

Influence of thermal conditions on the tensile properties of basalt fiber reinforced polypropylene-clay nanocomposites

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Abstract

In this paper, a comparative study on the tensile properties of clay reinforced polypropylene (PP) nanocomposites (PPCN) and chopped basalt fiber reinforced PP-clay nanocomposites (PPCN-B) is presented. PP matrix are filled with 1, 3 and 5 wt.% of nanoclays. The ultimate tensile strength, yield strength, Young's modulus and toughness are measured at various temperature conditions. The thermal conditions are included the room temperature (RT), low temperature (LT) and high temperature (HT). The basal spacing of clay in the composites is measured by X-ray diffraction (XRD). Nanoscale morphology of the samples is observed by transmission electron microscopy (TEM). Addition of nanoclay improves the yield strength and Young's modulus of PPCN and PPCN-B; however, it reduces the ultimate tensile strength. Furthermore, the addition of chopped basalt fibers to PPCN improves the Young's modulus of the composites. The Young's modulus and the yield strength of both PPCN and PPCN-B are significantly high at LT (-196 °C), descend at RT (25 °C) and then low at HT (120 °C).

Keywords: Polypropylene, Nanocomposites, Basalt fibers, Low temperature, High temperature, Tensile properties

1. Introduction

Nanotechnology is now recognized as one of the most fortunate areas for technological expansion in the 21st century [1]. In materials research, the development of polymer nanocomposites is rapidly emerging as a multidisciplinary research activity whose results could broaden the applications of polymers to the great benefit of many different industries. Polymer nanocomposites are polymers (thermoplastics, thermosets or elastomers) that have been reinforced with small quantities (less than 5% by weight) of nano-sized particles having high aspect ratios ($L/h > 300$) [2].

Clay nanoparticles, metal oxide nanoparticles, such as silica and titania nanoparticles, and carbon nanotubes increase the mechanical properties, especially, the elastic modulus of many kinds of polymer composites [3]. In the case of layered silicate (clay) nanocomposites, volume fractions of 2 to 5% by weight of clay result in mechanical properties similar to those found in conventional composites with 30 to 40% reinforcing material. Polyolefins as one of the most consumed resins, especially polyethylene (PE) and polypropylene (PP), are widely used in diverse applications, such as packaging, ornament, agriculture, and etc. [4].

Their general approaches have been adopted in attempts to improve the properties of polymeric composites by nanoparticles. For example, Yuan et al. [5] used clay nanoparticle added to PP matrix which increased the impact strength in the temperature range of 0 to 70 °C, while the toughness remained unaffected between -40 to 0 °C. The high toughness of clay reinforced PP nanocomposite was related to the crystal structure, the dispersion state of nanoclay particles, and the strong interfacial interaction between the nanoclay and the

polymer matrix. Svoboda et al. [6] reported that the addition of clay to PP always improved the tensile strength and tensile modulus, but reduced its ultimate elongation, regardless of the molecular weight of polypropylene-grafted-maleic anhydride (PP-g-MA). The most significant increase in tensile strength occurred with the addition of 1 to 2% of clay content. Selvakumar et al. [7], Kodgire et al. [8] and Saminathan et al. [9] reported similar results which with increasing nanoclay particles tensile properties increased. Yang et al. [10] investigated the mechanical behavior of montmorillonite-epoxy nanocomposites at both room temperature (RT) and low temperature (LT) in terms of tensile and impact properties. The strength and modulus of the nanocomposites were significantly higher at LT than at RT and these observations were explained in terms of the interfacial adhesion.

Fiber reinforced polymer is a composite material that has been developed in recent years. Reinforcement fibers are usually added in the form of continuous or chopped fibers to polymer matrix. A chopped fiber reinforced composites can have better processing properties and behave as isotropic materials at an expenses of light weight structure and can mold into complex shaped components [11].

Basalt fiber, known as the green industrial material of the 21st century, combines ecological safety, natural longevity and many other properties. It is not a new material, but its applications are surely innovative in many industrial and economic fields, from building and construction to energy efficiency, from automotive to aeronautic, due to its good mechanical and chemical performances [12]. Hence, the basalt fiber has gained increasing attention as a reinforcing material especially compared to traditional glass and carbon fibers. Basalt fiber can be provided at a cost considerably less than carbon, silica and other fibers. Basalt fiber has been comprehensively investigated as reinforcement to PP matrix composites [12].

For instance, Akinci [13] showed that the content of basalt fiber affected the structural integrity and the mechanical properties of composites. With increasing the amount of the basalt addition to the low density polyethylene (LDPE) results in a decrease in the elongation at breaking values. XRD investigations showed that the crystallization ratio changes in the LDPE composites. The crystallization was increased by increasing the basalt content and the basalt weight percent increases the hardness. If suitable coupling agents could be added to the basalt and LDPE mixtures, the mechanical properties can possibly be increased. Siddhartha et al. [14] investigated the mechanical characterization of bi-directional and chopped E-glass fiber reinforced epoxy composites. They showed when the amount of bi-directional E-glass fiber increased tensile strength of bi-directional E-glass fiber reinforced composites went up. However, in case of chopped E-glass fiber–epoxy composites a scatter in the tensile strength values was observed.

Mohan et al. [15] studied the effect of nanoclays (0–5 wt.%) on short glass fiber (GF)-reinforced PP composites. Addition of nanoclay reduced the melt flow rate of PP and PP-GF composites; however, it improved the crystallization characteristics due to their nucleating effect. This nucleating effect of nanoclay is due to the nanolevel dispersion in polymer matrix and this phenomenon is not observed in the unmodified microclay-filled PP composites. Improved tensile properties were observed in nanoclay filled PP-GF composites due to the intercalated/exfoliated nanocomposite structure. Furthermore, the addition of nanoclay in PP-GF composites improved the wear properties.

Almaadeed et al. [16] prepared different types of composites as wood flour reinforced recycled PP, GF reinforced recycled PP and wood flour-GF hybrid composites of recycled PP. They showed that tensile properties of recycled PP were improved by addition of wood flour. However, tensile Strength and tensile modulus of wood flour reinforced recycled

polypropylene were improved by adding or hybridizing of GF. Ramsaroop et al. [11] executed a comparative study on the fracture toughness of woven GF reinforced PP, chopped GF reinforced PP and nanoclay filled PP composites. PP composites contain 3 wt.% nanoclay showed superior crack containment properties over virgin PP. Furthermore, the woven fiber reinforced PP composites demonstrated superior crack resistant properties than that of clay filled nanocomposites and chopped fiber PP composites.

During the recent years, a few studies on materials particularly ceramic nanocomposites and cement composites were reported at HT [17]. Lonescu et al. [17] showed that the annealing experiments revealed the incorporation of Zirconium dioxide (ZrO_2) into the Silicon oxycarbide-based materials (SiOC) matrix which remarkably increases the thermal stability of the composites with respect to crystallization and decomposition at temperatures exceeding 1300 °C. The results indicated that the synthesized SiOC/ ZrO_2 nanocomposites are candidate materials for high-temperature applications, due to the fact that the presence of zirconia within the SiOC ceramic matrix was found to strongly suppress the carbothermal decomposition up to 1600 °C.

According to the study in the literature, no article was found to investigate both the effects of nanoparticles and fibers on PP nanocomposites at LT, RT and HT. However, for the first time, Soleimani et al. [18] reported that the notched impact strengths are increased at both 25 °C and -196 °C by increasing the weight percentage of nanoclay particles due to the reinforcement effect of these particles. The tensile modulus of nanocomposites at both 25 °C and -196 °C increased almost linearly with the increase of clay content. Moreover, both the tensile strength and tensile modulus at -196 °C were much higher than those at 25 °C. Eslami-Farsani et al. [19] reported that the addition of nanoclay has a significant enhancement in stiffness of PP/clay nanocomposites. Nearly 36% and 157% increase in the

tensile modulus at both RT and HT are observed, respectively. But, the increase in tensile strength is almost negligible.

The objective of the present paper is focused on the use of PP at LT, RT and HT and its reinforcement by nanoclay and chopped basalt fiber (BF) for their applications at medium load high and low temperature conditions for the first time.

In the present paper, PP nanocomposites contained clay and BF are prepared by melt mixing in a twin screw extruder followed by injection moulding, with different weight percentage of clay (1, 3 and 5 wt.%) and BF (10 wt.%) contents. PP-g-MA is added to matrix PP as a compatibilizer agent. The effect of adding various amounts of nanoclay particles and BF in matrix PP are investigated on tensile loading. Tensile properties as a function of nanoclay concentration are studied and also these properties of nanocomposites are compared to the properties of neat PP at LT, RT and HT. Tensile tests carried out according to ASTM D-638-10 standard. The dispersion characteristics of the nanoclay particles in PP matrix were determined by XRD and TEM.

2. Experimental procedure

2.1. Materials

The materials used for the preparation of PP nanocomposite were the commercialized PP with the trade name of Jampilen HP 500 M from Iran Petrochemical, JAM Products (melt flow rate (MFR) at 230 °C for 2.16 kg = 9 g/10 min), anti-peroxide Ciba-Irganox B215 from Iran Petrochemical, JAM Products and PP-g-MA with the trade name of Karabond ® PCH (Melt index at 190 °C for 2.16 kg = 6±0.5 g/10 min, melting point (1 kg) = 165 °C and graft efficiency = 0.6-1%) from Karangin Company, Iran. The nanoclay, Cloisite ®15A (Pishgaman Fanavari Asia, Iran) was a natural montmorillonite organically modified with a

quaternary ammonium salt, dimethyl, dehydrogenated tallow. The d-spacing of Cloisite ®15A was obtained to be 34.7 Å. The basalt roving fiber with the trade name of BCF13-2520-KV12 was supplied by Kamenny Vek Company from Russia.

2.2. Specimen preparation

Clay reinforced polypropylene nanocomposites (PPCN) were prepared using the melt blending technology in an intermeshing co-rotating twin screw extruder (Plasticorder Model PL2002 with L/D = 40, Germany) and temperature profile used, was from 165-195 °C (feed zone to die zone) with speed 150 rpm. After that, the specimens were designed by injection molding machine (Aslanian, Model EM80, Iran) at temperatures of 175–205 °C and injection pressure of 96 bar. The nanoclay was dried at 80 °C for 4 h in air-circulated oven prior to compounding to remove the moisture. For the preparation of chopped basalt fiber reinforced PP-clay nanocomposites (PPCN-B), the fibers were chopped into segments with a length from 5 to 8 mm. For achieving good mixing, it is better to used extruder twice. PPCN-B was included by 0.2 wt.% anti peroxide, 5 wt.% PP-g-MA, different amount of clay nanoparticles (1, 3 and 5 wt.%) and 10 wt.% chopped basalt fibers. The specimens were cut from the injection-moulded parts (3 mm thickness, 13 mm width and 165 mm length) for tensile tests considering the recommendations in the standard ASTM D-638-10.

All the specimens were coded according to their constituents' wt.% contents and the temperature conditions. P corresponds to PP and 0 to 5 are weight percentage of the nanoclay particles and R, L and H means the room temperature, low temperature and high temperature, respectively and T stands for tensile test and B corresponds to chopped basalt fibers.

2.3. Mechanical tests

Tensile tests at LT, RT and HT were carried out by Hounsfield (Model H25KS Co., England) testing machine with a load cell of 25 kN. The tensile properties of PPCN at 25 °C and 120 °C were measured by tensile testing machine with a crosshead speed of 25 mm/min. The crosshead speed of PPCN-B at 25 °C and 120 °C was set to 10 mm/min and the crosshead speed of PPCN and PPCN-B at -196 °C was set to 5 mm/min. The number of specimens tested in each case is in accordance with the standards (5 specimens). The LT and HT condition was achieved respectively, by dipping the samples in a liquid nitrogen for 20 min to reach to -196 °C and inserting samples in an Oven (Fan Azma Gostar Model BF55, Iran) for 20 min to reach to 120 °C. Then, the specimens were tested simultaneously in tensile loading at the same temperatures. The surface morphology of the fractured surfaces of the nanocomposite specimens and dispersion of the nanoclay and BF in PP matrix were investigated using a SEM (XL30 Philips, from Dutch).

2.4. Characterization

The structure of the nanocomposites was studied by using XRD and TEM methods. The XRD (Philips Analytical, model XPert MPD with Co radiation from Japan (0.154 nm wavelength at a generated voltage of 40 kV and current of 30 mA)) of the specimens were obtained. The diffractograms were scanned from 2.5° to 12° (2 θ) in steps of 0.02° using a scanning rate of 0.5°/min. X-ray diffractograms were taken on Cloisite ®15A clay particles and on PP/clay nanocomposites. Microscopic investigation of the selected nanocomposite specimens at various weight compositions were conducted using a TEM (Philips EM208, from Germany) with an operation voltage at 100 kV.

3. Results and discussion

3.1. Structure and morphology of PP-clay nanocomposites

The structure and morphology of PPCNs is examined using XRD and TEM methods. Figure 1 shows the XRD patterns of PP/clay nanocomposites. The Cloisite ®15A nanoclay shows a diffraction peak of 2θ at 3.2° and corresponds to an interlayer spacing of nanoclay (d-spacing) of 34.79 Å (calculated from Bragg's diffraction law of $2d\sin\theta = n\lambda$). From 1 to 5 wt.% of nanoclay in the PP polymer, there is an absence of a diffraction peak, and this suggests that the polymer matrix has entered into the interlayer spacing of the nanoclay and increased the original nanoclay interlayer spacing or the nanolayers of clays could have randomly dispersion in the PP polymer. Hence, it can be concluded that the nanoclays in the PP polymer from 1 to 5 wt.% formed an ordered exfoliated structure, or a randomly dispersed clay exfoliated structure. To further study the dispersion of nanoclays in the PP polymer, TEM morphology of the samples is examined. Figures 2a to 2c show the bright field TEM images of PPCNs. The bright phase of the picture is the matrix phase and the dark phase is the particle phase. Figures 2a, 2b and 2c show the TEM pictures of PP-clay (1 wt.%), PP-clay (3 wt.%) and PP-clay (5 wt.%) nanocomposites, respectively. With the addition of nanoclay in PP polymer matrix from 1 to 5 wt.% nanoclay, the content of the dark phase increases whereas the nanolayers of clays are well separated and dispersed randomly and show the formation of an exfoliated structure. The TEM pictures support the XRD results for the nanocomposites. Hence, these results show the improvement in tensile properties due to the fine dispersions of the particles.

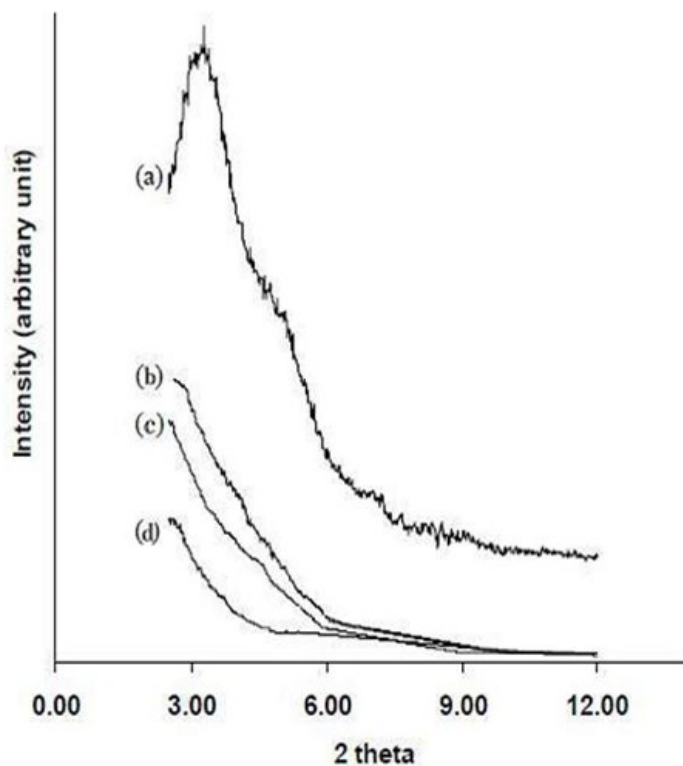


Figure 1. XRD patterns of (a) Cloisite®15A, PP with (b) 5 wt.% clay, (c) 3 wt.% clay, (d) 1 wt.% clay.

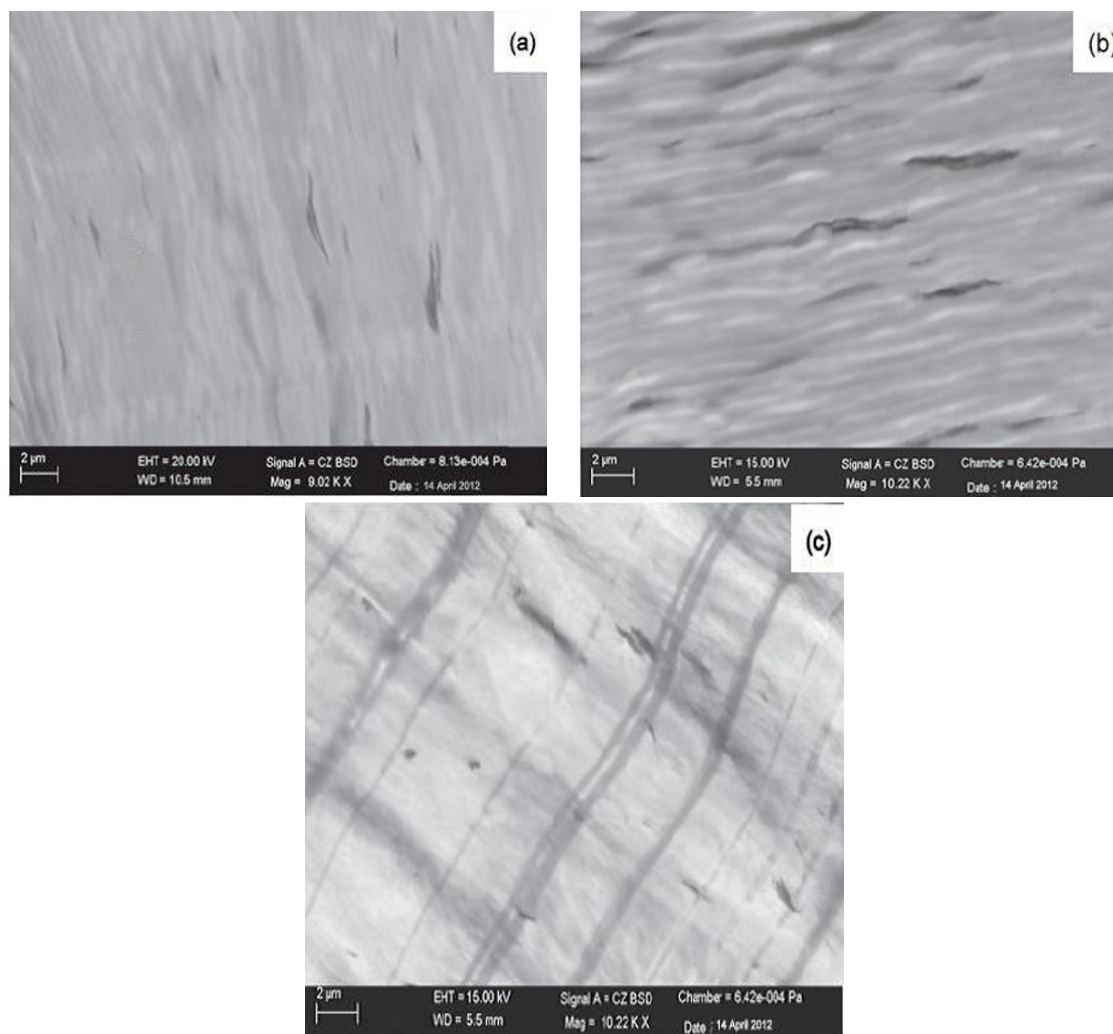


Figure 2. TEM pictures of PP with (a) 1 wt.%, (b) 3 wt.%, (c) 5 wt.% nanoclay particles.

3.2. Tensile test

3.2.1. Clay reinforced PP nanocomposites (PPCN)

In the first part of the discussion section, the tensile properties of nanocomposites were determined as a function of clay content (1, 3 and 5 wt.%). Tensile properties such as ultimate tensile strength, yield strength, Young's modulus, percentage of displacement at break and energy absorption (area under the strain-stress curves) for the neat PP and the

PPCNs and also PPCN-Bs at RT, HT and LT as a function of weight percentage of nanoclay are shown in Tables 1, 2 and 3, respectively. The PP nanocomposites exhibit relatively ductile behavior at RT compared to the results at other temperatures and obviously show ductile and brittle behaviors at HT and LT for all the compositions.

Table 1. Tensile properties of PP, PPCNs and PPCN-Bs at RT

Specimens codes	Room temperature						
	P0RT	P1RT	P3RT	P5RT	P1RTB	P3RTB	P5RTB
Displacement at break %	307.64	274.69	273.22	243.95	215.64	117.24	57.46
Yield strength (MPa)	24.4	23.16	23.76	24.12	23.21	23.92	24.38
Energy absorption (J)	156.68	151.89	131.99	118.23	134.6	60.7	25.3
Ultimate tensile strength (MPa)	19.76	18.06	16.68	15.53	17.45	16.28	15.33
Young's modulus (MPa)	523.42	588.17	612.33	714.22	656.86	729.35	832.64
Density (g/cm ³)	0.91	0.915	0.92	0.925	0.99	0.995	
Specific tensile ultimate strength (MPa/g/(cm ³))	21.71	19.73	18.13	16.78	17.62	16.36	15.33
Specific stiffness (MPa/g/(cm ³))	575.18	642.8	665.57	772.12	663.49	733.01	832.64
Specific toughness	172.17	166	143.46	127.81	135.95	61	25.3
Energy absorption/P0RT energy absorption	—	0.96	0.84	0.75	0.85	0.38	0.16
Specific ultimate tensile strength increase in comparison to P0RT (%)	—	-9.12	-16.5	-22.7	-0.19	-0.22	-0.29
Specific stiffness increase in comparison to P0RT (%)	-	11.75	15.71	34.23	-0.21	-0.64	-0.85

Table 2. Tensile properties of PP, PPCNs and PPCN-Bs at HT

Specimens codes	High temperature						
	P0HT	P1HT	P3HT	P5HT	P1HTB	P3HTB	P5HTB
Displacement at break %	584.51	527.41	532.77	483.21	405.41	223.92	106.19
Yield strength (MPa)	11.04	10.21	10.27	10.61	10.84	11.56	15.03
Energy absorption (J)	297.66	291.62	257.41	234.07	254.38	117.15	49.58
Ultimate tensile strength (MPa)	17.77	16.53	16.94	17.69	14.82	16.36	16.73
Young's modulus (MPa)	134.05	150.6	258.92	345.84	320.19	450.12	583.12
Density (g/cm ³)	0.91	0.915	0.92	0.925	0.99	0.995	1
Specific tensile ultimate strength (MPa/g/(cm ³))	19.52	18.06	18.41	19.12	14.96	16.44	16.73
Specific stiffness (MPa/g/(cm ³))	147.3	165.59	281.43	373.04	323.42	452.38	583.12
Specific toughness	327.09	318.71	279.79	253.04	256.94	117.73	49.58
Energy absorption/P0HT energy absorption	-	0.97	0.86	0.78	0.85	0.39	0.16
Specific ultimate tensile strength increase in comparison to P0HT (%)	-	-7.74	-5.68	-2.04	-0.23	-0.15	-0.14
Specific stiffness increase in comparison to P0HT (%)	-	11.73	91.05	153.82	1.19	2.07	2.95

Table 3. Tensile properties of PP, PPCNs and PPCN-Bs at LT

Specimens codes	Low temperature						
	P0LT	P1LT	P3LT	P5LT	P1LTB	P3LTB	P5LTB
Displacement at break %	584.51	527.41	532.77	483.21	405.41	223.92	106.19
Yield strength (MPa)	11.04	10.21	10.27	10.61	10.84	11.56	15.03
Energy absorption (J)	297.66	291.62	257.41	234.07	254.38	117.15	49.58
Ultimate tensile strength (MPa)	17.77	16.53	16.94	17.69	14.82	16.36	16.73
Young's modulus (MPa)	134.05	150.6	258.92	345.84	320.19	450.12	583.12
Density (g/cm ³)	0.91	0.915	0.92	0.925	0.99	0.995	1
Specific tensile ultimate strength (MPa/g/(cm ³))	19.52	18.06	18.41	19.12	14.96	16.44	16.73
Specific stiffness (MPa/g/(cm ³))	147.3	165.59	281.43	373.04	323.42	452.38	583.12
Specific toughness	327.09	318.71	279.79	253.04	256.94	117.73	49.58
Energy absorption/P0LT energy absorption	-	0.97	0.86	0.78	0.85	0.39	0.16
Specific ultimate tensile strength increase in comparison to P0LT (%)	-	-7.74	-5.68	-2.04	-0.23	-0.15	-0.14
Specific stiffness increase in comparison to P0LT (%)	-	11.73	91.05	153.82	1.19	2.07	2.95

Young's modulus and yield strength at RT, HT and LT are improved by increasing the amounts of nanoclay particles due to the better dispersion of clay layers in PP matrix. This improvement is due to the exfoliation of nanoscale clay particles in the matrix that restricts the mobility of polymer chains under loading. The orientation of clay platelets and polymer

chains with respect to the loading direction can also contribute to the reinforcement effect.

Figures 3 and 4 show the variation of Young's modulus and yield strength of the neat PP and PPCNs at RT, HT and LT as a function of nanoclay content, respectively. A number of recent papers which related to PPCN [7-9] and also some other papers which discussed about clay reinforced polymer [20,21] reported that Young's modulus of nanocomposites with increasing the amount of nanoparticles increased and approximately the maximum Young's modulus were belonged to the composites contain 5 wt.% of nanoclay particles.

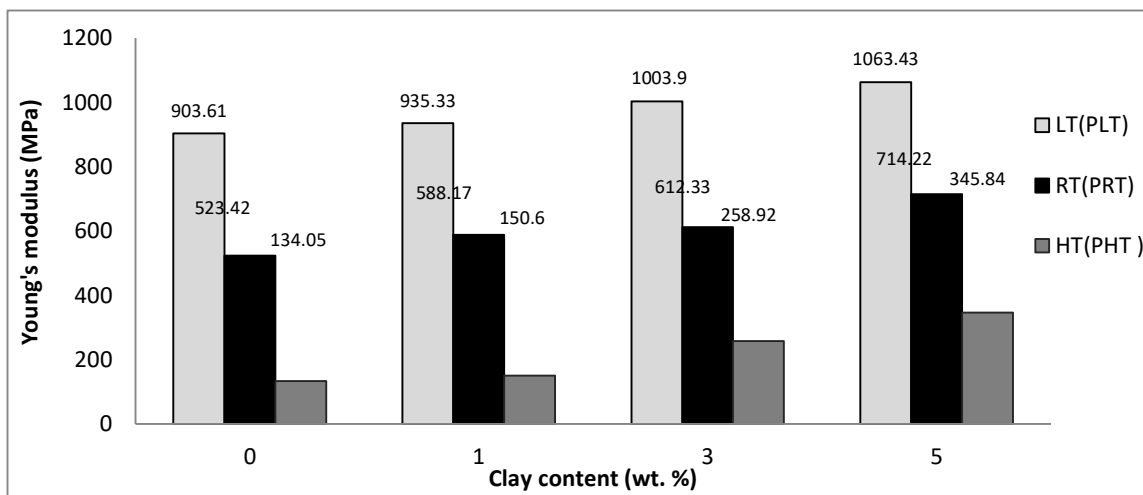


Figure 3. Young's modulus of PPCN at RT, HT and LT.

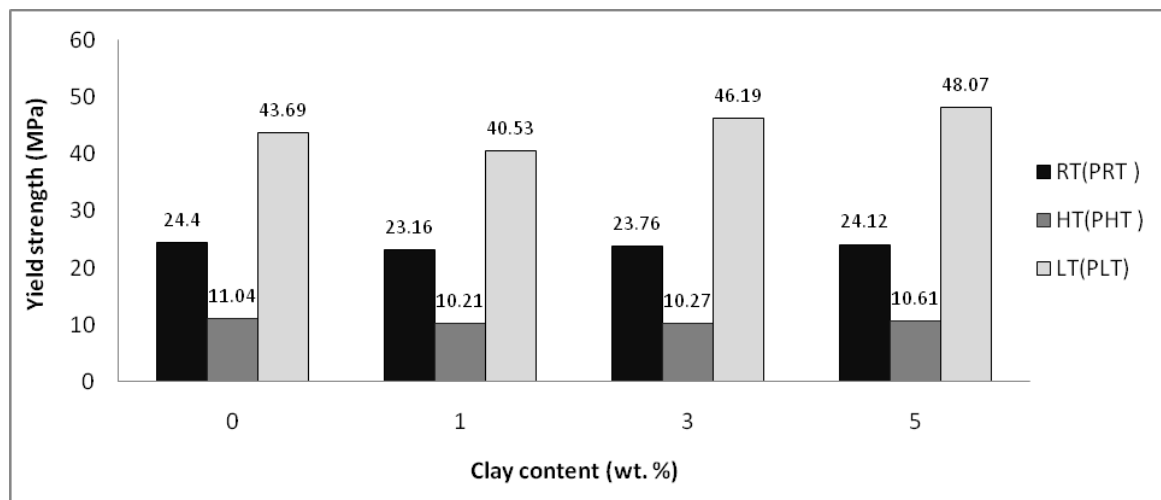


Figure 4. Yield strength of PPCN at RT, HT and LT.

The Young's modulus and yield strength at LT is much higher than that at RT and HT. It can be imagined out that the molecules are more closely compacted and the binding forces between the molecules are high at LT which makes the positive contributions to the Young's modulus and yield strength. On the other hand, many materials show higher modulus at lower temperature [10]. So, the modulus of clay would also be higher at LT, contributing to the higher modulus of the composites at LT [10]. The maximum Young's modulus are related to the composites contain 5 wt.% of nanoclay particles, i.e., P5RT, P5HT and P5LT specimens with the values of 714.22, 345.84 and 1063.43 MPa and the minimum Young's modulus are related to the neat PP, i.e., P0RT, P0HT and P0LT specimens with the values of 523.42, 134.05 and 903.61 MPa, respectively. When the clay content is 5 wt.%, the Young's modulus at LT is increased by 17.63% as compared to P0LT.

Although, the Young's modulus is improved, nanoclay had no considerable influence on the yield strength of the nanocomposites. According to Chen et al. [22] and Bahrami et al.

[23], the improvement in strength was quite gentle at low clay content (below 10 wt.%). The maximum yield strength are related to the composites contain 5 wt.%, i.e., P5RT, P5HT and P5LT specimens with the values of 24.12, 10.61 and 48.07 MPa and the minimum yield strength are related to the neat PP, i.e., P0RT, P0HT and P0LT specimens with the values of 24.4, 11.04 and 43.69 MPa, respectively. The yield strength at LT is consistently higher than that at RT and HT with the same composition. This is because of the nanolayers of clays which might be well separated and dispersed randomly in the polymer matrix at LT. A significant enhancement in the LT yield strength is observed, by the addition of clay contents. The results showed that with the addition of 5 wt.% clay content, the yield strength of PPCNs at RT, HT and LT reached the maximum increase by 4.1%, 3.9% and 18.6% as compared to P1RT, P1HT and P1LT, respectively. The effect of nanoclay particles on Young's modulus and yield strength is higher at LT.

The effect of nanoclay at HT is more significant than RT for ultimate tensile strength. The value of ultimate tensile strength for PP specimen contains 1 wt.% of nanoclay at RT (P1RT) is 18.06 MPa and at HT (P1HT) is 16.53 MPa, which show a reduction of 9.2% at HT. However, by adding nanoclay particles of 5 wt.% (P5RT), the ultimate tensile strength reduced to 15.53 MPa which shows a reduction of 16.3% as compared to P1RT, but P5HT shows a tensile strength of 17.69 MPa, which indicates an increase of approximately 7% as compared to P0HT. This is due to increase in temperature, the interaction between nanoparticles and matrix improved, and as a result, the ultimate tensile strength of specimens increased at HT.

The value of ultimate tensile strength at LT for PP specimen contains 1 wt.% (P1LT) is 40.53 MPa, which shows an increase of 124%, when compared to RT results. These results are nearly in accordance with those result of references [10,20,24]. The authors of Ref. [20]

noticed that the molecules of polymer matrix were tightly frozen at LT and also nanoparticles and matrix interface adhesion was stronger at LT than at RT because of the thermal shrinkage of matrix and tight clamping of the nanoparticles by the matrix at LT, leading to a higher composite strength.

P5LT specimen shows the strength of 48.07 MPa in which the comparison of this value to P1LT specimen indicates an increase of 18.6%. This can be explained as when the temperature decreases from RT to LT, the chemical bonds and the molecules of PP matrix shrunk and the bonding forces between the molecules become strong. Thus, a larger load is needed to break the PP matrix at LT, leading to a higher strength of the PP matrix at LT than at RT.

Ultimate tensile strength of PP nanocomposites at RT, HT and LT as a function of nanoclay content is shown in Figure 5. Ultimate tensile strength, percentage of displacement at break and energy absorption at RT and percentage of displacement at break and energy absorption at HT are decreased when increasing the clay content (1, 3 and 5 wt.%). These reductions are almost 21%, 20% and 24% for ultimate tensile strength, percentage of displacement at break and energy absorption at RT and also 17% and 21% for percentage of displacement at break and energy absorption at HT, respectively, for the specimens contained 5 wt.% of clay content as compared to the neat PP. The energy absorption is calculated by the area under stress-strain curves for different specimens.

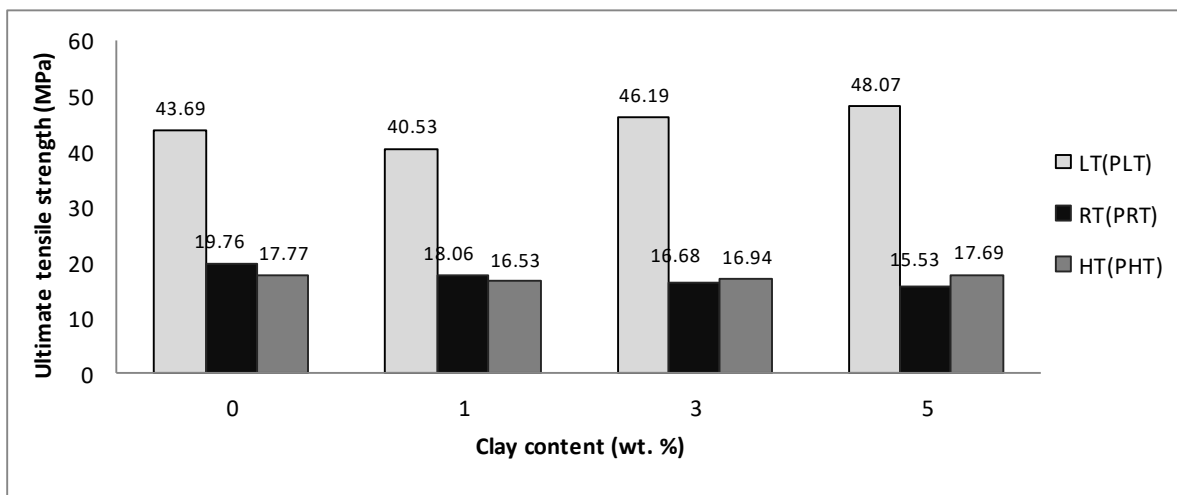


Figure 5. Ultimate tensile strength of PPCN at RT, HT and LT.

The presence of clay layers in the PP matrix prevented PP chains from free motions, thus decreasing the toughness and increasing the brittleness and therefore the plastic deformation of polymer matrices is limited by an increase in clay contents. However, ultimate tensile strength at HT increased by increasing the weight percentage of nanoclay, because the temperature affects the mobility of PP matrix and there is a good interface between the nanoparticles and the matrix. Approximately 7% increase is observed in ultimate tensile strength at HT with addition of 5 wt.% clay content as compared to 1 wt.%. The percentage of displacement at break and energy absorption at HT is higher than those at RT, because PPCNs are exhibited relatively ductile behavior at HT which shows higher toughness and hence causes later failure as compared to those at RT.

The energy absorption of nanocomposite specimens at LT is lower than RT. However, the energy absorption of those specimens with 5 wt.% of nanoclay particles was enhanced approximately by 6%, when compared to the neat PP. Yet, energy absorption at RT was obviously reduced with adding nanoparticles. The nanocomposites at LT are all brittle as compared to RT energy absorption. But, by adding nanoparticles, different effects for LT and

RT are observed. The effect of nanoparticles at RT is to reduce the energy absorption, but at LT, the materials show slight ductility at higher wt.% of nanoparticles.

The increase in the yield strength at RT, HT and LT and also the ultimate tensile strength at HT for the neat PP may be attributed to the tight arrangement of PP molecules and no different contractive coefficients in the homogeneous phase. Density of the neat PP composite specimens increased by adding the nanoclay particles and BF. It is due to nanoclay particles and BF added to PP which has higher densities than the neat PP.

3.2.2. Chopped basalt fiber reinforced PP-clay nanocomposite (PPCN-B)

In the second part of the discussion section, the tensile properties of the fiber nanocomposites are obtained as a function of clay content (1, 3 and 5 wt.%) and BF (10 wt.%) at RT, HT and LT. Tensile properties for PPCN-Bs at RT, HT and LT as a function of weight percentage of nanoclay and BF are shown in Tables 1, 2 and 3, respectively along with the neat PP and PPCN results. By adding BF to polymer matrix that contain nanoclay particles, the similar trend in variation (increase or decrease) are observed according to the results of tensile properties of PPCN specimens at RT, HT and LT.

Young's modulus and yield strength of PPCN-Bs at RT, HT and LT are improved by adding BF as compared to PPCNs. This improvement is due to the fiber like reinforcement in the matrix that restricts the mobility of polymer chains under loading, according to **the SEM images (Figs. 9 and 10)**. Those of samples prepared in Refs. [15,16] reported similar result in trend of tensile modulus. The authors of Ref. [15] mentioned that the improvement of Young's modulus is due to the exfoliation of nanoscale clay particles in the matrix and also it is better to consider that the orientation of nanoclay platelets and PP polymer chains with respect to the loading direction can contribute to the reinforcement effect.

The maximum Young's modulus are related to the composites contain 5 wt.% of nanoclay particles and 10 wt.% BF, i.e., P5RTB, P5HTB and P5LTB specimens with the values of 832.64, 583.12 and 1385.62 MPa, respectively, and the minimum Young's modulus are related to the composites contain 1 wt.% of nanoclay and 10 wt.% BF, i.e., P1RTB, P1HTB and P1LTB specimens with the values of 656.86, 320.19 and 955.21 MPa, respectively. Young's modulus of nanocomposite specimens contains 5 wt.% of nanoclay particles and 10 wt.% of BF at RT, HT and LT is approximately 17%, 68% and 30% higher than the nanocomposite specimens with 5 wt.% of nanoclay particles without fibers, respectively. Considering all the specimens, the highest Young's modulus and the yield strength belong to P5LTB specimen with the values of 1385.62 MPa and 48.21 MPa respectively, in which contains 5 wt.% of nanoclay particles and 10 wt.% BF at LT. Ref. [24] compared tensile modulus of chopped glass fiber reinforced polymer in different range temperatures (-253 °C, -197 °C, 22 °C), they found out that the tensile modulus at LT is higher than those at RT. Figures 6 and 7 show the variation of Young's modulus and yield strength of the PPCN-Bs at RT, HT and LT as a function of nanoclay content.

Brittle nature of the BF causes the fracture of the specimens to occur earlier as compared to the specimens without BF. The percentage of displacement at break for P1RT and P1HT is 274.69% and 527.41%, while by adding BF to polymer matrix, these values reduce to 215.64% and 405.41%. Also, the values of energy absorption of P1RT and P1HT are 151.89 and 291.62 J, and by addition of BF to polymer matrix, the values reached to 134.6 and 254.38 J, thus the energy absorption of P1RT and P1HT specimens reduce when compared to the P1RTB and P1HTB specimens by approximately 12% and 14%, respectively. The percentage of displacement at break and energy absorption of PPCNs is higher than PPCN-Bs at RT and HT, except the nanocomposite specimens at LT. It can be concluded that the

interface adhesion between BF and PP matrix becomes stronger, because of the thermal shrinkage of PP matrix and tight clamping of the BFs by the PP matrix at LT. Therefore, the percentage of displacement at break and energy absorption of fiber nanocomposites are higher than the specimens without fiber at LT. The percentages of displacement at break and energy absorption of P5LTB specimen are approximately 7.3% and 5.25% higher than the P5LT specimen, respectively.

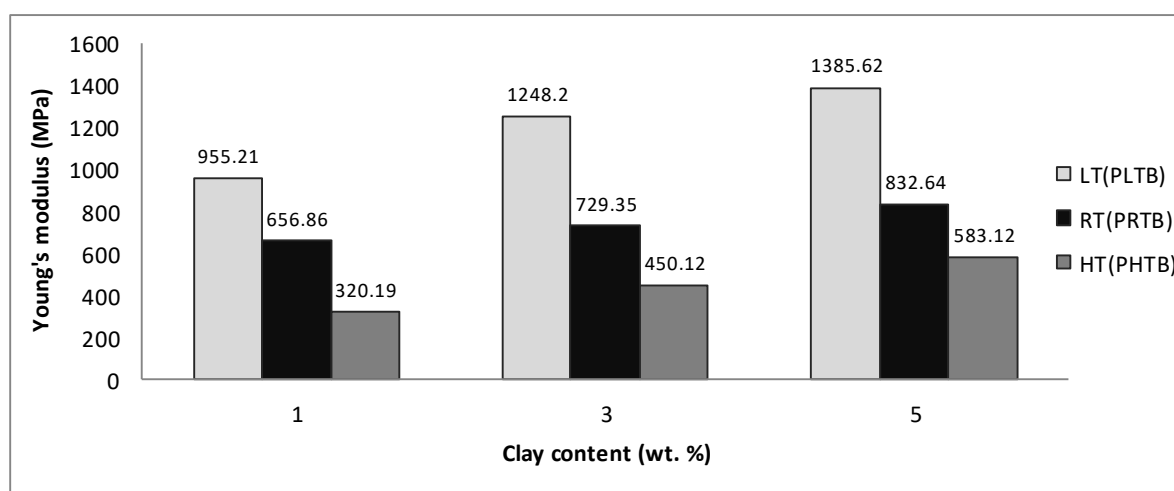


Figure 6. Young's modulus of PPCN-B at RT, HT and LT.

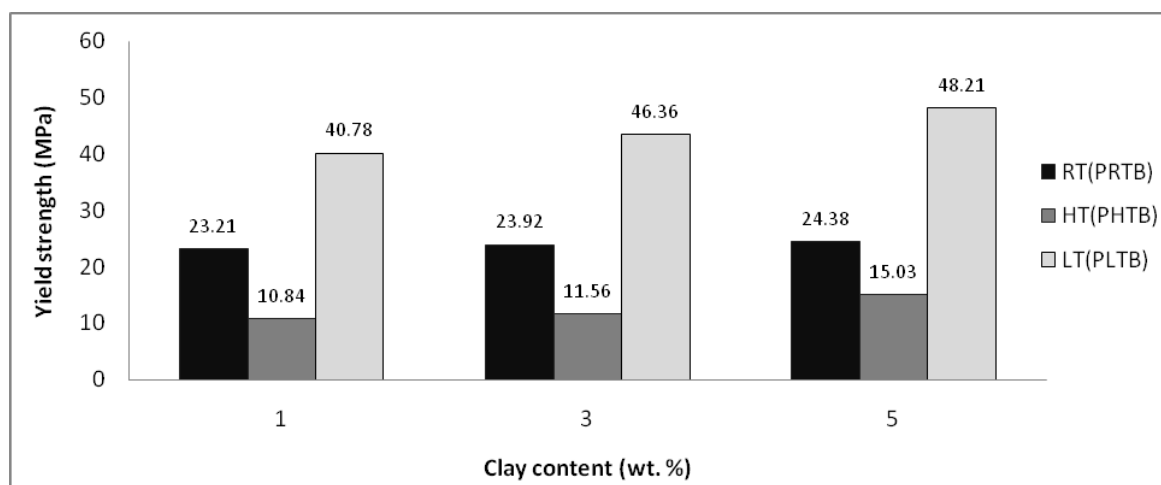


Figure 7. Yield strength of PPCN-B at RT, HT and LT.

Ultimate tensile strength of PPCN-Bs at RT, HT and LT as a function of nanoclay content is shown in Figure 8. Also, the ultimate tensile strength of PPCNs is higher than PPCN-Bs at RT and HT. The values of ultimate tensile strength for P1RT and P1HT are 18.06 MPa and 16.53 MPa, and for the specimens contain BF, i.e., P1RTB and P1HTB are 17.45 MPa and 14.82 MPa which indicates a reduction of almost 5% and 10%, respectively. Tensile strength to fracture and elongation at break of Ref. [13] decreased when basalt fiber added to polymer matrix and is stated this reduction is due the bonding strength is poor.

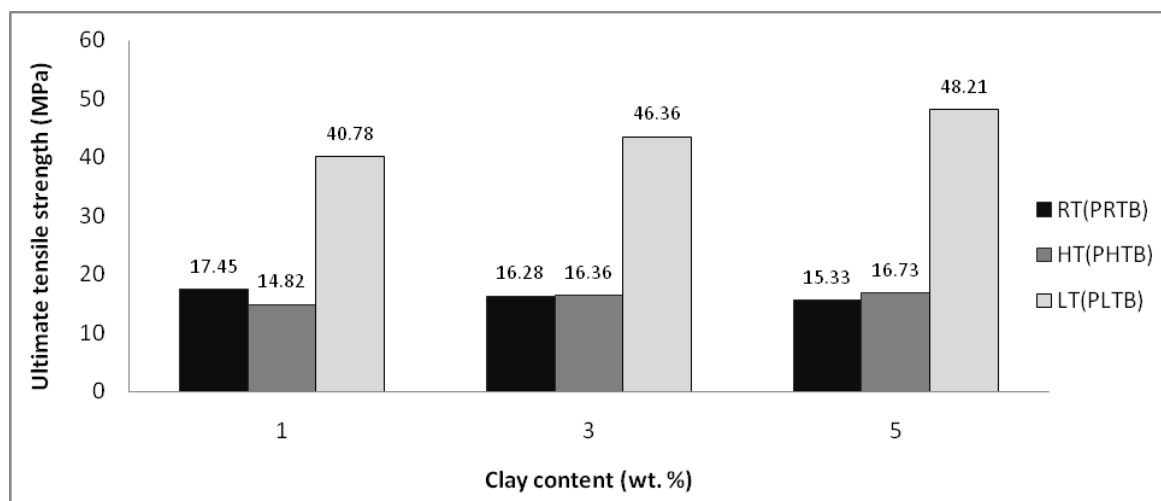


Figure 8. Ultimate tensile strength of PPCN-B at RT, HT and LT.

3.3. Scanning electron microscope (SEM)

The phase morphology of the nanocomposites is observed using SEM. Figures 9 and 10 illustrate some representative SEM micrographs of the fracture surfaces at RT with different magnifications. SEM micrographs on the failure surfaces indicate that the interfacial bonding in the PPCN-B specimen contains 5 wt.% of nanoclay particles is superior to that in the PPCN-B specimen contains 1 wt.% of nanoclay particles.

It is found that for the P5RTB specimen (Figure 9b), the fibers are still surrounded and adhered with the matrix and nanoparticles. Consequently, the matrix cracking is the primary failure mechanism [25]. On the other hand, for the P1RTB specimen (Figure 9a), the failure surfaces of the fibers are relatively featureless and smooth, which provide an indication that the interfacial de-bonding is the main failure mechanism [25]. Matrix residues that are observed on fiber bundles are unequivocal signs of effective fiber–matrix adhesion. It should also be noted that, for the specimen contains 5 wt.% of nanoclay particles (Figure 9b), matrix–nanoclay residue around the fibers is significantly more than that specimen contains 1 wt.% of nanoclay particles (Figure 9a). Figure 10a indicates that P1RTB specimen contains the matrix regions that are quite even, indicating the brittle fracture. However, significant de-bonding of the basalt fiber is also visible, with clean basalt surface, characteristic of poor interfacial adhesion. The matrix is significantly rougher for the P5RTB (Figure 10b), possibly reflecting the matrix failure mode. Furthermore, the matrix residues are visible at the surface of the basalt fibers indicating better interfacial adhesion.

From the SEM observations, it appears that the PPCN-B specimens contain 5 wt.% of nanoclay particles possess better interfacial bonding than the PPCN-B specimens contain 1 wt.% of nanoclay particles. As a result, the increasing behavior of the Young's modulus and the yield strength in the nanocomposites could be attributed to the improved interfacial strength modified by the clay particles.

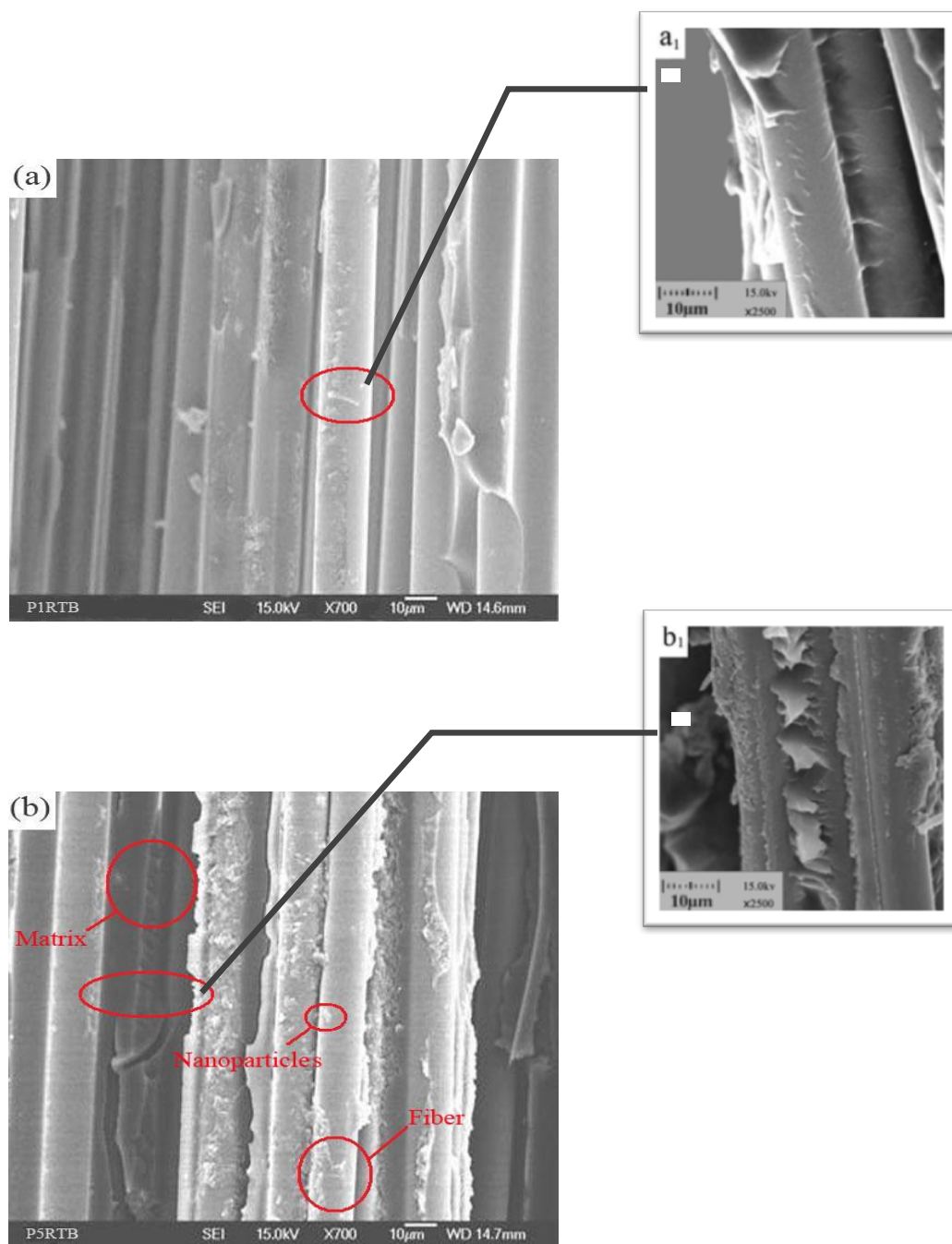


Figure 9. SEM micrographs of BF composites fracture surfaces with 700 magnification for (a) PP with 1 wt.% nanoclay and (b) PP with 5 wt.% nanoclay.

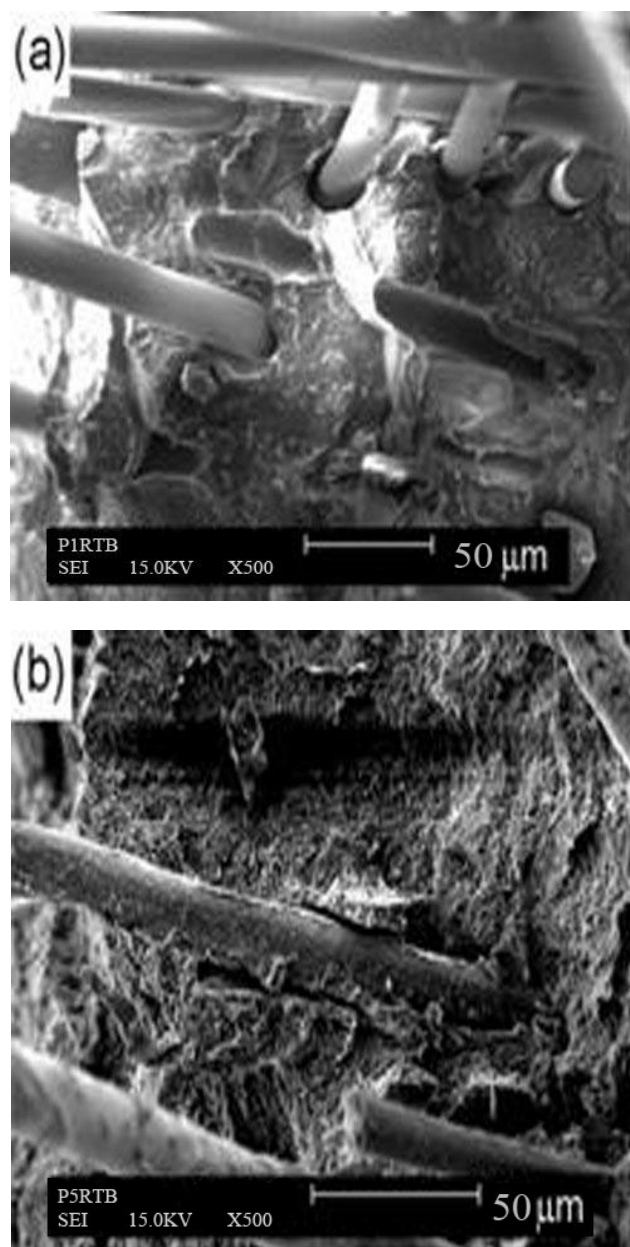


Figure 10. SEM micrographs of BF composites fracture surfaces with 500 magnification for (a) PP with 1 wt.% nanoclay and (b) PP with 5 wt.% nanoclay.

4. Conclusions

A relatively new class of composite material consisting of two reinforcements in matrix is studied with emphasis on the tensile mechanical properties. Material used is thermoplastic

PP polymer, which acts as a matrix material with the major reinforcement as nanoclay particles and the secondary reinforcement as BF. The composites are prepared using the melt mixing technique and the tensile properties of nanocomposites are obtained at RT (25 °C), HT (120 °C) and LT (-196 °C) and compared to the properties of the neat PP. The following conclusions can be drawn:

- 1) X-ray diffraction analyses indicate the exfoliation for the samples containing 1, 3 and 5 wt.% nanoclay and also the transmission electron microscopy results show that the general dispersion is at the nanolevel in the samples containing clay with some evidence of exfoliation.
- 2) Young's modulus and yield strength of PP nanocomposites is increased by increasing the weight percentage of nanoclay particles (up to 5 wt.%) and BF, because of their reinforcement effect. However, the percentage of displacement at break, energy absorption and ultimate tensile strength are decreased due to the limited plastic deformation of the polymer matrix.
- 3) The reinforcing efficiency of nanoclay particles and BF for the tensile properties of PP composites is higher at LT than at RT and HT, since the interfacial bonding between PP matrix, nanoclay and BF becomes stronger at LT than at RT and HT, due to the thermal contraction effect.
- 4) Basalt fibers have a significant effect in increasing the Young's modulus and the yield strength and result in a decrease in the percentage of displacement at break and the energy absorption at RT, HT and LT.
- 5) Young's modulus and yield strength values for specimen contain 5 wt.% of nanoclay particles and 10 wt.% BF at LT are the highest as compared to the other specimens at RT and HT. Also, low temperature causes that the percentage of displacement at break and the

energy absorption of the specimens contain BF and without BF improve by adding nanoclay particles.

- 6) Scanning electron microscopy studies of the tensile fractured surfaces reveal improved fiber matrix adhesion for samples containing nanoclay, which may be responsible for the improvement in tensile properties. The enhancing behavior could be due to the improved interfacial bonding between the fibers and the surrounding matrix by the nanoclay particles.
- 7) The outcome of this study suggests that the nanoclay particles can be added in to the fiber reinforced composites as a filler or third phase additive to enhance the tensile mechanical properties such as Young's modulus and yield strength even at considerably low clay concentrations.

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