

Talcum Powder as a Nucleating Agent and Reinforcing Filler in PHBV Composites

Arjang Aminishahsavarani¹, Ali Salimian¹, Karnik Tarverdi², Hari Upadhyaya¹

¹Centre for Advanced Materials, School of Engineering, London South Bank University, London, UK

²Wolfson Centre for Material Processing, Brunel University London, London, UK

Email address:

aminisha@lsbu.ac.uk (A. Aminishahsavarani), upadhyah@lsbu.ac.uk (H. Upadhyaya)

To cite this article:

Arjang Aminishahsavarani, Ali Salimian, Karnik Tarverdi, Hari Upadhyaya. Talcum Powder as a Nucleating Agent and Reinforcing Filler in PHBV Composites. *Composite Materials*. Vol. 6, No. 1, 2022, pp. 7-16. doi: 10.11648/j.cm.20220601.12

Received: September 8, 2020; **Accepted:** September 19, 2020; **Published:** February 5, 2022

Abstract: PHBV/talc composites at concentrations of 100/0, 90/10, 85/15, and 80/20 were prepared by extrusion compounding followed by injection molding. The effect of talcum powder on crystallinity, thermal and thermomechanical, mechanical and morphological properties of PHBV/talc composites were investigated by DSC, XRD, TGA, SEM, DMA, and mechanical testing. It was found that talc can change the sluggish crystallinity of PHBV. The talc enhanced the nucleation of the PHBV in the composites which lead to a faster crystallization rate. The heat distortion temperature, crystallinity, and the modulus of PHBV/talc composite also increased. The HDT value of the talc-filled PHBV is significantly higher than the pure PHBV, The HDT value of PHBV increases from 129.87°C to 145.48°C with adding the 20% weight fraction of talc. The DMA result revealed that the storage modulus of the composites increased with an increase in the content of talc. The change in storage modulus demonstrated the reinforcing effect of talc. The isothermal crystallization behavior of PHBV studied by DSC and analyzed by Avrami equation indicate that with the addition of the talc, the crystallization rate of the PHBV increases in the composites. Talc therefore enhances the nucleation of the PHBV in the composites. SEM images showed a fine dispersion of talc in the polymer matrix. The tensile modulus results were theoretically supported by the application of the Halpin-Tsai equation which supported the accuracy of the results obtained from the tensile tests.

Keywords: Bioplastic, Nucleating Agent, Reinforcing Filler, Extrusion, Crystallization Composite

1. Introduction

The global consumption of conventional plastics has increased noticeably in recent years. However, the depletion and price fluctuation of petroleum resources and the escalated rising environmental awareness about the effects of synthetically produced materials have attracted a lot of attention to biologically derived polymers. Poly (3-hydroxybutyrate-co-3-hydroxyvalerate), PHBV, belongs to the family of biodegradable bacterial bio-polyesters which have gained a lot of interest with researchers due to their ability to be a substitute for many conventional petroleum-based polymers. There have been several studies on the properties of PHB and PHBV concerning issues like their brittleness, narrow processing window, and the slow rate of crystallinity. These are properties that have hindered the commercial usage of these materials [1, 2]. The slow crystallization rate causes films made of

PHBV stick to itself even after cooling. The reason for this is that a considerable fraction of the PHBV remains amorphous and tacky for long periods [3]. According to Kai, He, and Inoue, there are several possible causes for their brittleness. The bacterially synthesized PHB or its copolymer PHBV is completely known as isotactic stereoregular polyester, with a high tendency to crystallize. However, the nucleation density of bacterial PHBV is too low to initiate efficient crystallization. Consequently, the crystal spherulite size is exceptionally large and thus the possibility of brittle failure by cracks is high among PHB and the PHBV copolymer [4].

Nucleating agents are widely used to modify the crystallization characteristics of various polymers. The rate of crystallization and the size of the crystals have a strong influence on the mechanical and optical properties

after processing. The addition of nucleating agents to semi-crystalline polymers provides a surface on which the crystal growth can start. As a consequence, fast crystal formation will result in many small crystal domains. Cycle times in injection moulding will be reduced and physical properties such as flexural modulus, strength, heat distortion temperature, and hardness will increase [5].

Nucleating agents also decrease the average size of spherulites and prevent the formation of large, interspherulitic cracks that cause embrittlement. In summary, the nucleating agents are small crystalline particles that are dispersed in the melt and remain solid in the process; a large number of tiny crystals form from the melt on them at the start of the crystallization process. The size and number of the crystalline structures will alter the impact strength [6]. Talcum powder is a low-cost mineral and is one of the softest naturally occurring minerals. It is used as a reinforcing filler and nucleating agent for thermoplastics such as polypropylene, polyethylene, etc. [7]. Talc is characterized as a hydrated magnesium sheet silicate with the formula $Mg_3Si_4O_{10}(OH)_2$. Talc's particles are in a lamellar (platy) form, and it exists with a variable aspect ratio.

2. Experimental

2.1. Material & Sample Preparation

The PHBV used in this study was ENMATTM Y1000 with 3 mol% of hydroxyvalerate (HV) content without any additive substances and was supplied in a white powder form manufactured by Tianan Biologic Material Co. (Ningbo, P. R. China). The talc was kindly provided by Imerys under the trade name of Crys-talc R7, fine white powder with median particle diameter: d50 1.9 μm and d95 7.6 μm .

Before processing through an extruder, the PHBV powder was first dried in a vacuum oven at a temperature of 60°C for 24 hours to remove moisture. The talc powder was used as received. Four batches of PHBV/talc with weight ratios (w/w) of 100/0, 90/10, 85/15, 80/20 were prepared. All the components were premixed in a plastic bag by manually tumbling for 5 mins and were fed by a calibrated powder twin screw feeder into the extruder. The extruder used was a Betol co-rotating intermeshing twin-screw extruder (40 mm diameter, L/D=21/1, Amp=5-10) at 200 rpm. The specimens for mechanical properties were obtained by injection moulding in a Demag NC III, 150 Tone, injection moulding machine.

2.2. Characterization

Differential Scanning Calorimetry (DSC) analyses were performed with TA Instruments DSC/Q2000 with Universal Analysis 2000 software. For non-isothermal crystallization, the samples were first heated to 200°C at a heating rate of 10°C/min and isothermally held for 5 min to eliminate any thermal history. The samples were then cooled at the same heating rate of 10°C/min to -20°C and then again heated to 200°C with the same heating rate for obtaining the second

heating cycle. To evaluate isothermal crystallization values, the samples were heated up to approximately 30°C above the melting point (about 200°C) and held isothermally for 5 minutes to eliminate any thermal history. The samples were then rapidly cooled down at the rate of 80°C/min to the pre-determined isothermal temperatures and kept at these points until crystallization was completed. The procedure was carried out for the three pre-determined temperatures of 110°C, 120°C, and 130°C for each of the compounds.

Thermogravimetric analysis (TGA) was performed using a TA instrument "The New Discovery TGA", with TRIOS software version 3.3.0.4055 under a nitrogen atmosphere. The temperature range was from room temperature to 650°C with a heating rate of 10°C/min.

X-ray diffraction analyses of Neat PHBV and its composites with talc were carried out with A Buker D8 advanced Copper-tube diffractometer equipped with a Linx Eye Detector PSD (position sensitive) detector. Diffraction Data were acquired at ambient temperature in the angular region (2θ) of 5-60°, with a time of 3.5 seconds per step and with an increment of 0.01°/step.

The morphology of the specimens was examined with a SUPRA ZEISS 35VP with a 20KV accelerating voltage using an SE detector. The scanning electron microscopy of fractured samples from the Charpy impact testing was conducted at room temperature. The specimens were dried for two hours before the gold coating.

Tensile tests were performed with an Instron testing machine (model 3366) according to ASTM D 638 standard for tensile testing. A 10 KN load cell was used with a crosshead speed of 5 mm/min. At least five samples were tested for each reported value. The impact test was performed using a CEAST Fractovis Plus impact tester Model 7520. The samples were injection moulded 150x150x4 mm plates that were cut into 60x60 mm square impact test plates.

Dynamic Mechanical Analysis (DMTA) was performed with a TA Instruments DMA Q800. The accurately prepared rectangular samples with dimensions 127x12x4 mm were cooled to -50°C and then heated up to 150°C, with a heating rate of 2°C/min, under a maximum force of 1 N at a frequency of 1 Hz and an amplitude of 5 μm using the single cantilever system.

The heat distortion temperature (HDT) was performed with a TA Instruments DMA Q800 using rectangular specimens dimensions 50x13x4 mm at a 3-point bend system.

3. Results and discussion

3.1. Thermal Analysis

Figure 1 shows the non-isothermal DSC curves of PHBV and PHBV/talc composites with concentrations of 90/10 and 80/20.

All the non-isothermal DSC measurements of PHBV/talc composites produced two melting point peaks (second heating cycle). These were shifted slightly by the different

concentrations of talc in the composites. The phenomena of two endothermic peaks in the DSC curve could be caused by the reorganization of crystals during the low chosen heating rate of 10°C/min. Liu and Gunaratne & Shanks and Wang et

al also stated that the double melting peaks of PHBV were caused by melting, recrystallization, and re-melting during heating [3, 8, 9].

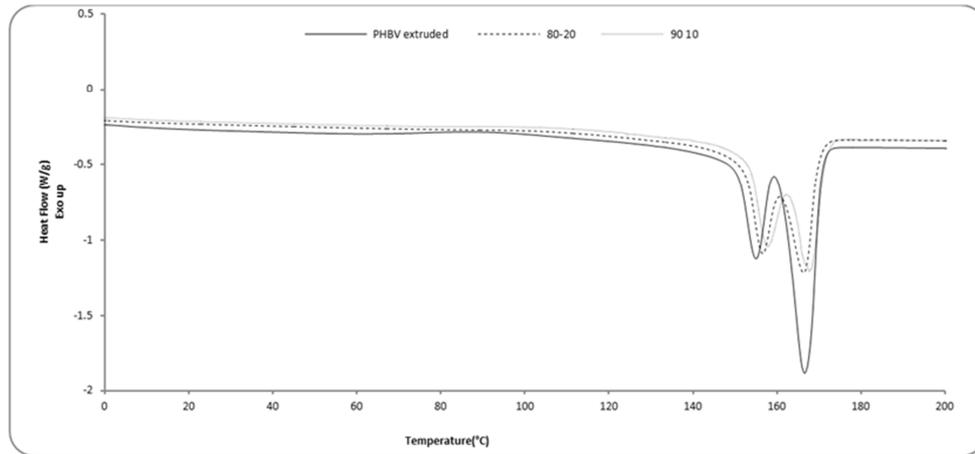


Figure 1. DSC analyses of second heating curves (10°C/min 0–230°C) of PHBV/talc samples (neat, 90/10, 80/20).

The isothermal crystallization behavior of PHBV and different concentration of PHBV/talc can be described by the Avrami equation. The relative degree of crystallinity X_{rel} at time t is given by the following:

$$X_{rel} = \frac{X_C(t)}{X_C(\infty)} = \int_0^t \frac{dH(t)}{dt} dt / \int_0^\infty \frac{dH(t)}{dt} dt \quad (1)$$

Where $X_C(t)$ and $X_C(\infty)$ are the degrees of crystallinity at time t and that at the end of crystallization, respectively, and $dH(t)/dt$ is the rate of heat flow during the crystallization process at time t . The latter was measured from the moment when the sample was cooled to the appropriate crystallization temperature. X_{rel} can be obtained from the following expression:

$$1 - X_{rel} = \exp(-ktn) \quad (2)$$

Here, n is the Avrami exponent, which is determined by the mode of crystal nucleation and the crystal growth geometry under the actual conditions. The parameter k is an isothermal crystallization rate constant. Taking a ‘double logarithm’ of Equation (2) gives the following:

$$\log[-\ln(1 - X_{rel})] = n \log t + \log k \quad (3)$$

The plot of $\log(-\ln(1 - X_{rel}))$ against $\log t$ gives a straight line, whose slope is n and its intercept on the ordinate is $\log k$. In the investigations of isothermal crystallization at time t , $dH(t)/dt$ was recorded and then integrated against the time, t , to give the values of $X_C(t)$ and $X_C(\infty)$. When $X_{rel}=0.5$ in Equation (3), the half crystallization time, $t_{0.5}$, which is the time taken for 50% of ‘total-volume’ of crystallization is given by the following:

$$t_{0.5} = (\ln 2 / K) 1/n \quad (4)$$

Figure 2 presents the effect of the talc concentration on the relative crystallinity of the PHBV/talc composites.

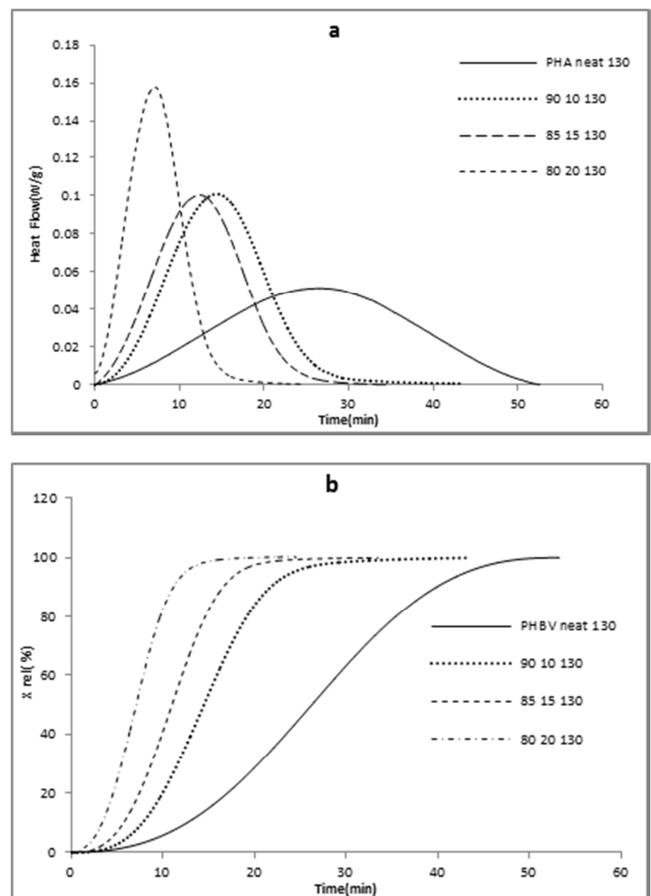


Figure 2. Comparison between (a) the isothermal crystallization and (b) the relative crystallinity of PHBV & PHBV/talc.

While it takes about 50 min for the neat PHBV to completely crystallize at 130°C, The crystallization time decreases to less than 20 min for the composite with 20% talc.

Figure 3 illustrates the $\log[-\ln(1 - X_{rel})]$ vs $\log(t)$.

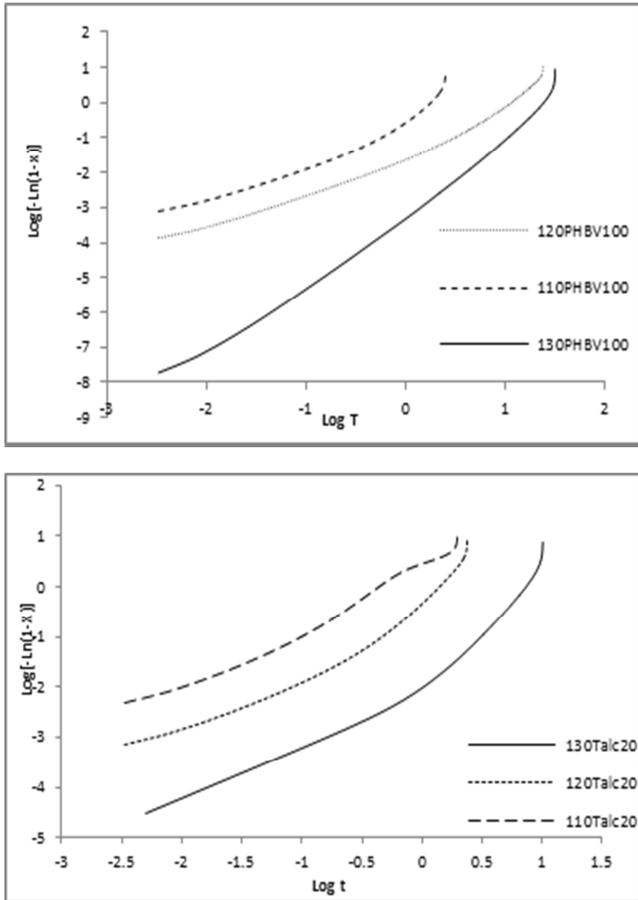


Figure 3. Avrami plots for the isothermal crystallization of PHBV & PHBV/talc.

From the slope and the intercept of the graphs in figure 3 the Avrami's components, n and k were calculated and are shown in table 1. Time at half crystallinity $t_{0.5}$ has been calculated from the formula (4).

Table 1. Avrami's components for PHBV neat and PHBV/talc composites.

Sample PHBV/Talc	Tc (°C)	n	k (min ⁻¹)	t _{0.5} (min)
100-0	110	1.59	0.34	1.85
	120	1.65	0.02	8.49
	130	2.43	0.000382	21.71
90-10	110	1.58	0.55	1.14
	120	1.78	0.18	1.92
	130	2.82	0.0012	14.5
85-15	110	1.56	2.19	0.48
	120	1.85	0.20	1.85
	130	2.92	0.002	12.45
80-20	110	1.58	2.68	0.4243
	120	1.74	0.50	1.21
	130	2.96	0.00297	6.30

From table 1 it can be seen that at a specific temperature the value of n for PHBV/talc compounds with different concentrations hasn't shown a dramatic change which indicates that the mechanism of crystallization after adding talc was not affected by the different concentrations of talc.

For each sample, the amount of k reduces with increasing the crystallization temperature, while the crystallization half time ($t_{0.5}$) value increases with temperature. It could be justified that with increasing temperature the crystallization rate decreases because the melt crystallization is temperature-dependent. Moreover, the k value for the PHBV/talc composites is increased by an increase of the talc concentration in the composite at a particular temperature.

The value of $t_{0.5}$ reduces with an increase of the talc content. The above results indicate that with the addition of the talc, the crystallization rate of the PHBV increases in the composites. Talc therefore apparently enhances the nucleation of the PHBV in the composites.

3.2. Thermogravimetric Analysis (TGA)

The results of the TGA analysis of pure PHBV and PHBV/talc composites are presented in Figure 4 and Table 2.

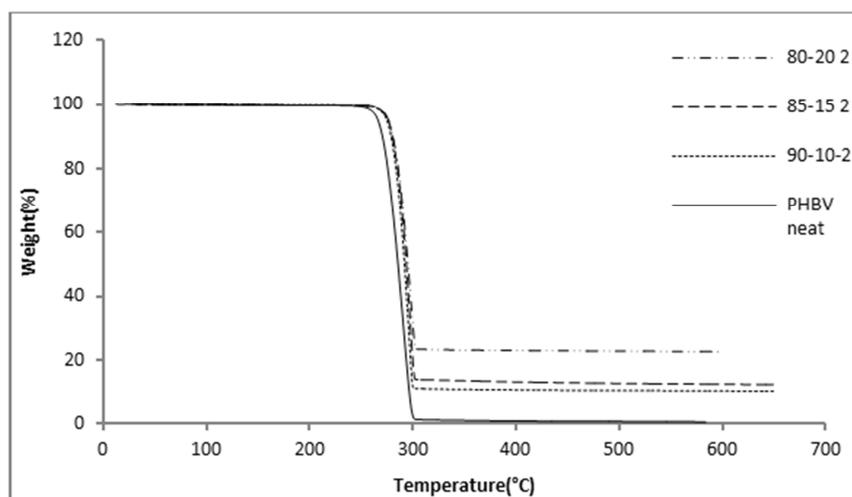


Figure 4. TGA graph of PHBV neat and PHBV/talc.

These results show that the thermal decomposition of PHBV started at 253.5°C and then accelerated rapidly to a peak rate of 285.87°C (Figure 4). The thermal stability of the

composites didn't increase significantly with increasing the amount of talc. However, with 20% talc in the compound, T_i (the initial decomposition temperature) has changed to

263.86°C, and thermal degradation was retarded by almost 10°C compared to the neat PHBV. The residue at 600°C (%)

could be referred to as the amount of talc concentration in the composites.

Table 2. The values of characteristic temperatures of TGA and DTG graphs, T_i =the initial decomposition temperature and T_{end} =the end decomposition temperature, Δm_i =Mass loss in T_i (%), and residue at 600°C (%).

Specimens PHA/Talc	T_i (°C)	Δm_i (%) (Mass loss)	T_c (°C)	Residue at 600°C (%)
100/0	253.50	98.45	294.83	0.64
90/10	263.77	88.720	300.69	10.47
85/15	262.67	85.804	303.50	13.54
80/20	263.86	77.823	303.89	22.11

3.3. X-ray Powder Diffraction (XRD)

X-ray diffraction 1D patterns of the Extruded PHBV and PHBV/talc composites are shown in Figure 5.

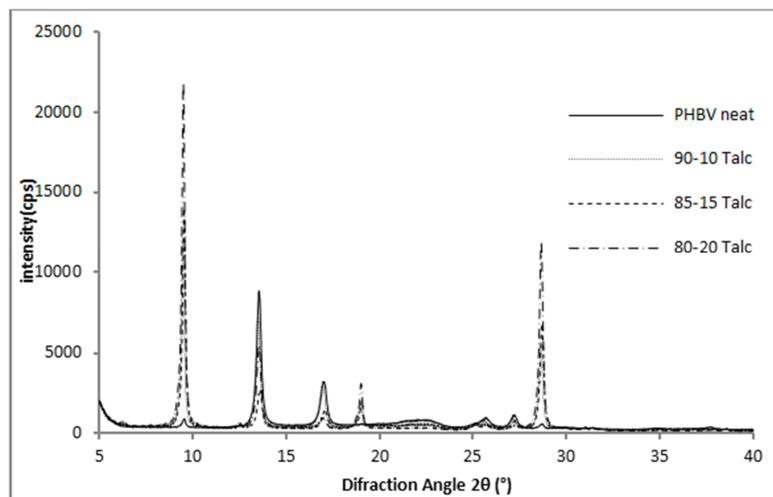


Figure 5. XRD graph of PHBV extruded and PHBV composite with talc at different concentrations.

The graph illustrates that the neat PHBV presents two strong diffraction peaks at around 13.54° and 17.00° corresponding to (020) and (110) planes (Miller index), respectively of the orthorhombic crystal structure. The peaks at 19°, 25°, and 12.5° correspond to the nucleation effect of talc in the compound. Wu et al (2004) and Obata et al (2001) reported that three sharp diffraction peaks assigned to the reflection of talc are at ca $2\theta=9.5^\circ$, 19.0° , and 28.7° , and are attributed to the (002), (020), and (006) reflections of the talc crystals [10, 11] The crystalline structure of the polymer matrix is not, therefore, affected by the presence of the talc. The PHBV/talc composites show the presence of the three talc peaks, $2\theta=9.5^\circ$, $2\theta=19^\circ$, $2\theta=28.7^\circ$ (Figure 5). However,

it has to be stated that the intensities of the three talc peaks are proportional to the talc content. Kunioka et al. stated that PHBV with less than 40% 3HV crystallized in the P (3HB) lattice, while those with a 3HV composition more than 50% mol, crystallized in the P (3HV) lattice. This phenomenon is called isodimorphism [12]. The graph in Figure 5 shows that the amorphous parts of the graph were decreased in composites with talc.

3.4. Mechanical Properties: Tensile and Flexural Testing

The tensile and flexural properties of PHBV and PHBV/talc composites are illustrated in table 3:

Table 3. The tensile and flexural properties of PHBV and PHBV/talc composite.

PHBV/ Talc %	Tensile strength MPa (SD)	Elongation at break %	Elasticity Modulus GPa	Flexural Modulus GPa
100/0	32.68 (3.5)	1.2 (0.18)	3.75 (0.42)	3.9 (0.69)
90/10	20.35 (2.1)	0.9 (0.13)	5.22 (0.4)	4.77 (0.57)
85/15	21.75 (3.1)	0.7 (0.45)	5.46 (0.42)	5.07 (0.69)
80/20	26.48 (3.8)	0.8 (0.15)	6.54 (0.046)	5.94 (0.33)

From table 3, it can be seen that the tensile strength of PHBV and PHBV/talc composites decreased with the addition of 10% talc and then increased with the addition of more talc. Similar phenomena were reported by Whaling, Bhardwaj, and Mohanty, it was stated that at the higher concentrations of talc,

the talc particles prevent the matrix from deforming and thus the composite has a higher modulus than the matrix resin [7]. However, the non-uniform size of the talc particles based on the morphology studies of specimens by SEM (figure 9) could be another reason for that. Li et al stated that if the talc

particles are not uniform with a spread of different sizes, the amount of small particles rises with increasing the talc volume fraction. The result is that the composite becomes more compacted because the smaller particles occupy the free spaces between the large particles. The density of particles distributed may account for the increase in the tensile strength of the composite at the higher talc concentrations [13]. Table 3 shows that there is an increase in Young's modulus from a value of 3.75 GPa for the neat PHBV up to 6.54 GPa with the addition of a 20% weight fraction of talc. This effect is due to the addition of the high modulus platy filler to a significantly lower modulus polymer matrix. De Armitt stated that platy fillers including mica generally increase the polymer modulus significantly more than isotropic fillers such as calcium carbonate, silica, dolomite, and fly ash. The improvement is strongly dependent on the aspect ratio of the filler. Fillers with a large aspect ratio have a greater effect and it is similar for both the Young's and the flexural moduli. The tensile strength of the composites, however, is also affected by the level of adhesion between the filler and polymer. A coupling agent can enhance the effect of fillers. Moreover, the modification of the filler's surface area also may increase the adhesion with the help of more contact area between the filler and matrix of polymer [14, 15].

The elongation at break (%) decreases by increasing the amount of talc in the composites (Table 3). This behavior can be justified by the effect of fillers on the matrix by restricting the chain mobility which reduces the level of plastic deformation before fracture that results in the matrix reinforcement [16, 17].

The Halpin-Tsai equation (shown below) provides a mathematical model for predicting the elasticity of composite materials based on the geometry and orientation of the filler

and the elastic properties of the filler and matrix. It is valid for high aspect ratio fillers; therefore it could be used for the talc particles platy structure.

$$Y_c/Y_m = (1 + \zeta \eta V_f) / (1 - \eta V_f) \quad (\text{Halpin-Tsai equation}) \quad (5)$$

Where:

$$\eta = \frac{Y_f Y_m - 1}{Y_f Y_m + \zeta} \quad (6)$$

Y_c = composite Young's modulus,

Y_m = corresponding matrix Young's modulus

Y_f = corresponding filler Young's modulus

ζ = a measure of the reinforcement that is equal to $2(L/D)$, depends on the boundary conditions (the geometries of the inclusions and loading conditions) where (L/D) is the aspect ratio of the filler (L =length, D =thickness of the particles).

V_f = volume fraction of filler in the composite. This could be calculated from the following equation:

$$V_f = \frac{W_f}{W_f + (1 - W_f) \rho_f / \rho_m} \quad (7)$$

Where W_f is the weight fraction of filler and ρ_f and ρ_m are the specific gravity of filler and matrix respectively [18].

Y_m is 3.75 GPa as measured,

Y_f is taken as 70 GPa which is Young's modulus of other silicate fillers (such as glass)

$$\rho_f = 2.78 \text{ g/cm}^3, \rho_m = 1.24 \text{ g/cm}^3$$

ζ is calculated from the aspect ratio of the average of 20 talcum powder particles observed in the SEM images (Figure 10) with Microsoft Visio & excel software. The result was an aspect ratio of 10.

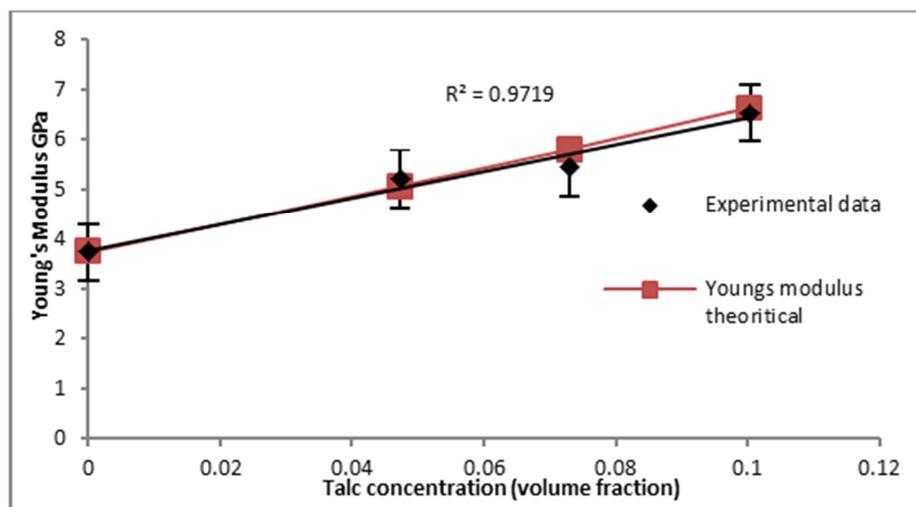


Figure 6. The experimental Young's Modulus and theoretically based on Halpin-Tsai equation.

It can be seen in figure 6, that the experimental data is very close to the theoretical data and the correlation factor is about 0.97 which indicates the accuracy of the results obtained from the tensile tests.

3.5. Thermomechanical Properties: Dynamic Mechanical Properties

The temperature dependence of the dynamic storage modulus (E_1) and $\tan \delta$ (the ratio of the loss modulus to

the storage modulus, E_2/E_1) of the PHBV composites with talc are given in Figure 7. Figure 7a shows that with an increase in the amount of talc in the composite there is a substantial increase in the storage modulus. This is shown by the upward shift in the curves from 100/0 to 90/10 and 80/20 with approximately a linear response. The composite with 85/15 did not, however, show the expected

modulus increase based on the other specimens. This irregular trend could have resulted from the low accuracy of the measurement of the talc concentration in the compound. The change in the storage modulus with the increase in the talc content is evidence of the reinforcing effect of talc.

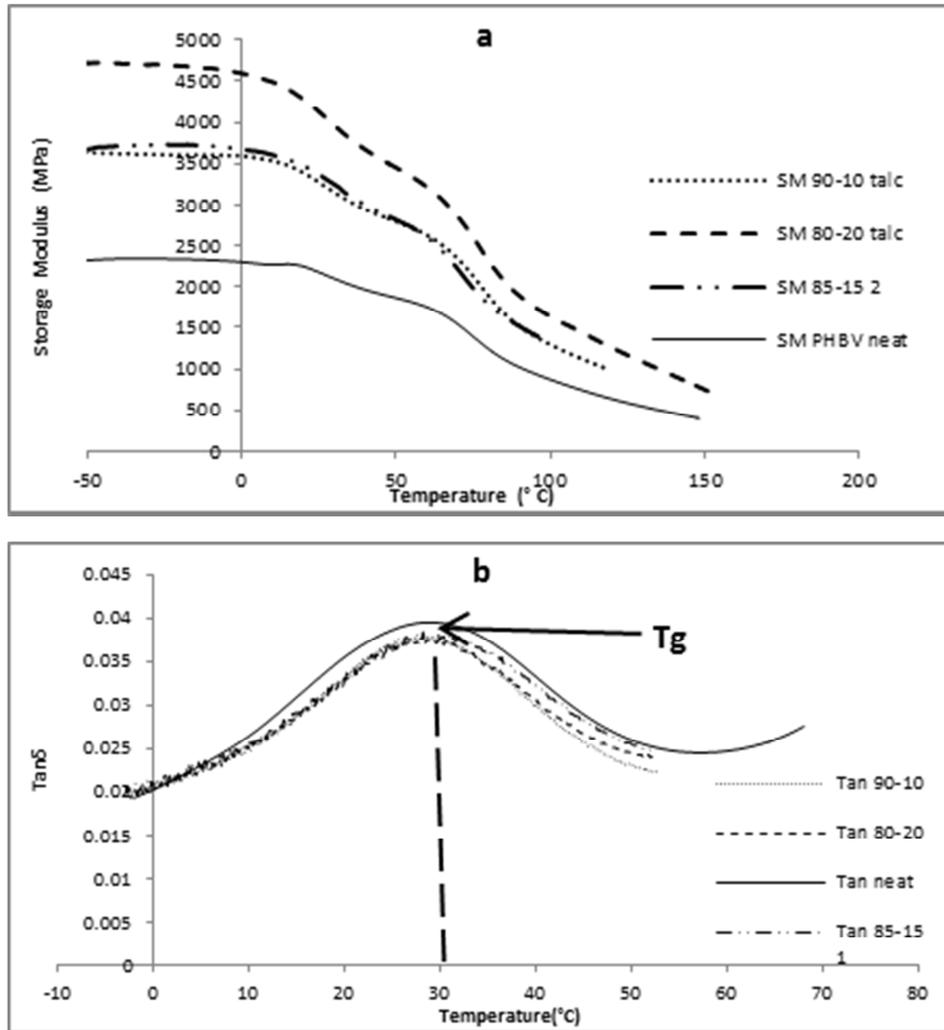


Figure 7. The storage modulus (a) and $\tan \delta$ (b) for PHBV and PHBV/Talc composites.

Figure 7b shows that there is no distinguishable change in the glass transition temperatures of the composites with an increasing amount of talc compared to the neat polymer. Landel and Nielsen declared that fillers have a larger effect in increasing the storage modulus of polymers above T_g than that below T_g . The main reason for this could be the large modulus ratio E_2/E_1 of the polymer above the T_g in the rubbery phase compared to the rigid glassy state. A less important reason would be the larger Poisson's ratio above T_g and the presence of induced thermal stresses below T_g in the glassy state [19].

3.6. The Heat Distortion Temperature (HDT)

The heat deflection temperatures (HDTs) of PHBV and its talc-filled composites are presented in Figure 8.

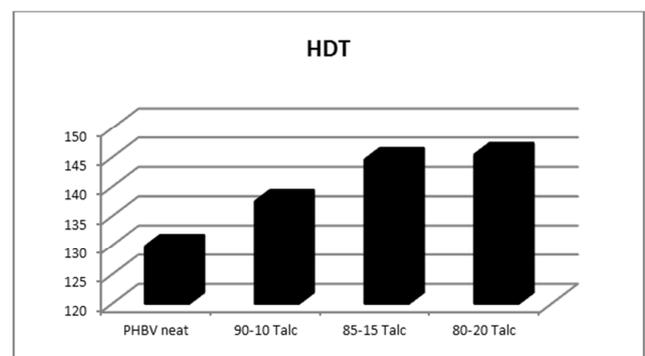


Figure 8. The heat deflection temperatures (HDTs) of neat PHBV and its talc-filled composites.

The HDT value of PHBV is 129.87°C. The HDT value of the talc-filled PHBV is significantly higher than the pure PHBV. For the 10% weight fraction of talc, it has a value of 137.652°C. This increases further to 144.61°C with the 15% weight fraction of talc. Only a slight further increase to 145.48°C was recorded with the 20% weight fraction of talc.

The increases in the modulus and the reduction of the high temperature creep performance for the filled polymers be the key factors for the improvement of the HDT value. The modulus-temperature dependency is also a critical factor in determining the HDT value of the material (Whaling et al, 2006). It has been shown from the DMA results, that the talc-filled PHBV composites exhibit higher storage modulus

values than the neat PHBV at low temperatures with them coming closer together at the higher temperatures (see figure 7). The DMA result could also be associated with the improvement in the HDT values for the talc-filled PHBV composites. The improving HDT properties of talc-filled PHBV is supported by the DSC and TGA results (figures 2, 3, 4) which indicate that talc plays an important role in enhancing the crystallization and also heat resistance of PHBV and its composites.

Scanning Electron Microscopy In general, two frequently used concepts for describing the structural character of polymeric composite materials are the composition and dispersion of the modified agent in the polymeric matrix [20].

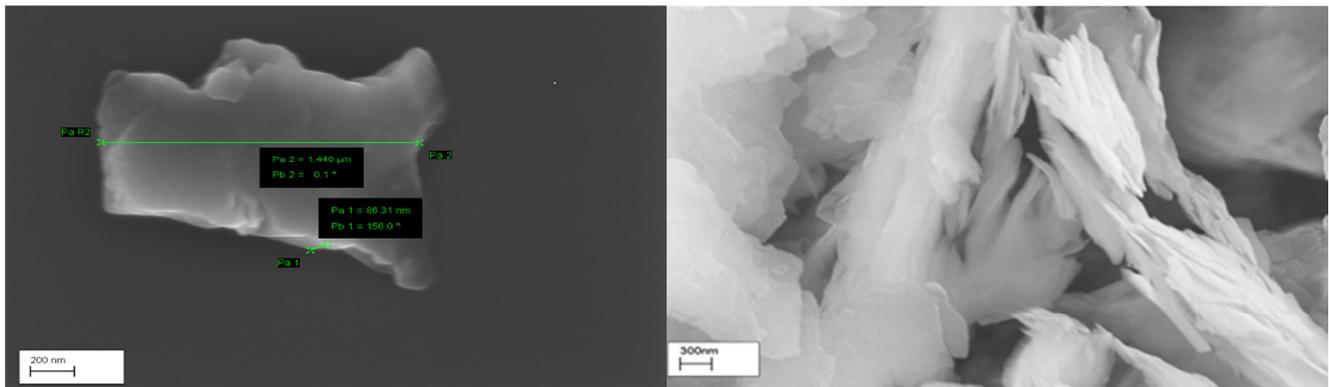


Figure 9. SEM images of talc particles.

The morphology of pure Talc is illustrated in figure 9. It can be observed that the platy shape of talc particles dominates the whole morphology. However, spherical

morphologies are also evident. The particles have a median diameter of $d_{50}=1.9 \mu\text{m}$ and $d_{95}=7.6 \mu\text{m}$, and can be considered to be very fine talc.

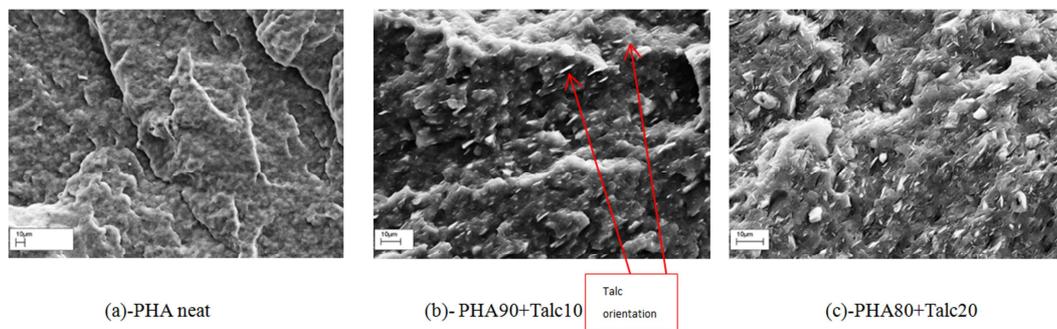


Figure 10. SEM images of the fracture surfaces of the PHA/talc composite tensile bars with different talc concentrations.

The figures 10(b & c) were taken from the edge of specimens and the image 10(a) from the center of the specimen to have a comparison of the orientation of the talc in the whole cross-section of the moulding. The images clearly show that the talc particles were randomly dispersed and oriented in the PHA matrix. A strong parallel orientation of particles aligns with the flow direction at the wall of the mould (figures 10b, c). The lamellae of the talc particles and the polymer melt flow that are frozen close to the surface (skin) have an orientation favorable to the mechanical loading intension. These phenomena result from the fountain flow effect of the melt filling the mould (figure 10). In the core of the specimens, the particles show a more random

orientation. A similar phenomenon has also been reported by Whaling et al. and in the work of Pukanszky and Moezo which indicated that talc particles tend to orient in the flow direction in processing in conventional plastic machinery due to their anisotropic structure when subjected to the shear stress and flow pattern during the processing. According to Pukanszky et al, the orientation and orientation distribution of particles in the matrix is dependent on factors such as shear condition, flow pattern, mould filling rate, and cooling condition [20]. Whaling, Bhardwaj, and Mohanty declared that the dispersion of particles in a polymer matrix also depends on the shear stress developed to separate the particles during processing and the relative magnitudes of the

adhesion and separating forces of the particles [7].

4. Conclusion

All non-isothermal DSC of the PHBV and PHBV/talc composites showed two peaks of the melting point due to reorganization and recrystallization of the polymer close and before the melting point.

Isothermal crystallization kinetics of the PHBV has been analyzed using the JMAK equation and it showed how the talc accelerated the crystallization of the PHBV. The Avramis component proved that the mechanism of crystallization did not change with the different concentrations of talc. It was also revealed that the value of the isothermal crystallization rate constant, k , reduced and the time at half crystallinity, $t_{0.5}$ is increased with an increase in temperature. The value of $t_{0.5}$ was reduced with an increase in the amount of talc at a specific temperature.

The above results indicate that the addition of talc increased the crystallization rate of PHBV in the composites. Therefore, talc enhances the nucleation of the PHBV in the composites which leads to a faster crystallization rate.

The XRD result showed that the crystalline structure of the polymer matrix is not affected by the presence of talc.

The TGA results indicated that the addition of talc could increase the temperature of degradation of PHBV/talc composite with 10% talc. However, thermal stability doesn't improve with increasing the amount of talc.

The DMA result revealed that the storage modulus of the composites increased with an increase in the content of talc. However, the phenomenon was not similar to the 85/15 talc concentration. This might be due to an insufficient amount of talc inside the composite. The change in storage modulus demonstrated the reinforcing effect of talc.

There were no distinguishable changes in the glass transition temperatures with the addition of the talc to PHBV.

The heat distortion temperature of PHBV/talc composite increased significantly with an increase in the amount of talc.

The Young's Modulus and the Flexural Modulus increased with the addition of talc. The mathematical prediction of the modulus of elasticity of the composites using the Halpin-Tsai equation closely matched the experimental results presented.

Finally, SEM revealed the platy shape structure of the talc powder. The aspect ratio was calculated from the SEM images of the composites. The images also showed a good dispersion of the talc particles inside the polymer matrix. The orientation of the particles resulting from the shearing of the melt at the mould walls and the cold surface of mould was also observed in the SEM images.

References

- [1] Vidhate, S, Innocentini-Mei, L, D'Souza, N, A, (2012), "Mechanical and electrical multifunctional poly (3-hydroxybutyrate-co-3-hydroxyvalerate)—multiwall carbon nanotube nanocomposites", *Journal of polymer engineering & science*, Vol 52, issue 6, 1367-1374.
- [2] Bugnicourt, E, Cinelli, P, Lazzeri, A, Alvarez, V, (2014), "Polyhydroxyalkanoate (PHA): Review of synthesis, characteristics, processing and potential applications in packaging", *eXPRESS Polymer Letters*, Vol. 8, No. 11, 791–808 Available [online] at www.expresspolymlett.com (Accessed 18 Aug 2016).
- [3] Liu, W, J, Yang, H, L, Wang, Z, Dong, L, S, Liu, J, J, (2002), "Effect of nucleating agents on the crystallization of Poly(3-Hydroxybutyrate-co-3-Hydroxyvalerate)", *Journal of Applied Polymer Science*, Vol. 86, Pages 2145–2152, Wiley Periodicals, Inc.
- [4] Kai, W, He, Y, Inoue, Y, (2005), "Fast crystallization of poly(3-hydroxybutyrate) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) with talc and boron nitride as nucleating agents", *Journal of Polymer International*, Volume 54, Issue 5, Pages 780–789.
- [5] Kucerova, J, (2008), "Nucleating and clarifying agents for polymers", [online] Available at http://digilib.k.utb.cz/bitstream/handle/10563/7290/ku%C4%8Derov%C3%A1_2008_bp.pdf?sequence=1 (Accessed 17 Aug 2016).
- [6] El-Hadi, A, Schnabel, R, Straube, E, Müller, G, Riemschneider, M, (2002), "Effect of melt processing on crystallization behavior and rheology of poly (3-hydroxybutyrate)(PHB) and its blends", *Macromolecular Materials and Engineering Journal*, Volume 287, Issue 5, Pages 363-372.
- [7] Whaling, A, Bhardwaj, R, Mohanty, A, (2006), "Novel Talc-Filled Biodegradable Bacterial Polyester Composite", *Ind. Eng. Chem. Res.*, Vol 45, Issue 22, pages 7497–7503.
- [8] Gunaratne, L. M. W. K, Shanks, R. A, (2005), "Multiple melting behavior of poly(3-hydroxybutyrate-co-hydroxyvalerate) using step-scan DSC", *European Polymer Journal*, Vol: 41, Pages 2980–2988.
- [9] Wang, Y. D., Yamamoto, T, Cakmak, M, (1996), "Processing characteristics and structure development in the solid-state extrusion of bacterial copolyesters: PHBV", *J Applied Polymer Science*, Volume 61, Issue 11, Pages 1957–1970.
- [10] Wu, G, Wen, B, Hou, S, (2004), "Preparation and structural study of polypropylene-talc gradient materials", *Journal Polymer Int.*, Vol 53, Pages 749-755.
- [11] Obata, Y, Sumitomo, T, (2001), "The effect of talc on the crystal orientation in polypropylene/ethylene-propylene rubber/talc polymer blends in injection molding" *Polymer Engineering & Science*, Vol 41, Issue 3, pages 408–416.
- [12] Kunioka, M, Tamaki, A, and Doi, Y., (1989), "Crystalline and thermal properties of bacterial copolyesters: poly (3-hydroxybutyrate-co-3-hydroxyvalerate) and poly (3-hydroxybutyrate-co-4-hydroxybutyrate)", *Macromolecules*, vol. 22, no. 2, pp. 694–697.
- [13] Li, G.; Helms, J. E.; Pang, S. S., Schulz, K, (2001), "Analytical Modeling of Tensile Strength of Particulate-Filled Composites". *Polym. Compos.* Vol 22, Pages 593-603.
- [14] De Armit, C, (2011), "functional fillers for plastics", in book *Applied Plastics Engineering Handbook*, by Kutz, Elsevier, page 458.
- [15] Xanthos, M, (2010), "Functional Fillers for Plastics", Wiley-VCH Verlag GmbH & co, page 35.

- [16] Castillo, A, L, Barbosa, S, E, Capiati, N, J, (2013), "Influence of talc morphology on the mechanical properties of talc-filled polypropylene", *J Polym Res*, vol 20, page152.
- [17] Echevarria GG, Eguiazabal JI, Nazabal J (1998), "influence of molding conditions and talc content on the properties of polypropylene composites", *Eur. Polym. J.* Vol. 34, No. 8, pp 1213-1219.
- [18] Halpin, (1969), "Stiffness and Expansion Estimates for Oriented Short Fiber Composites" *Journal of composite Materials*, Volume: 3 issue: 4, page (s): 732-734.
- [19] Landel, R, F, Nielsen, E, L,(1994)," *Mechanical Properties of Polymers and Composites, Second Edition*", Marcel Dekker Inc, New York, page 425.
- [20] Pukanszky, B, Belina, K, Rockenbauer, A, Maurer, F, H, J. (1994), "Effect of nucleation, filler anisotropy and orientation on the properties of PP composites", *Composites*, Vol 25, Issue 3, Pages 205-214.