Mechanical properties and structure development in poly(butylene succinate)/organo-montmorillonite nanocomposites under uniaxial cold rolling

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Abstract. Polymer nanocomposites have potentially enhanced properties when the molecular orientations of the polymer chains can be controlled. In this study, the mechanical and structural properties of poly(butylene succinate) (PBS) and 2wt% organo-montmorillonite (OMMT) filled PBS nanocomposites were modified by uniaxial cold rolling. Cold rolling was carried out to different compression ratios. The mechanical properties of rolled samples were studied in both the machine direction (MD) and the transverse direction (TD). Along the MD, distinct improvements in tensile strength and elongation at break were observed. However, the tensile strength degraded along the TD. Wide angle X-ray diffraction (WAXD) and microwave molecular orientation analysis reported on the degree of molecular orientation after rolling. Further, degree of crystallinity was reduced after cold rolling.

Keywords: nanocomposites, molecular orientation, cold rolling, poly(butylene succinate), organo-montmorillonite

1. Introduction

Aliphatic polyesters have been recognized as environmentally friendly biodegradable polymers. Poly(butylene succinate) (PBS) is one of the most promising biodegradable aliphatic polyesters. PBS is commercially available with many desirable properties including biodegradability, melt processability, thermal and chemical resistance [1–7]. Addition of organo-montmorillonite (OMMT) has been reported to increase the strength and modulus of PBS [1–3]. However, the extent of these improvements is rather limited. As the structure of molecular orientation is an important factor in producing polymer materials with outstanding properties, orientating the polymer chains using various methods such as cold rolling should be able to further improve polymer strength and ductility [8, 9].

Cold rolling is a process by which a polymer sheet is introduced between two unheated rollers and then compressed and squeezed. It is usually carried out at temperature below the crystallization temperature of the polymer. The technical merits offered by cold rolling process are the controllability, energy-saving and better dimensional retention after rolling due to the lower operation temperature. Basically, the rolling conditions, including temperature, time, and final thickness, determine the properties of the rolled product. Understanding the relationship between the deformation characteristics and the induced microstructure is essential to enable prediction on the final properties of the product [8–12]. Although studies on polymer chain orientation are rather abundant, research on the deformation of polymer nanocomposites is rare. Abu-Zurayk *et al.*

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[13] reported that biaxial hot stretching on the nanocomposites has caused the delamination of clay stacks and orientation of clay. However, there is no relevant work has been reported on the uniaxial cold rolling of polymer nanocomposites. It is an interesting field of study in order to further enhance the material properties by using a relatively simple process. During uniaxial cold rolling, the direction of the molecular orientation relative to the applied stress direction is of particular importance [14]. In this study, uniaxial cold rolling has been carried out on PBS and 2 wt% OMMT filled PBS nanocomposites. Sheets are reduced in thickness by 20–60% which defined by the compression ratio (λ). Uniaxial cold rolling is believed to improve the mechanical properties of nanocomposites. Generally, tensile strength of rigid polymers increases in the direction parallel to the rolling direction, which is known as the machine direction (MD). However, such strength decreases in the direction perpendicular to the rolling direction or known as the transverse direction (TD) [14, 15]. Vega-Baudrit *et al.* [15] have previously reported on the dramatic enhancement of strength and modulus of PBS along the MD after uniaxial rolling process.

In this research, the mechanical properties of the rolled samples were investigated both in the MD and in the TD. The mechanical properties are greatly influenced by the polymer chain orientation that develops during cold rolling. Birefringence generated by microwave molecular orientation analyzer provides a quantitative study on the molecular orientation of polymers at different λ . Moreover, it provides the information on the molecular orientation angle (MOA) and molecular orientation ratio (MOR) of polymer chains. Wide angle X-ray diffraction (WAXD) is another common method used to observe the molecular orientation of crystalline phase in PBS. The effects of cold rolling on the degree of crystallinity were studied using WAXD and differential scanning calorimetry (DSC).

2. Experimental details

2.1. Materials

PBS (Bionolle #1020) was supplied by Showa Highpolymer Co., Ltd., Japan with MFI value of 25 g/10 min (190°C, 2.16 kg), melting temperature

of 115°C and density of 1.26 g/cm³. OMMT (Nanomer® I.30TC, Nanocor Inc, USA) with cation exchange capacity (CEC) of 110 mequiv/100 g was used in this study.

2.2. Preparation of nanocomposites

In this research, PBS was incorporated with 2 wt% of OMMT to form a nanocomposite (PBS/2%OMMT). First, PBS pellets and OMMT were dried at 60°C for 24 hours. Melt-mixing of PBS with OMMT was performed using an internal mixer (Haake PolyDrive R600, Thermo Electron Cooperation, Germany). The mixing process was carried out for 5 minutes at a temperature of 135°C and a rotary speed of 50 rpm. The mixed compound was dried at 60°C for 24 hours. The dried compound was then molded on a compression molding machine (GT 7014-A30C, GOTECH Testing Machines Inc., Taiwan). The compound was pre-heated at 135°C for 7 minutes, followed by compression molding for 3 minutes. After that, the sample was cooled through a cold-pressing at 15°C for 5 minutes.

2.3. Uniaxial cold rolling

The two-roll mill machine (XK-160, Shanghai rubber-machine work, China) consists of two rotating rollers with diameter of 160 mm, length of 320 mm and rotating speed of 60 rpm. PBS and nanocomposite sheets with original thickness of 1 mm were rolled between the unheated rollers at room temperature. The sheets were rolled for several times in one direction to reduce the thickness to 20, 40 and 60% (~0.8, 0.6 and 0.4 mm, respectively) by controlling the gap between the two rollers. The sample thickness was measured after each rolling cycle to enable the control of final thickness. The compression ratio (λ) is defined by d_0/d where d_0 and d are the sample thickness before and after rolling. The relationship between the sample thickness and λ are shown in Table 1.

Table 1. Compression ratio with different thickness reduction

Thickness reduction [%]	d_0 [mm]	d [mm]	λ
20	1	0.8	1.25
40	1	0.6	1.67
60	1	0.4	2.50

2.4. Sample characterizations

2.4.1. Mechanical properties

Tensile properties were studied by using a universal testing machine (Instron 3366, Instron Co., Ltd., USA) at $23 \pm 2^\circ\text{C}$ and $50 \pm 5\%$ relative humidity. Tensile test was carried out according to the ASTM D638-03 (Type IV) standard with a gauge length of 50 mm and a cross-head speed of 5 mm/min. The tensile properties such as tensile strength, modulus and elongation at break were investigated in both the MD and TD. Five measurements were conducted on each sample.

2.4.2. Differential scanning calorimetry (DSC)

DSC analysis was carried out using Perkin-Elmer DSC-6 (PerkinElmer Inc., USA) under a nitrogen atmosphere. The sample was heated from 30 to 150°C at a heating rate of $10^\circ\text{C}/\text{min}$ and followed by a cooling stage from 150 to 30°C at the same rate. The first heating is to eliminate the thermal history in the sample. A second heating was then performed from 30 to 150°C . Finally, samples were cooled to room temperature. The data was analyzed to determine the melting temperature, T_m , and crystallization temperature, T_c , of PBS. Degree of crystallinity (χ_c) was calculated by using Equation (1) for pure PBS:

$$\chi_c = \frac{\Delta H_c}{\Delta H_m^0} \cdot 100\% \quad (1)$$

where ΔH_c – crystallization enthalpy of sample, ΔH_m^0 – melting enthalpy of 100% crystalline PBS (110.3 J/g) and using Equation (2) for polymer nanocomposites:

$$\chi_c = \frac{\Delta H_c}{\Delta H_m^0(1 - W_f)} \cdot 100\% \quad (2)$$

where W_f – weight fraction of fillers in the nanocomposite.

2.4.3. Microwave molecular orientation analysis

The effects of uniaxial cold rolling process on the development of polymer chain alignments were investigated by microwave molecular orientation analyzer (MOA-6015), Oji Scientific Instrument, Japan. This is a simple technique to determine the molecular orientation and dielectric anisotropy of sheet materials. Sample was inserted into the gap between a pair of rectangular waveguides of the

cavity resonator system. Then, polarized microwaves were irradiated perpendicular to the sample [16, 17]. The sample was rotated around the central axis normal to the sheet plane at a speed of 6.0 s per turn. The transmitted wave intensity is measured at every 1° of rotation angles. The orientation patterns are obtained by detecting the transmitted microwave intensity at a fixed frequency. It provides the information on molecular orientation angle (MOA). The molecules in polymer sheets are aligned on average in the direction specified by the MOA. Molecular orientation ratio (MOR) can be measured to describe the extent of alignment of molecular chains with reference to the rolling direction. Besides that, birefringence (Δn) was determined as the difference between the refractive indices along the MD and TD [18].

2.4.4. Wide angle X-ray diffraction (WAXD)

The molecular orientation of rolled samples was investigated by using $\text{CuK}\alpha$ radiation with a wavelength of 0.154 nm in a RINT2100FSL diffractometer (Rigakudenki Ltd, Japan). The samples were scanned in a scan range from 2 – 40° by using $2.0^\circ/\text{min}$ scanning rate. WAXD patterns and diffractograms were recorded. The results were analyzed by using X'Pert HighScore Plus software. χ_c were calculated via the software on the basis of Equation (3):

$$\chi_c = \frac{A_c}{A_T} \cdot 100\% \quad (3)$$

where A_c – area of the peak due to crystal diffraction of the sample, A_T – total area of the crystal and amorphous from the sample diffractograms.

3. Results and discussion

3.1. Mechanical properties

After uniaxial cold rolling, the PBS and PBS/2%OMMT nanocomposite were subjected to the tensile test in both the MD and TD, as illustrated in Figure 1.

Table 2 summarizes the tensile characteristics of PBS and PBS/2%OMMT before and after cold rolling. In the MD, distinct differences in the tensile strength and elongation at break could be seen on the PBS and PBS/2%OMMT after uniaxial cold rolling. As the λ increases, tensile strength and elongation at break improved significantly, with

Table 2. Tensile properties of PBS and PBS/2%OMMT nanocomposites along the MD and TD

Rolling direction	λ	Compound	Tensile strength [MPa]	Modulus [MPa]	Elongation at break [%]
Unrolled	–	PBS	32.6 ± 2.7	589 ± 6.8	10.9 ± 2.6
		PBS/2%OMMT	33.6 ± 1.2	632 ± 9.1	12.9 ± 2.4
MD	1.25	PBS	38.3 ± 3.4 (+17.5)	526 ± 10 (–10.7)	38.3 ± 16 (+251.4)
		PBS/2%OMMT	38.5 ± 0.86 (+14.7)	578 ± 23 (–8.6)	22.3 ± 1.8 (+72.9)
	1.67	PBS	57.4 ± 6.2 (+76.0)	563 ± 35 (–4.4)	119 ± 25 (+991.7)
		PBS/2%OMMT	58.8 ± 2.2 (+75.2)	599 ± 32 (–5.2)	113 ± 23 (+776.0)
	2.50	PBS	96.7 ± 2.2 (+196.5)	526 ± 50 (–10.7)	123 ± 7.0 (+1030.3)
		PBS/2%OMMT	98.1 ± 3.7 (+192.4)	568 ± 15 (–10.1)	116 ± 14 (+797.7)
TD	1.25	PBS	32.3 ± 0.40 (–1.0)	606 ± 33 (+2.94)	27.5 ± 3.0 (+152.3)
		PBS/2%OMMT	30.8 ± 0.58 (–8.1)	641 ± 20 (+1.4)	20.5 ± 8.6 (+58.9)
	1.67	PBS	31.0 ± 0.90 (–4.8)	688 ± 10 (+16.8)	17.8 ± 1.6 (+63.3)
		PBS/2%OMMT	30.4 ± 0.51 (–9.3)	748 ± 42 (+18.4)	17.0 ± 1.8 (+31.8)
	2.50	PBS	28.8 ± 0.33 (–11.6)	757 ± 21 (+28.6)	17.4 ± 0.06 (+59.6)
		PBS/2%OMMT	28.0 ± 0.68 (–16.6)	837 ± 6.6 (+32.5)	10.0 ± 0.06 (–22.5)

() Percentage of changes in the tensile properties after cold rolling

Figure 1. Schematic diagram of sample preparation in the machine direction (MD) and transverse direction (TD) after uniaxial cold rolling process

greatest improvement visible in samples with the highest $\lambda = 2.50$. Strength improved by 192–196%, and elongation at break improved by 700–1000%, respectively.

Generally, polymer chains will align along the rolling direction to form a more anisotropic material. Most commonly, enhanced properties have been observed along the direction parallel to the rolling direction (MD) in which the molecules are

Figure 2. Illustration of molecular orientation and clay alignment after uniaxial cold rolling

aligned/oriented, while poorer properties have been observed perpendicular to the molecular orientation (TD). The enhancement in strength along the MD could be due to increased molecular orientation and enhanced clay alignment after rolling [13], as illustrated in Figure 2.

Herewith, the anisotropy of the material can be derived from the ratio of strength along the MD to strength along the TD, as presented in Figure 3. It is found that the anisotropy improved with the increment of λ , indicates a better molecular orientation and clay alignment at high λ . Furthermore,

Figure 3. Anisotropy of PBS and PBS/2%OMMT at various compression ratios

PBS/2%OMMT nanocomposite exhibits higher anisotropy than pure PBS due to clay alignment. This indicates that the anisotropy derived from the enhancement of strength is influenced by both the anisotropy in polymer chains and the clay alignment, which differs from the determination via birefringence that will be discussed later.

Both of the tensile stress-strain curves of PBS and PBS/2%OMMT nanocomposite are showing a similar trend. The typical stress-strain curves of PBS and PBS/2%OMMT along the MD are presented in Figure 4. The unrolled PBS and PBS/2%OMMT nanocomposite fractured in a brittle mode. Upon uniaxial cold rolling, plastic deformation occurred on the rolled samples in the MD, which was manifested by the occurrence of yielding as observed in the stress-strain curves. Plastic deformation which involves both breaking of van der Waals bonds between molecules and also scission of some covalent bonds occurred [19]. The force required to break a covalent bond is relatively higher than that required for breaking van der Waals bonds. Orienta-

tion of the polymer chains along the MD results in the presence of a larger number of covalent bonds which must be overcome by a larger tensile force [18]. Thus, the tensile strength of the material increases. In addition, more rolling actions as measured by the λ will likely lead to higher molecular orientation, and commensurately to increased strength [8, 19]. Further, it is believed that uniaxial cold rolling could lead to the enhancement of the degree of clay alignment. Investigation on the effects of various rolling conditions to the clay alignment will be reported in our future publication. As observed in Figure 5, elongation at break increased drastically from unrolled sample to $\lambda = 2.50$ in the MD, outlining the occurrence of the brittle-to-ductile transition. Parallel to the orientation direction, the polymer has become ductile and has a yield point and high elongation [20]. This is due to the more ordered polymer chains alignment in the MD, which reduces the chain entanglements and increases the chain flexibility and mobility to flow and slide [21]. The presence of ‘necking’ on the rolled samples after yield point indicates that plastic

Figure 5. Elongation at break of PBS and PBS/2%OMMT at various compression ratios along the MD

Figure 4. Typical tensile stress-strain curves of (a) PBS and (b) PBS/2%OMMT at various compression ratios along the MD

deformation occurred [22]. During plastic deformation, polymer chains slide among each other and thereby permit the polymer to be elongated more than it could otherwise [20]. A slight decrement in the modulus of PBS and PBS/2%OMMT nanocomposite in the MD is a result of brittle-to-ductile transition. The ductility after uniaxial cold rolling enables the polymer chains to flow and slide during stretching. Thereby, it would reduce the stiffness of the material and subsequently reduce the modulus along the MD.

When tested in the TD, however, opposite trends were observed. As the λ increased, tensile strength was reduced, whilst the modulus increased. Anisotropy generally weakens a polymer specimen perpendicular to the direction of orientation [14, 20, 23], which in this case corresponds to the TD of the cold rolling process. In the TD, loads are carried primarily by weak van der Waals bonds. Fracture in the TD only requires breakage of these much weaker bonds [23, 24]. Further, if there are small cracks or other imperfections in the polymer, they become oriented parallel to the rolling direction. These oriented cracks are strong stress concentrators for loads applied perpendicular to the orientation direction [20], leading to the fracture at a lower tensile force.

Table 2 shows that, even for the sheets with the lower λ (1.25 and 1.67), elongation at break increased in the TD. Stretching along the TD involves the disorientation and reorientation of the polymer molecules [23]. Upon stretching the previously oriented material in the TD, molecules will first disorient and then reorient themselves along the direction of the applied force [20]. The disorientation and reorientation processes lead to plastic deformation of the material and causes a slight increment in the elongation at break. For the PBS/2%OMMT nanocomposite, there is a slight decrease in the elongation at break for the highest λ . This is due to the high clay orientation and exfoliation, which limited the disorientation and reorientation processes. Moreover, the materials become rigid with an increasing modulus with λ along the TD. Unlike uniaxial stretching, uniaxial rolling process could induce a biaxial orientation since the rolling will result in the expansion of samples both in the MD and TD direction. However, the orientation along the TD is relatively lower than that of along

the MD [24]. Thus, it could only be traced from the modulus which obtained at the low strain level. Further research to ascertain this phenomenon is in progress by using a higher λ up to 4.0 in order to investigate the changes in modulus along the TD at high λ . It will be reported in our future publication.

3.2. Microwave molecular orientation analysis

Generally, the polymer chains tend to orient parallel to the MD with uniaxial rolling process, leading to the enhancement of the mechanical properties [8–10, 12–15] as discussed above. Therefore, the investigation upon the orientation of polymer chains is essential to understand the effects of uniaxial cold rolling on the anisotropy of polymers. Microwave molecular orientation analysis by using polarized microwaves is able to provide information on the birefringence of a material [25]. Birefringence is a measurement of the total molecular orientation of both crystalline and amorphous region in a semi-crystalline polymer such as PBS [26–28]. It is able to provide a quantitative measurement on the overall molecular orientation by detecting the differences in polarizability of molecular chains at two perpendicular directions [29].

Figure 6 shows the birefringence, Δn as a function of λ . The value of Δn is often taken as a measure of molecular orientation. Both of the PBS and PBS/2%OMMT are showing a similar trend. The Δn for unrolled samples is very low, which is 0.0001 and 0.0003 for PBS and PBS/2%OMMT, respectively. After subjected to uniaxial cold rolling, Δn increases with the λ . This indicates that higher λ during uniaxial cold rolling is able to induce higher molecular orientation to the polymer chains. The Δn of PBS is higher than that of PBS/2%OMMT, which con-

Figure 6. Birefringence of PBS and PBS/2%OMMT at various compression ratios

forms to the WAXD results. Δn may arise from the molecular anisotropy but also from the ordered alignment of similar particles such as OMMT. However, as reported by Yalcin *et al.* [12], the formation of Δn due to the ordered alignments of OMMT is negligible. The nanometer size OMMT has similar refractive index as the polymer matrix and will not influence the Δn . Thus in this case, the effect of clay alignment is neglected in the determination of anisotropy. As mentioned above, anisotropy derived from Δn and WAXD show a different trend than that of derived from strength. Besides that, the microwave molecular orientation analysis can provide the study on molecular orien-

tation angle (MOA) and molecular orientation ratio (MOR) of the polymer chains. MOA represents the magnitude of the chain alignment angle diverted from the MD. MOA is approximately zero when the polymer chains are aligned parallel to the MD. The MOR value reveals the relative number of polymer chains orientating to the direction specified by MOA [30]. Typical orientation patterns of PBS and PBS/2%OMMT are presented in Figure 7. The vertical axis is corresponding to the MD; whilst the horizontal axis is corresponding to the TD.

Figure 8 shows a comparison of the MOA and MOR according to their respective λ . Both PBS and PBS/2%OMMT are showing a similar trend. After subjected to uniaxial cold rolling, MOA decreased significantly. This indicates that the polymer chains tend to align in the direction more parallel to the MD as compared with the unrolled samples. Generally, the MOA reduces with the increment of λ due to a more parallel orientation with the MD [30]. The polymer chains aligned most parallel to the MD at $\lambda = 2.50$, which is manifested by the lowest MOA. At the $\lambda = 2.50$, higher rolling actions has contributed to a better molecular orientation, leading to a better enhancement of the mechanical properties. The MOA of the samples which rolled at $\lambda = 1.67$ is slightly higher than that at the $\lambda = 1.25$. However, the difference is insignificant, which is 3 and 4° for PBS and PBS/2%OMMT, respectively.

Another important indication of molecular orientation in a sample is the MOR. For both PBS and PBS/2%OMMT, MOR increased with the increment of λ . The highest MOR is observed at $\lambda = 2.50$, reveals a higher quantity of polymer chains aligned close to the MD with the angle defined by MOA [25]. The relationship between MOA and

Figure 7. Typical orientation patterns of (a) PBS and (b) PBS/2%OMMT obtained at various compression ratios

Figure 8. Molecular orientation angle and molecular orientation ratio as a function of compression ratio for (a) PBS and (b) PBS/2%OMMT

MOR determines the molecular orientation of the polymers. The polymer chains are oriented slightly close to the MD at $\lambda = 1.25$, comparing with the $\lambda = 1.67$ as verified by MOA. However, a better molecular orientation can be observed at the $\lambda = 1.67$ with better properties enhancement is attributed to the relatively higher MOR. The higher MOR at $\lambda = 1.67$ has compensated the slight increment in MOA, leading to a better molecular orientation. Thus, it can be concluded that the degree of molecular orientation along the MD increased when subjected to greater rolling action (or higher λ). The results are conforming to the mechanical properties and WAXD.

3.3. Wide angle X-ray diffraction (WAXD)

Details of the molecular orientation and degree of crystallinity of PBS and PBS/2%OMMT were obtained by WAXD. WAXD is a common technique to evaluate the molecular orientation of crystalline region in a semicrystalline polymer, such as PBS. Figures 9 and 10 show the WAXD patterns for PBS and PBS/2%OMMT at different λ , where the uniaxial rolling direction is vertical. The Debye rings indicate that PBS is an isotropic material, which becomes orientated as the thickness is reduced by uniaxial cold rolling. For unrolled PBS and PBS/2%OMMT, the azimuthal intensity distri-

Figure 9. WAXD patterns of rolled PBS sheets at various compression ratios: (a) unrolled, (b) $\lambda = 1.25$, (c) $\lambda = 1.67$, (d) $\lambda = 2.50$

Figure 10. WAXD patterns of rolled PBS/2%OMMT sheets at various compression ratios: (a) unrolled, (b) $\lambda = 1.25$, (c) $\lambda = 1.67$, (d) $\lambda = 2.50$

bution for each reflection is uniform, confirming that PBS is an isotropic material. Upon uniaxial cold rolling to a higher λ , gradual intensification of the amorphous halo in the equator has been observed. At $\lambda = 2.50$, a clear intensity difference between meridian and equator indicates the development of molecular orientation [10, 12, 31, 32]. Moreover, rolled PBS has higher molecular orientation than does rolled PBS/2%OMMT. This appears in the WAXD patterns as a more dramatic intensity change in PBS after rolling. This result can be correlated with the anisotropy determined by microwave molecular orientation analysis.

Figure 11. WAXD diffractograms of PBS at various compression ratios: (a) unrolled, (b) $\lambda = 1.25$, (c) $\lambda = 1.67$, (d) $\lambda = 2.50$

Figure 12. WAXD diffractograms of PBS/2%OMMT at various compression ratios: (a) unrolled, (b) $\lambda = 1.25$, (c) $\lambda = 1.67$, (d) $\lambda = 2.50$

Table 3. Degree of crystallinity verified by WAXD at various compression ratios

Compound	λ	χ_c [%]
PBS	unrolled	49.37
	1.25	46.98
	1.67	46.75
	2.50	40.74
PBS/2%OMMT	unrolled	40.87
	1.25	39.52
	1.67	39.31
	2.50	38.07

Figures 11 and 12 show the WAXD diffractograms of PBS and PBS/2%OMMT at different λ . Degree of crystallinity, χ_c , are identified from the diffractograms, as presented in Table 3. Cold rolling action decreased the χ_c due to the destruction of crystalline

regions as large lamellae (folded chain structures) were subjected to rolling to form microfibrils (extended chain structures). The transition from folded chain structures to extended chain structures after cold rolling resulted in thinner lamellae and lower crystallinity [33].

3.4. Differential scanning calorimetry (DSC)

Uniaxial cold rolling does not show significant effect on the melting and crystallization behaviour of PBS and PBS/2%OMMT nanocomposites, as observed in Figure 13 and Table 4. Figure 13a shows that there are no distinct differences in DSC patterns as well as in the melting peaks for rolled and unrolled samples. The presence of two melting peaks corresponds to the two different types of crystalline lamellae present in PBS [6]. Vega-Baudrit *et al.* (2005) [15] suggested that the low endotherm, 'y' is corresponds to the melting of the original crystallites; and the high endotherm, 'x' corresponds to the melting of the recrystallized one. As presented in Table 4, no notable changes in melting temperatures, $T_{m,x}$ or $T_{m,y}$ were observed after the cold rolling process.

Table 4 shows that rolling and clay addition do not significantly impact the crystallization temperature, T_c . No shifting of the crystallization peaks was observed in Figure 13b. However, the degree of crystallinity, χ_c decreased after clay addition and uniaxial cold rolling process as discussed previ-

Figure 13. DSC thermograms at (a) melting and (b) crystallization

Table 4. DSC results of rolled and unrolled PBS and PBS/2%OMMT nanocomposite

Compound	$T_{m,x}$ [°C]	$T_{m,y}$ [°C]	ΔH_m [J/g]	T_c [°C]	χ_c [%]
PBS (unrolled)	112.4	102.2	63.6	85.9	57.6
PBS ($\lambda = 2.50$)	112.9	102.4	59.8	85.9	54.2
PBS/2%OMMT (unrolled)	113.4	102.1	60.3	85.6	55.7
PBS/2%OMMT ($\lambda = 2.50$)	112.6	102.2	50.9	85.7	47.1

ously. According to Dubnikova *et al.* [34], the crystallization of polymer chains decreases as a result of their confinement between the intercalated and exfoliated clay layers. χ_c is also most reduced for samples with the highest λ . The χ_c values of DSC are slightly different from that of obtained from WAXD, however, the trend appears to be the same. The variation is believed to be a result of errors between different characterization methods and equipments. The DSC results show that any enhancement in mechanical properties after cold rolling is not a result of crystallinity enhancement.

4. Conclusions

The addition of 2 wt% OMMT to PBS via melt mixing slightly improved both the strength and the elongation at break of the nanocomposites. When PBS and PBS/2%OMMT sheets were subjected to uniaxial cold rolling, tensile strength along the MD increased substantially. This is mainly due to the increased molecular orientation after cold rolling, which is verifiable by microwave molecular orientation analysis and WAXD. A brittle-to-ductile transition was also observed along the MD, identifiable by a substantial increase in elongation at break and a reduction of the modulus. The strength of the rolled samples degraded along the TD. However, the modulus and elongation at break increased along the TD. Thus, it is concluded that PBS is an isotropic material, whose properties are greatly reliant on molecular chain alignment. WAXD and DSC demonstrated a decrease in crystallinity after cold rolling. This reduction is due to the destruction of crystalline regions during cold rolling. Hence, it indicates that any enhancement in mechanical properties observed is not a result of crystallinity enhancement. Moreover, according to DSC thermograms, no notable changes in T_m and T_c were observed after cold rolling. As a conclusion, uniaxial cold rolling does not influence the thermal properties of PBS or of its nanocomposites.

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