

Thermal and Mechanical Properties of Chitosan Reinforced Polyhydroxybutyrate Composites

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ABSTRACT: The article reports the results of studies on the effect of chitosan (0, 5, 10, 20, 30, and 40 wt %) on thermal and mechanical properties of poly(hydroxybutyrate) composites. The addition of chitosan causes an increase in the glass transition temperature (T_g) while a decrease in the enthalpy of fusion (ΔH_{fus}), crystallization (ΔH_{cry}) and percentage of crystallinity as determined by differential scanning calorimeter (DSC). The thermogravimetric analysis reveals that high amount of chitosan decreases the thermal stability of the composites. The

Young's modulus of the composite increases and is high for the composite having 40 wt % of chitosan. Increase in the amount of chitosan decreases the elongation at break and impact strength of composites. Finally, the Young's modulus of the composites has been compared with the theoretical predictions. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 3357–3362, 2012

Key words: polyhydroxybutyrate; mechanical properties; thermal properties

INTRODUCTION

In the recent years, ecological concern has resulted in a renewed interest in the development of biodegradable polymers from renewable resources; so that the onetime use items can be disposed with the peace of mind that they will not remain for centuries in a landfill, or as litter. Among several biodegradable polymers, poly(hydroxybutyrate) (PHB) is hydrophobic in nature and have high melting temperature and crystallinity. However, its strength, thermal stability, gas permeability, and solvent resistance are sometimes not enough for end use applications. For these reasons, several studies were conducted in the preparation and characterization of blends and composites based on PHB.^{1–8} Zhang et al.⁶ investigated the thermal behavior, miscibility, and phase morphology of PHB and ethyl cellulose blends. El-Shafee et al.⁷ characterized the properties of PHB with cellulose acetate butyrate blends at different compositions. Bledzki et al.⁸ showed that the addition of man-made cellulose, jute, and abaca fibers in polylactic acid (PLA) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) will increase its ten-

sile strength and stiffness. Similarly Mohanty et al.⁹ indicated that the addition of 30 wt % fibers in PHB matrix can increase the Young's modulus. Wong et al.¹⁰ prepared flax fiber reinforced PHB composites, modified with different plasticizers and found that poly(ethylene glycol) and tributyl citrate are the most effective plasticizers for native PHB. Cyrus et al.¹¹ succeeded in producing double-layer films using PHB and cellulose paper through solution casting method. In the case of PHB/layered silicate nanocomposites, Maiti et al.¹² found that the extent of intercalation depends on the amount of silicate and the nature of organic modifier present in the layered silicate. The nano-hybrids show significant improvement in thermal and mechanical properties of the matrix compared to the neat polymer.

Similar to cellulose and other fillers, chitosan are also used as reinforcing agent in various polymer matrixes.^{13–16} Suyatma et al.¹³ reported that incorporation of PLA with chitosan improved the water barrier properties and decreased the tensile strength and elastic modulus of the film. Ikejima et al.¹⁴ investigated the crystallization behavior and environmental biodegradability of chitin and chitosan reinforced PHB. Shih et al.¹⁵ synthesized drug releasing microspheres of PHB/chitosan with various compositions through both single and double emulsion methods.

This article reports the effect of chitosan on the mechanical and thermal properties of PHB

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TABLE I
Properties of PHB

Density (g/cm ³)	1.29
Tensile strength (MPa)	8.9
Tensile modulus (MPa)	7.5
Elongation (%)	7.6
MFI (180°C) at 21.6 kg	10

composites fabricated by mixing followed by injection moulding.

EXPERIMENTAL

Materials

Polyhydroxybutyrate 209 (PHB) was provided by Biomer (Krailling, Germany). The chitosan was procured from Meron Chemicals (Kerala, India). The properties of the PHB and chitosan used for this study are given in Tables I and II, respectively.

Preparation of composites

PHB/chitosan composites were prepared using a micro compounder (DSM Xplore). The temperature was maintained at $175 \pm 2^\circ\text{C}$ and the screw rpm was fixed at 100. Initially PHB was melted; afterwards the chitosan (5, 10, 20, 30, and 40 wt %) were introduced to the mixer. The pelletized samples were then injection molded using a microinjection molding machine attached with DSM Explore with a capacity of 10 cc. The mould temperature was set at 50°C and the cylinder temperature was set at 175°C . Test specimens were injection molded under these conditions.

Characterization

DSC analysis

The melting and crystallization behavior of the composites were determined using DSC-Q1000, Universal V4.2E TA Instruments. The first heating was done from a temperature of -20 to 200°C at a rate of $10^\circ\text{C}/\text{min}$ followed by isothermal heating for 5 min. The first cooling and second heating were performed at $10^\circ\text{C}/\text{min}$ in nitrogen atmosphere.

Thermal stability

Thermal degradation studies were performed by thermogravimetric measurements using TGA (TA Q500). The measurements were carried out in nitrogen atmosphere from 25 to 800°C at a heating rate of $10^\circ\text{C}/\text{min}$.

Tensile properties

Tensile tests were carried out by using a universal testing machine (Tinius Olsen H10 kT) at a speed of

2 mm/min and gauge length of 25 mm. The tests were performed according to ASTM D638-03 standard. The data presented correspond to the average value of five measurements.

Impact testing

The impact test was performed on notched samples using a charpy impact testing machine, ZWICK D-7900 according to ASTM D 6110-06. Five specimens were tested in each case and the average values were reported.

RESULTS AND DISCUSSION

Thermal properties

Figure 1(a,b) represent the heating and cooling curves for the chitosan/PHB composites at different loading. All materials exhibit two peaks at higher temperature (T_{m1} and T_{m2}) for the heating curves as a result of melting of the primary crystallites and recrystallized crystallites having different stability.¹⁷ It is usually proposed to link either to the process of partial melting and recrystallisation and remelting or to melting of crystal with different lamellar thickness and/or different crystal structures.¹⁸ The thermal properties such as, glass transition temperature (T_g), melting temperature (T_m), crystallization temperature (T_{cry}), enthalpy of fusion (ΔH_{fus}), and crystallization (ΔH_{cry}) obtained from the DSC scans are summarized in Table III. Incorporation of chitosan to the PHB increases the T_g while a decrease in T_{m1} and T_{m2} . In the polymer blend containing a crystallizable component, the miscibility of the components in the amorphous phase is one of the causes for the lowering of melting temperature.¹⁹ Here the decrease in lamellar thickness of PHB suppresses the T_m of PHB composites. This decrease in lamellar thickness of PHB can be due to the slight reduction in crystal size and lower degree of crystallinity as a result of the restricted polymer chain mobility in the presence of the filler.²⁰ The significant variation in the ΔH_{fus} and ΔH_{cry} values of composites also indicates that the addition of fillers can affect the crystallinity of the PHB. The degree of crystallinity (χ) of the PHB and composites were determined using the following relationship²¹ and shown in Table III.

TABLE II
Properties of Chitosan

Appearance	Powder
Color	Off white
Mesh size	35 and 50 μm
Solubility	97% in 1% Acetic acid
Ash content	2% max
Deacetylation	Above 90%
pH	6.5–8
Moisture	10% max

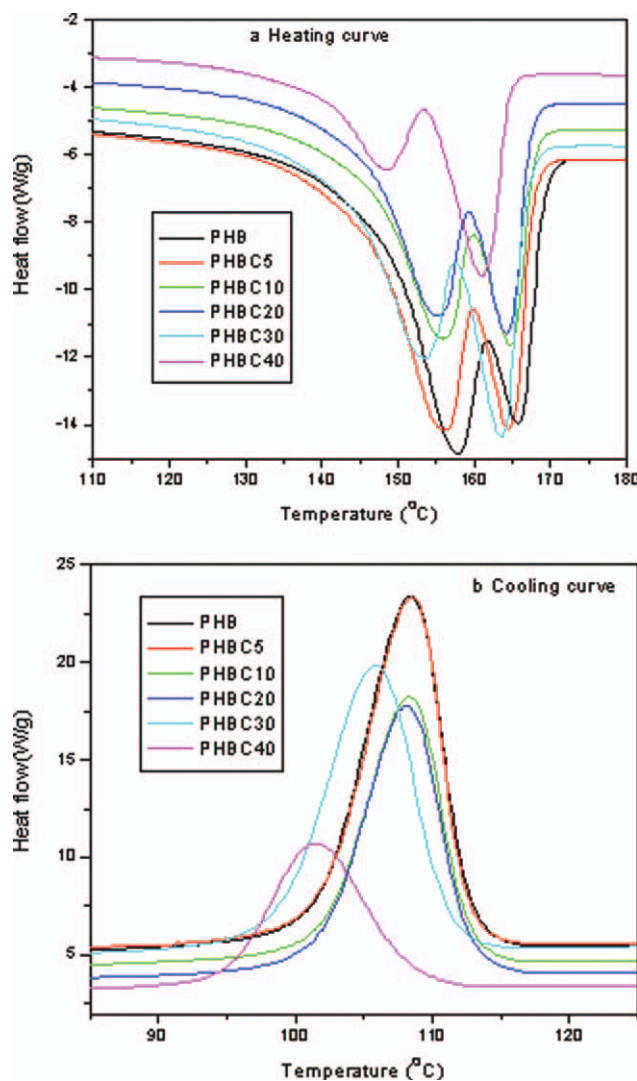


Figure 1 DSC thermograms of the chitosan/PHB composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\chi = \left(\frac{\Delta H_f}{\Delta H_f^0} \right) \times \frac{100}{w} \quad (1)$$

where ΔH_f is the enthalpy of fusion of the composite, ΔH_f^0 is the enthalpy of fusion of the 100% crystalline PHB, and w is the mass fraction of PHB in the composite. ΔH_{fus}^0 of PHB was taken as 146 J/g.²¹

Incorporation of 10 wt % of chitosan decreases the percentage of crystallinity of the chitosan/PHB composite, while further increase in the concentration of the chitosan does not cause significant variation. This is because, the presence of highly rigid chitosan molecules surrounding PHB molecules will make PHB molecules in the composites inflexible and will induce insufficient crystallization when compared with the case of neat PHB.

The TG and DTG plot for the chitosan is given in Figure 2. Here the mass loss occurs in two stages in the temperature of 50–100°C and 250–350°C. The initial mass loss around 100°C is due to the evaporation of water whereas the second peak at 301°C corresponds to the degradation and deacetylation of chitosan.²² The TG and DTG curves for the chitosan/PHB composites are given in the Figure 3(a,b), respectively, and the results are summarized in Table IV. It can be seen that as temperature increases the degradation of the composite increases and the nature of degradation depends on the amount of chitosan. At lower temperature region, the composite PHB40 shows more degradation than the PHB due to the evaporation of water which is associated with the chitosan. Addition of more amount of chitosan decreases the thermal stability of the composites. Increase in the amount of chitosan increased the residual mass (d_m residue) due to the better thermal stability of chitosan at higher temperature which is clear in the Table IV. Similar trend was observed by Mir et al.²³ in chitosan reinforced HDPE blends. The DTG plot indicates that the main decomposition for the PHB and composites are in the region between 260 and 315°C. Addition of more chitosan shifts the maximum degradation temperature (T_m) of PHB from 293 to 274°C. This decomposition stage is ascribed to the degradation of PHB, which occurs via random chain scission (*cis*-elimination).²⁴

Now, more information regarding thermal stability of the composites can be obtained by sophisticated analysis of the signals where the degradation starts. The kinetic aspect of the thermal degradation of polymeric material can be obtained by using Broido method.²⁵ Here we assume that degradation is a first order or a superposition of first order process. This assumption has been already been verified

TABLE III
 T_{cry} , T_m , ΔH_{cry} , ΔH_{fus} , and Degree of Crystallinity of Chitosan/PHB Containing Different Amounts of Chitosan

Composites	T_g (°C)	T_{cry} (°C)	T_{m1} (°C)	T_{m2} (°C)	ΔH_{fus} (J/g)	ΔH_{cry} (J/g)	χ (%)
PHB	40	108	158	166	65	56	45
PHBC5	44	108	156	165	59	53	43
PHBC10	45	108	155	165	53	50	40
PHBC20	45	108	154	164	48	48	41
PHBC30	45	105	153	163	40	40	40
PHBC40	47	101	148	161	35	34	40

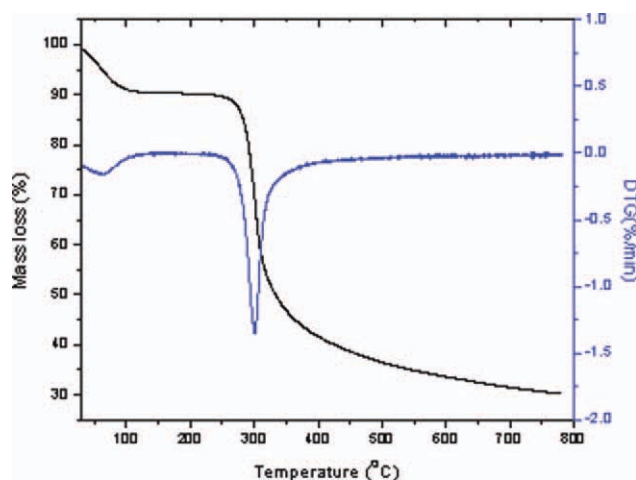


Figure 2 TG and DTG plots for the chitosan. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

for cellulosic fibers.²⁶ Hence the assumption of Broido leads to:

$$\ln[-\ln(1-\alpha)] = \ln K - \frac{\Delta E}{RT} \quad (2)$$

where α is the amount of fiber degraded at time t , ΔE is the change in activation energy, R is the universal gas constant, and T is the temperature in Kelvin scale. In this, α can be calculated using the following equation:

$$\alpha = \frac{W_0 - W_t}{W_0 - W_\infty} \quad (3)$$

where W_t is the mass at time t , W_0 is the initial mass, and W_∞ is the mass after infinite time. The interesting point associated with Broido's method is that the result does not depend upon the value of heating rate and also gives us the activation energy independently of the value of T_m at which the reaction is maximum. The results obtained by using Broido's method for the chitosan/PHB composites are given in Table IV. Here the decrease in activation energy from 180 to 141 kJ mol⁻¹ with increase in the amount of chitosan is due to the decrease in the thermal stability of composites.

Mechanical properties

The tensile strength, elongation at break, and Young's modulus of chitosan/PHB composites are summarized in Table V. It can be seen that incorporation of chitosan to matrix decreases the percentage of elongation. The maximum decrease is for the composites having 40% w/w chitosan content. This indicates that the addition of chitosan to matrix decreases the ductile nature of polymeric matrix. It is interesting to note that the incorporation of chitosan decreases the tensile strength of composite

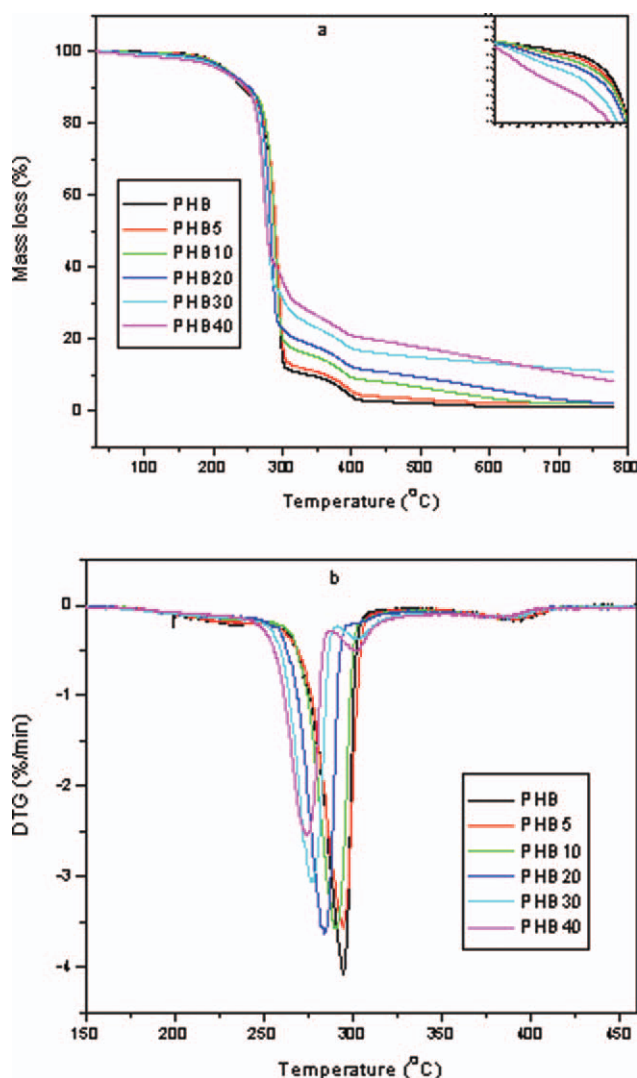


Figure 3 (a) TG plots of chitosan/PHB composites and (b) DTG plots of chitosan/PHB composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

slightly due to the partial incompatibility between chitosan and PHB. Correlo et al.¹⁶ also observed a decrease in tensile strength during the addition of chitosan in aliphatic polyester. As the chitosan content increases from 0 to 40 wt %, the Young's modulus increases from 1044 to 2499 MPa, that is, an increment of 58%. This increment is primarily due to

TABLE IV
Results of Thermogravimetric Studies of the Chitosan/PHB Containing Different Amounts of Chitosan

Composites	T_m (°C)	d_m residue (% w/w)	ΔE_a (kJ/mol)
PHB	293	1.20	181
PHBC5	292	1.85	176
PHBC10	290	1.87	175
PHBC20	286	2.23	169
PHBC30	276	9.70	145
PHBC40	274	8.90	142

the reinforcing effect imparted by the van der Waals force of attraction between fillers and matrix. Similar observation was also made by Choi et al.²⁷ in poly(-hydroxybutyrate-co-hydroxyvalerate)-organoclay composites. The impact strength of the composites also decreases with increase in filler loading from 1595 to 159 kJ/m². The poor adhesion between the filler and PHB cause micro-cracks when impact occurs, thus allowing the cracks to easily propagate which ultimately results in lower impact strength. Similar trend was observed by Kim et al.²⁸ in agro-flour reinforced polybutylene succinate composite.

Theoretical modeling

The mechanical properties of particulate filled composites can be affected by a number of parameters such as filler orientation, particle size of the filler, and filler/matrix adhesion. As a result, great number of studies has been conducted for mechanical properties of two-phase composites. Hence a variety of models are available to describe the modulus, tensile strength, and elongation at break as a function of filler content. Several theories have been proposed to model the tensile modulus of "noninteractive" composite materials in terms of different parameters. Among the most prominent are those developed by Guth,²⁹ Quemeda,³⁰ and Thomas et al.³¹ The comparison of the experimental values with these theoretical predictions is represented in Figure 4.

Guth equation

$$M_C = 1 + 2.5V_f + 14.1V_f^2 \quad (4)$$

Guth's equation is an expansion of Einstein, to account for the inter particle interactions at higher filler concentrations.

Quemeda equation

$$M_c = M_m \left[\frac{1}{1 - 0.5KV_f^2} \right] \quad (5)$$

where K is a constant and normally its value is 2.5 for noninteractive fillers. This variable coefficient is

TABLE V
Stress-Strain Properties of the Chitosan/PHB Composites Containing Different Amounts of Chitosan

Composites	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Impact strength (kJ/m ²)
PHB	11 ± 0.2	1044 ± 1	1.92 ± 0.4	1595 ± 5
PHB5	8.9 ± 0.5	1083 ± 2	1.14 ± 0.3	367 ± 2
PHB10	7.5 ± 0.3	1434 ± 2	0.59 ± 0.1	375 ± 3
PHB20	7.6 ± 0.5	1753 ± 1	0.47 ± 0.2	354 ± 1
PHB30	8.2 ± 0.2	1940 ± 3	0.46 ± 0.1	252 ± 2
PHB40	8.5 ± 0.3	2499 ± 2	0.36 ± 0.2	159 ± 3

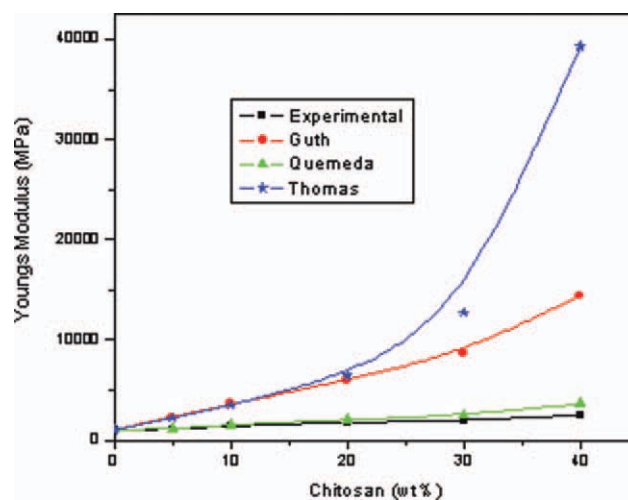


Figure 4 Theoretical modeling of Young's modulus of composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

introduced to account for the inter-particle interactions and difference in particle geometry.

Thomas equation

$$M_c = M_m(1 + 2.5V_f + 10.05V_f^2 + 0.00273e^{16.6V_f}) \quad (6)$$

Thomas equation is an empirical relationship based on the data generated with dispersed spherical particles in polymer matrices.

Many investigations showed that the effect of solid fillers on the tensile properties of polymers might be positive or negative, depending on filler size and shape, internal stresses, surface nature, and aspect ratio. The particles restrict the mobility and deformability of the matrix by introducing a mechanical restraint. The most important feature that affects the interfacial adhesion is believed to be the mechanical stresses, chemical interactions, and physico-chemical weak boundary layers. From Figure 4, it can be seen that especially at higher loading the experimental curve does not fit with the theoretical predictions. Since all these predictions assume that matrix and filler have no appreciable degree of interaction. Any interaction operative would only be physical. Here the polymer matrix is stiffened by the particulate and also in most of the conventionally filled polymer systems, the modulus value increases linearly with the filler volume fraction.

CONCLUSION

The present investigation regarding the reinforcing effect of chitosan in PHB matrix reveal that incorporation of chitosan in the PHB matrix increases the T_g values while a decrease in the T_{cry} , T_m , and percentage of crystallinity. TGA analysis indicates that

addition of more chitosan decreases the thermal stability of the composites which is also confirmed by the activation energy calculated using Broido's plot. As the filler loading increases, the Young's modulus of the composites increase from 1044 to 2499 MPa. However, the tensile strength and impact strength decrease at all loadings. Also experimental values of tensile properties deviate more from the theoretical prediction due to the variation in the filler-polymer interaction.

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