant improvements in melt strength, and crystallinity [54]. The present work implements this approach to modify the chain architecture of PHB. Depending on the amounts of DCP and TAM, chain extended, or cross-linked PHB with high amounts of gel, is obtained for the first time to be best of our knowledge. We further report substantial improvements in the melt-state properties, modulus and thermal stability of the polymer.

2. Experimental

2.1 Materials and compounding

Additive-free PHB with a weight-average molecular weight of 1,416 kg/mol and polydispersity of 7 (as reported by the supplier), was supplied by BIOMER, Krailling, Germany. Triallyl trimesate (TAM, 98%) and dicumyl peroxide (DCP, 98%) were used as received from Sigma–Aldrich. JoncrylTM 4368 a multifunctional epoxide styrene-acrylic oligomeric chain extender, containing glycidyl methacrylate (GMA) functions was supplied by BASF.

DCP (0.2,0.3 wt%) and TAM (0.2–1 wt%) were dissolved in acetone and coated onto PHB powders in a Petri dish. The coated pellets were placed in a vacuum oven overnight at 60 °C to remove the solvent and moisture. Subsequently the mixtures were mixed in a DSM microcompounder at 190 °C for 6 min at a

screw speed of 100 rpm to ensure complete reaction. The curing time is estimated from the half-life of the peroxide at the curing temperature. Usually, the peroxide curing process is estimated to end after a period of five times of that of the half-life of the peroxide (the half-life time of the DCP at 190°C is around 1 min). The resulting compounds are designated using the name of the polymer, followed by the amounts of DCP and TAM (e.g. PHB/0.3/1 denotes PHB reacted with 0.3 wt.% DCP and 1 wt.% TAM).

To provide a suitable comparison, 2 wt% Joncryl[®], which is one the most common used polymer branching agent used in polyesters, was blended with PHB using the DSM microcompounder under the same conditions as described above.

2.2 Characterization

2.2.1 Rheology

The rheological properties were measured using an MCR-301 Anton Paar rheometer. Compression-molded disks, having 20 mm diameter and 2 mm thickness, were prepared using a Carver press at 190 °C. The viscoelastic properties were measured in the shear oscillatory mode by means of 25 mm parallel plate geometry at 190 °C. Frequency sweeps were conducted at 190°C at a frequency range between 1 and 250 rad·s⁻¹. The lowest frequency was kept at 1 rad/s, to limit the exposure time of the samples, as PHB is known to suffer from extensive thermal degradation. Time sweeps were conducted at a frequency of 1 Hz and 190 °C to assess the stability of PHB and the modified samples.

Samples were further characterized in uniaxial extension using an SER-2 universal testing platform from expansion instruments hosted on an MCR-301 by Anton Paar. In the SER fixture 10 mm wide × about 700 μm thick rectangular polymeric film specimens were fixed with clamps on two counter-rotating cylindrical drums. While one cylinder is driven by the MCR-301 motor, the other rotates in the opposite direction and is directly coupled with the torque transducer of the rheometer to measure the torque on the sample. The transient uniaxial elongational viscosity was calculated from the measured force and the applied Hencky strain rate. For the present case, measurements were conducted at 190 °C at Hencky strain rates of 0.10 and 1 s⁻¹. The linear viscoelastic (LVE) oscillatory measurements obtained at 190 °C were used to calculate the LVE stress growth curve, η^+ , and to check the consistency of the extensional measurements. The curve corresponding to $3\eta^+$ represents the LVE envelope in uniaxial extension, according to Trouton's law.

2.2.2 Thermal analysis

Differential Scanning Calorimetry (DSC) was performed on a Q100 DSC from TA Instruments, under dry nitrogen. All samples were first heated to 200 °C at a heating rate of 5°C·min⁻¹ and maintained at this temperature for 3 min to erase previous thermal history, then cooled to -70 °C and reheated to 200 °C. The cooling and reheating rates were 5 °C·min⁻¹. The crystallinity of the PHB was calculated via Eq. (1):

$$X_c = \frac{\Delta H_m}{\Delta H_{100}} \times 100 \quad (1)$$

where ΔH_m is the thermodynamic enthalpy of fusion per gram of PHB and ΔH_{100} is the theoretical fusion enthalpy of a polymer with 100% crystallinity which is 146.6 J·g⁻¹ for PHB.

Thermogravimetric analysis (TGA) was conducted on a Q500 TGA from TA Instruments under nitrogen atmosphere. The weight loss was recorded by heating to 700 °C at a heating rate of 20 °C·min⁻¹. Isothermal experiments were also conducted at the blending temperature of 190 °C for 20 min.

2.2.3 Gel content

To calculate the gel content, the samples were Soxhlet-extracted with boiling chloroform for 18 h to thoroughly remove the soluble fractions. Approximately 0.35 g of the samples were cut into small pieces and wrapped in a pre-weighted standard wire mesh. The swelled samples were dried in a vacuum oven. The gel fraction were calculated by dividing the final weights with the initial weights of the gels as Eq. (2):

$$\text{Gel content} = \frac{\text{Final weight of sample}}{\text{Initial weight of sample}} \times 100 \quad (2)$$

2.2.4 Optical microscopy

Isothermal crystallization experiments were carried out using a Linkam CSS 450 hot stage mounted on an Olympus BX51 optical microscope. Disk-shaped samples were first heated to 200 °C at a rate of 30 °C·min⁻¹ and then cooled to 120 and 130 °C at 30 °C·min⁻¹. The crystallization process was recorded isothermally at 135 °C using a Sony ExwaveHAD 3 CCD digital recorder.

2.2.5 Dynamic mechanical thermal analysis (DMTA)

DMTA was carried out using a TA Instruments DMA 2980 from -20 to 80 °C at a heating rate of 5 °C min⁻¹ and a frequency of 1 Hz. The measurements were carried out using the dual cantilever clamp mode on samples of size 41.24 × 9.66 × 3.05 mm³. The samples were prepared via compression molding in a hot press at 190 °C under nitrogen atmosphere, followed by quenching at ambient temperature using a cold press for 5 min.

3. Results and Discussion

3.1 Rheology

Reactive modification of polyolefins in the presence of peroxide and coagent involves hydrogen abstraction from the tertiary carbon to form a free radical, which subsequently reacts with the coagent to generate bimodal molecular weight and branched distributions, resulting in dramatic changes in the rheological and thermal properties of the polymers [51]. Similarly, in polyesters hydrogen abstraction from the tertiary carbon of the polyesters may form a free radical, which would subsequently react with the coagent to generate branching and/or cross-linking [54]. A possible product of the reaction of PHB with peroxide and TAM coagent is shown in Scheme 1.

Scheme 1: Possible products from the reaction of PHB with DCP and TAM.

Depending on the amount of DCP used in the formulations, two series of coagent-modified PHB were prepared; the first series was prepared using 0.2 wt% DCP and amounts of TAM ranging from 0.2-0.8

wt%, whereas the second one was prepared using 0.3 wt% DCP and the same range of TAM. The viscoelastic properties of these materials at a frequency of 1 rad/s are compared to those of the parent PHB, as well as PHB reacted with DCP alone and with Joncryl[®], in Table 1.

As depicted in Figure 1, the unmodified PHB had a very low viscosity, and displayed a Newtonian plateau, with minimal shear thinning. Represented on a Van Gorp Palmen plot (Figure 2) the phase angle of the neat PHB at low frequency approached 90°, which is indicative of a linear structure. Samples reacted with DCP alone (PHB/0.2 DCP and PHB/0.3 DCP) had slightly lower viscosity, because of degradation, attributed to chain scission. Furthermore PHB reacted with 2 wt% of a multi-functional epoxide oligomeric chain extender (Joncryl[®]) displayed essentially identical rheological properties with the neat PHB (Table 1). Even though Joncryl[®] is a commonly used chain extender for polyesters such as PLA [48], these results prove that it is ineffective in the case of PHB.

On the other hand, adding TAM coagent, while keeping the amount of peroxide constant at 0.2 wt% resulted in progressively higher values of viscosity, with loss of the Newtonian plateau and increased shear thinning (Figure 1), accompanied by an increase storage modulus, as well as decrease in the loss tangent (Table 1). The Van Gorp Palmen plots (Figure 2) showed a pronounced decrease in the phase angle upon increasing the amount of TAM, indicating enhanced elasticity, because of chain extension, formation of branches and/or cross-linking, similar to what we have observed in other coagent-modified polymers, such as polypropylene [52] and PLA [53].

Coagent-modified samples also exhibited significant strain hardening, under extensional deformation, as shown by extensional stress growth experiments (Figure 3). It should be noted that it was not possible to measure the extensional viscosity of the parent PHB material, due to its very low viscosity and sagging. To our knowledge this is the first time that PHB with enhanced melt strength is produced.

Similar trends were obtained by using 0.3 wt% DCP and varying amounts of TAM. However when the amount of DCP increased to 0.3 wt%, less amount of coagent was needed to achieve similar effects (Table 1). Out of the formulations shown in Table 1, those reacted with 0.2 wt% DCP and amounts of TAM higher than 0.6 wt%, as well as those containing 0.3 wt% DCP and amounts of TAM up to 0.4 wt% had gel contents around 30 wt%, indicative of partial cross-linking.

Adding TAM beyond this level, resulted in very high viscosities, above 10,000 Pa·s, (see Figure 4) with a pronounced viscoelastic solid-like behaviour, values of $\tan\delta$ below 1 (Table 1) and gel contents above 60%. This behavior is indicative of a high degree of cross-linking, suggesting that TAM was a very effective branching/cross-linking agent for PHB. Because of the highly cross-linked structure of these

samples it was impossible to prepare thin strips and to obtain accurate extensional strain hardening measurements.

Table 1. Rheological properties of neat PHB, and reactively modified PHB at a frequency of 1 rad/s

Sample (PHB/DCP/TAM)	Complex Viscosity Pa·s	Storage modulus Pa	Phase angle degree	tan delta
PHB neat	607	13.3	88	21.0
PHB/0.2	435	28.2	85	11.3
PHB/0.3	444	30.8	84	10.0
PHB/0.2/0.2	784	227	73	3.0
PHB/0.2/0.4	2170	1200	57	1.5
PHB/0.2/0.6	3330	2050	52	1.3
PHB/0.2/0.8	5640	4530	42	0.9
PHB/0.3/0.2	3970	2450	52	1.3
PHB/0.3/0.4	4200	2830	47	1.1
PHB/0.3/0.6	11700	9950	31	0.6
PHB/0.3/0.8	17100	15700	27	0.5
PHB/2% Joncryl	632	19.7	87	20.2

90 °C.

3.2 Thermal analysis

Coagent modification resulted in a significant increase in the crystallization temperature, T_c , of PHB, by more than 15°C (Figure 5 and Table 2). This observation is consistent with our previous reports on coagent-modified polypropylene and PLA [55, 56]. The shift in the crystallization temperature can be attributed a nucleating effect, attributed to the presence of gels, as well as to the formation of a separate phase of coagent-rich particles that forms upon reactive modification and promotes spherulite nucleation [55, 56].

of strain
arbitrary

n

Table 2. Crystallization temperature (T_c), % crystallinity, crystallization onset temperature (T_{on}), heat of fusion and degradation onset temperature for neat PHB and DCP-TAM modified PHBs

Samples	T_c (°C)	ΔH (J/g)	X_c (%)	T_{on} (°C)	Degradation onset temp (°C)
PHB neat	96	94.9	65	107	258
PHB/0.2	97	95.1	65	106	255
PHB/0.2/0.2	115	100.1	69	127	260
PHB/0.2/0.4	115	100.4	71	125	260
PHB/0.2/0.6	115	94.9	65	125	273
PHB/0.2/0.8	117	96.4	66	127	272
PHB/0.3/0.2	117	96.4	66	126	260
PHB/0.3/0.4	118	96.4	66	126	259
PHB/0.3/0.6	118	97.8	67	128	272
PHB/0.3/0.8	119	97.8	67	128	271

Clear evidence of enhanced nucleation is also shown in Figure 6 by representative light microscope images of spherulites obtained during isothermal crystallization experiments. As expected, large spherulites were formed in the neat PHB at the crystallization temperature of 120 °C in agreement with literature reports [57, 58]. It is clearly seen that the spherulite size of PHB was dramatically reduced in the reactively modified samples. The reduction was more pronounced when higher amounts of the reagents

1 d)

were used. Given that crystallization of the coagent modified samples was very fast at 120°C, attributed to the significantly enhanced crystallization kinetics, these experiments were done at a crystallization temperature of 130°C.

As shown in Figure 7, upon melting PHB typically has a broad melting peak, attributed to the formation of different crystal types, caused by the melt-cold crystallization process during heating, resulting in unstable imperfect crystals [54]. Both melting peaks for the modified samples shifted around 5 °C to lower temperatures, suggesting that the lamellar thickness was affected significantly by the presence of branching.

TAM

3.3 Thermal Degradation

The results obtained from non-isothermal TGA under nitrogen, are displayed in Fig. 8. The thermal degradation process of all the samples occurred in a single stage, in the temperature range of 260–300°C. The neat PHB sample began to lose weight at about 265°C. The major weight loss (approximately 50% decrease) occurred just after around 285°C. PHB degrades at high temperature via random chain scission reaction, through intramolecular stereoselective cis-elimination with the formation of oligomers containing trans-crotonate end groups [59, 60]. There was no carbonaceous residue at the end of the TGA degradation experiment, confirming that thermal degradation of the PHB and the modified PHBs is a one-step reaction attributed to the free-radical random scission mechanism.

The onset temperature for thermal degradation did not change significantly for the samples reacted with up to 0.4 wt% coagent (TAM). The samples reacted with 0.6 wt% or higher concentration of TAM, which had high gel contents, showed higher onset degradation temperature (Table 2). Hence, it can be deduced that the formation of cross-links through incorporation of TAM improved the thermal stability.

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Isothermal weight loss–time analysis was also studied for PHB, and its coagent modified derivatives at 190°C by TGA. Only slight weight loss was observed at this temperature under nitrogen up to 10 minutes suggesting that the samples remained relatively stable under these conditions.

Oscillatory rheometry was further used to monitor the degradation of the samples under isothermal conditions and air, by measuring the storage moduli as a function of time. Fig. 9 shows the effect of residence time at 190 °C on the normalized modulus of PHB and modified PHB samples. A pronounced decrease in the normalized modulus is visible, confirming that PHB is very prone to degradation, which can be attributed to hydrolysis of PHB and a subsequent reduction in molecular weight [60]. On the contrary, the coagent modified samples were more stable, suggesting that the degradation process was inhibited, and the degradation kinetics were delayed. It appears that the presence of crosslinked structures delays the thermal degradation process onset and reduces the rate of degradation. Even though it is also expected that the biodegradability of these materials would also be compromised, this modification approach can be very beneficial in terms of stabilizing these inherently unstable materials during processing and enhancing their stability during their life-time.

Fig. 9. Time sweep test for neat PHB and DCP-TAM modified PHBs at a frequency of 1Hz and 190 °C.

3.4 Dynamic Mechanical Analysis

The temperature dependence of the dynamic moduli of PHB and coagent-modified PHB were investigated in the solid state using DMTA (Fig. 10). The data demonstrate that below the glass transition temperature, T_g , there was a significant increase in modulus, with the addition of DCP and TAM. For example, the modulus for the crosslinked PHB samples increased by around 65% compared to neat PHB, due to the reinforcement effect imparted by the crosslinking in the presence of peroxide and coagent. The differences are less pronounced, but still noticeable above the T_g .

Fig. 11 shows the loss tangent, $\tan \delta$, as function of temperature for the prepared samples. T_g here is calculated as the temperature at which the maximum in $\tan \delta$ occurs, for the branched and crosslinked PHB with DCP and TAM. A decrease in T_g with adding crosslinking contents (DCP & TAM) is observed, compared to neat PHB. While such a decrease is counter-intuitive for fully crosslinked samples, it should be noted that these samples are only partially crosslinked. The decrease in T_g may be attributed to enhanced molecular motions of the amorphous phase due to chain branching leading to an increase in free volume. The free volume may also increase as a result of restriction of the chain packing due to crosslinking of the polymer chains [61, 62].

Fig. 10. Temperature dependence of storage modulus of neat and DCP-TAM modified PHB

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4. Conclusions

This work demonstrates for the first time an easy to implement reactive extrusion approach in the melt state to achieve high degrees of PHB branching and/or crosslinking. The rheology results and gel content evaluations showed that the combination of dicumyl peroxide (DCP) initiator and triallyl trimellate multifunctional coagent (TAM) provided an effective branching/crosslinking agent for PHB. With added amounts of DCP (0.2 and 0.3 wt%) and TAM (up to 1 wt%), a gel fraction of up to 65 wt% was obtained and the viscosity of PHB increased about 2 orders of magnitude.

Investigation of the samples' thermal properties showed a significant increase in the crystallization temperature, finer spherulitic structure and faster crystallization kinetics. PHB with high degrees of crosslinking also had improved thermal stability. These traits have the potential to expand the use of PHB in many common polymer processing applications.

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