CHEMICALLY CHITOSAN MODIFIED WITH METHYL METHACRYLATE AND ITS EFFECT ON MECHANICAL AND THERMAL PROPERTIES OF POLYPROPYLENE COMPOSITES

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ABSTRACT

Effects of methyl methacrylate on the properties of chitosan-filled polypropylene (PP) composites has been investigated. Mechanical and thermal properties of the composites were analyzed according to ASTM D 638-91, thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC). The results showed that tensile strength of PP composites decreased upon the addition of chitosan, while Young's modulus improved. At a similar filler loading, the treated PP/chitosan composites were found to have higher tensile strength and Young's modulus as compared with the untreated composites. Thermal analysis results showed that thermal stability and crystallinity of the treated composites were higher than the untreated ones. Scanning electron microscopy (SEM) and Fourier transforms infrared (FTIR) studies revealed less detached filler from matrix on tensile surface of the treated composites as an evidence of enhanced filler-matrix interfacial adhesion due to formation of ester-bridge between the chitosan and the methyl methacrylate.

Keywords: polypropylene; chitosan; composites; methyl methacrylate; interfacial adhesion

ABSTRAK

Pengaruh metil metakrilat terhadap sifat-sifat komposit polipropilena (PP) terisi kitosan telah diteliti. Sifat mekanik dan sifat termal komposit dianalisis menggunakan ASTM D 638-91, analisis thermogravimetri and differential scanning calorimetry (DSC). Hasil-hasil yang diperoleh menunjukkan bahwa kekuatan tarik komposit PP menurun dengan penambahan kitosan, sedangkan modulus Young meningkat. Pada jumlah pengisi yang sama, komposit PP/kitosan dengan perlakuan ternyata memiliki kekuatan tarik dan modulus Young yang lebih tinggi dibandingkan dengan komposit tanpa perlakuan. Analisis termal menunjukkan bahwa kestabilan termal dan kristalinitas komposit dengan perlakuan lebih tinggi daripada komposit tanpa perlakuan. Kajian SEM dan FTIR menunjukkan pengurangan pengisi yang terlepas dari matriks pada permukaan patahan komposit dengan perlakuan sebagai sebuah bukti peningkatan ikatan antarmuka pengisi dan matriks yang disebabkan pembentukan jembatan-ester antara kitosan dan metil metakrilat.

Kata Kunci: polipropilena; kitosan; komposit; metil metakrilat; ikatan antarmuka

INTRODUCTION

Recently, the utilization of natural fibers as filler or reinforcement in thermoplastic composites is being more attractive. This trend is mainly encouraged by economic and environmental factors [1]. Since thermoplastic composites prepared using natural fibers are inexpensive and could minimize environmental pollution due to their characteristics bio-degradability, they could play a vital role in solving the environmental problems [2-3]. Among the advantages of using natural fibers in thermoplastic composites are low density, low abrasion to equipment, increase in modulus of elasticity (Young's modulus) and renewability [4]. However, some drawbacks are lower ultimate strength and elongation, increased water sorption, and difficulty in processing [5]. In general, when natural fillers or fibers are added to thermoplastics, properties such as elastic modulus, heat deflection temperature, moisture sorption and viscosity are increased whereas impact performance is reduced [6-8].

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A large number of natural fibers are being used as filler to replace mineral fillers, such as wood fiber [9], sawdust [10], waste paper [11], jute [12], rice husk [13], sisal [14], and chitosan [15]. Chitosan is known as the second most abundant natural fiber after cellulose. It is extracted from crustaceous shells such as crabs, shrimp and prawns [16]. Currently, active researches have been conducted in the application of chitosan as biomaterials due to its biodegradability, biocompatibility and non toxicity, in spite of low cost, resource abundances, lightness and non abrasive nature [17].

The mechanical and physical properties of natural fiber filled thermoplastic composites are strongly influenced by the interaction on the interface between filler and matrix [18]. The interaction between the two components can be enhanced by physical and chemical modification of the filler or by using suitable coupling agents. Coupling agents are able to react with both components during the preparation of the composites, creating a chemical bridge at the filler–matrix interface [19-20].

Chitosan is a natural polysaccharide which tends to absorb water due to its hydrophilic characteristic, responsible to poor filler and matrix interfacial interaction. This becomes major drawback of using chitosan as filler in thermoplastic composites. This problem could be overcome by treating the filler. A number of attempts have been carried out in order to enhance the interaction between chitosan fiber and hydrophobic matrix. Salmah et al. [21] reported that the interfacial adhesion between chitosan and PP matrix was significantly enhanced by employing the 3-aminopropyltriethoxysilane (3-APE) as the chemical modifying agent in composite systems. In addition, in our previous work we have reported that better interfacial bonding and higher tensile strength of chitosan filled polypropylene (PP) composites were obtained by chemically treating the chitosan with sodium dodecyl sulfate [22].

In this study, methyl methacrylate was used as chemical modifying agent for treating the chitosan filler to enhance the interfacial interaction with PP matrix. Methyl methacrylate was chosen due to its reactive chemical moieties that may react with polar groups of chitosan i.e. hydroxyl and amine groups, to form a chemical bonding [23]. The formation of chemical bonding between chitosan and methyl methacrylate is expected to decrease the hydrophilic character of chitosan leading to enhance interfacial adhesion. Therefore, this study was aimed to investigate the effect of chemical treatment of chitosan by using methyl methacrylate on mechanical and thermal properties of polypropylene (PP) composites, while varying the chitosan loading.

EXPERIMENTAL SECTION

Materials

Polypropylene (PP) homopolymer used in this study was injection molding grade S11232 G112, from Polypropylenas Sdn Bhd (Malaysia) with MFI (melt flow index) value of 45 g/10 min at 230 °C. Chitosan was obtained from Hunza Nutriceuticals Sdn Bhd (Malaysia) with average size of 80 µm and degree of deacetylation (DD) of 90%. Ethanol (98%.v/v) and methyl methacrylate were obtained from Aldrich.

Instrumentation

A Z-blade Mixer (MCN ELEC Co., Taiwan) was used for preparation of the composite. Tensile tests were carried out according to ASTM D 638-91 on an Instron 5582. Thermal analyses were investigated by using TGA Q500 Perkin Elmer Instrument and Perkin Elmer TA Instrument DSC Q 1000. A scanning electron microscope (SEM), model JSM 6260 LE JEOL, was used to study surface morphology of composites. FTIR spectroscopy analysis of untreated and treated chitosan was carried out in ATR mode by using Perkin-Elmer 1600 Series.

Procedure

Preparation of treated chitosan

Methyl methacrylate solution was prepared in ethanol at temperature of 40 °C. The amount of methyl methacrylate used was 3 vol.% of filler. The solution was then cooled down to room temperature. Afterward, chitosan was gradually added to the solution while slowly stirred. The mixture was mechanically stirred for 2 h in order to be homogenized and stayed overnight. The precipitate was filtered and then dried in the oven at 80 °C for 24 h to remove ethanol residue.

Preparation of PP/chitosan composites

PP/chitosan composites were prepared in a Z-blade Mixer at temperature of 190 °C and rotor speed of 50 rpm. PP was first loaded to start the melt mixing. After 12 min, the chitosan was added. Mixing was continued for another 3 min. At the end of 15 min, the PP/chitosan composites were taken out and sheeted through a laboratory mill at 2.0 mm nip setting. Samples of PP/chitosan composites were compression molded in an electrically heated hydraulic press. Hot-press procedures involved preheating at 190 °C for 9 min followed by compressing for 3 min at the same temperature and subsequent cooling under pressure for 3 min. The same procedure was conducted for the preparation of treated PP/chitosan composites. The

Table 1. Formulation of untreated and treated PP/chitosan composites

Materials	Untreated composites	Treated composites
Polypropylene (PP) (php)	100	100
Chitosan (php)	0, 10, 20, 30, 40	10, 20, 30, 40
Methyl methacrylate (vol.%)	-	3

php = part per-hundred polymer
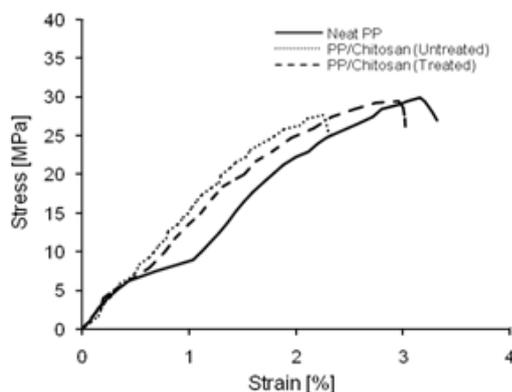
Fig 1. Stress *versus* strain traces of neat PP and PP/chitosan composites with and without treatment
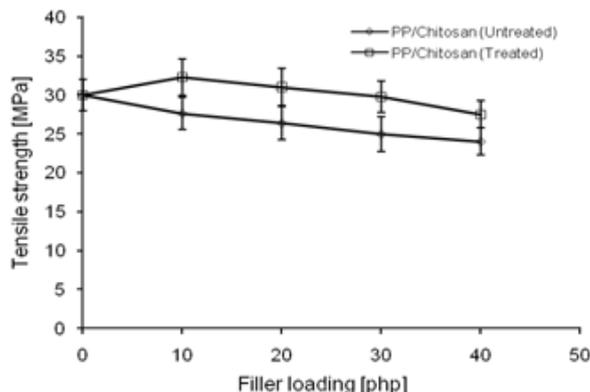
Fig 2. Effect of filler loading on tensile strength of PP/chitosan composites
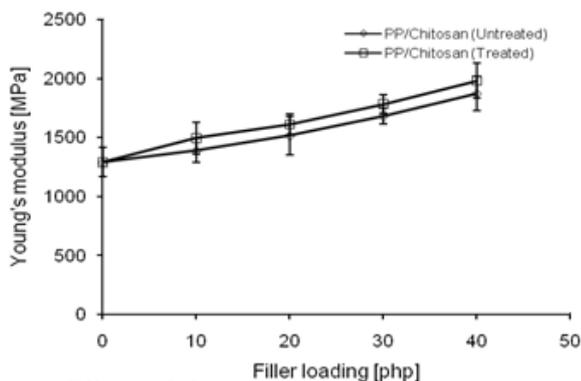
Fig 3. Effect of filler loading on Young's modulus of PP/chitosan composites

formulation of untreated and treated PP/chitosan composites is summarized in Table 1.

Characterizations

Tensile tests were carried out according to ASTM D 638-91. At least, five dumbbell specimens of each composition with thickness 1 mm were cut from the molded sheets with a Wallace die cutter. A cross head speed of 20 mm/min was used and the test was performed at 25 ± 3 °C.

Thermogravimetric (TGA) and derivative thermogravimetric (DTG) analyses were investigated to study the thermal stability of the composites. Samples were scanned on TGA, from 30 to 600 °C at a heating rate of 20 °C/min using a nitrogen flow of 50 mL/min. On DSC analysis, samples were scanned from 25 to 250 °C at a heating rate of 20 °C/min using nitrogen flow of 50 mL/min. The melting and enthalpy of PP/chitosan

composites were automatically calculated by the instrument software. The crystallinity of composites (X_c) was determined using Equation 1:

$$X_c = \Delta H_f \, x \, 100 \, / \, \Delta H_f^o \tag{1}$$

where ΔH_f is the heat of fusion of the PP and composites, ΔH_f^o is the thermodynamic heat of fusion of fully crystalline PP (209 J/g) [24]. A mean value of three replicates of each specimen was recorded.

Study on the morphology of the tensile fracture surface of the PP/chitosan composites was carried out by using a scanning electron microscope (SEM). The fracture ends of specimens were mounted on aluminium stubs and sputter coated with a thin layer of palladium to avoid electrostatic charging during examination.

Fourier transforms infra red (FTIR) spectroscopy analysis of untreated and treated chitosan was carried out. Samples were scanned from 650 to 4000 cm^{-1} with resolution of 4 cm^{-1}.

RESULT AND DISCUSSION

Tensile Properties of PP/Chitosan Composites

Tensile test has been conducted to determine the strength of PP/chitosan composites when the force is given in tension. Stress *versus* strain traces recorded tensile testing for neat PP, untreated and treated PP composites containing 20 php chitosan filler are presented in Fig. 1. All traces exhibited a similar character; however, in some extent both untreated and treated PP composites showed lower strength and
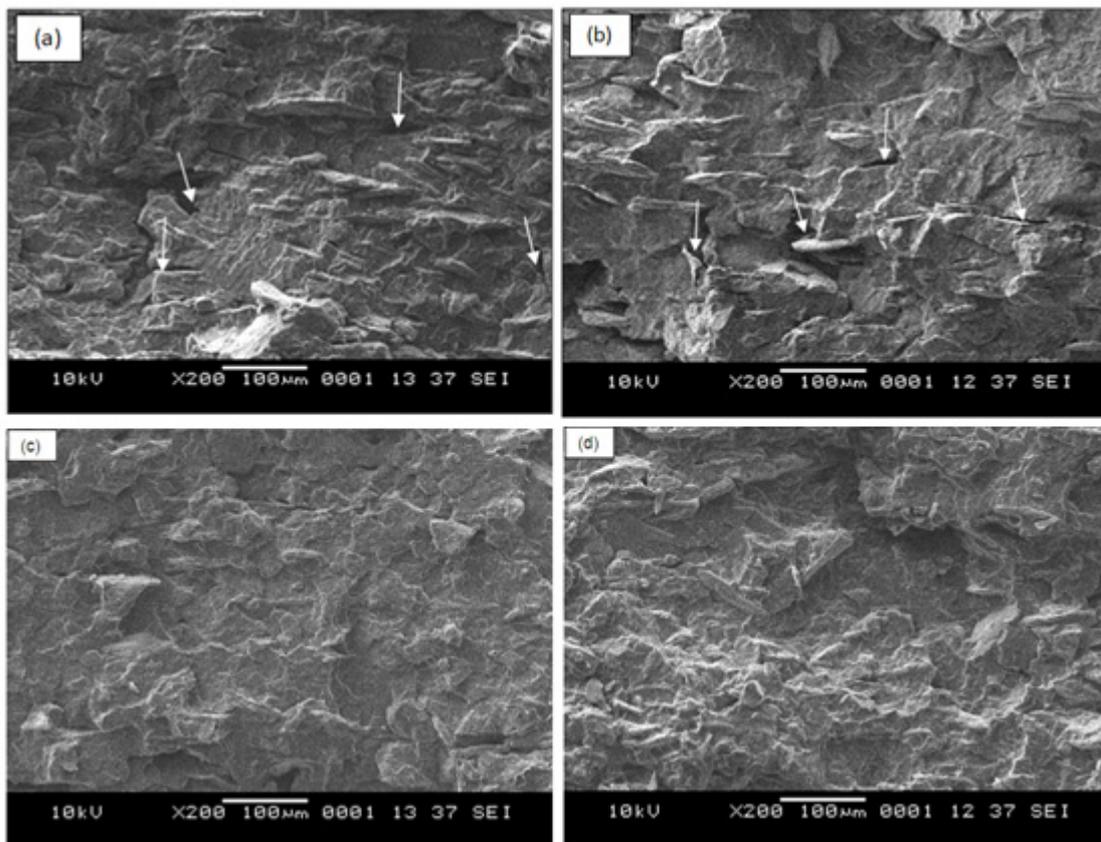
Fig 4. SEM micrograph of tensile surface; (a) untreated PP/chitosan composite (20 php); (b) untreated PP/chitosan composite (40 php); (c) treated PP/chitosan composite (20 php); (d) treated PP/chitosan composite (40 php); all magnifications are 200X. Arrows indicate traces of pulled out filler

ultimate strain than neat PP. The presence of chitosan as filler significantly influenced the strength of PP composites. Chemical treatment did not apparently change the stress *versus* strain trace character of the treated PP composites, but influenced the measured strength at failure. The use of methyl methacrylate increased both strength and ultimate strain of treated PP composites when compared to untreated ones.

Tensile strength of PP/chitosan composites as a function of filler loading is depicted in Fig. 2. Tensile strength of PP/chitosan composites decreased with the increasing of filler loading, which considerably due to the lack interfacial interaction between chitosan and PP matrix. Chitosan is natural polysaccharide with hydrophilic character, while PP is hydrophobic polymer. The different polarities diminish filler-matrix interfacial adhesion [25]. Hence, as the chitosan loading increased thereby increasing the interfacial area, the worsening interfacial interaction between filler and matrix has caused decreasing tensile strength. However, as the presence of methyl methacrylate on the chitosan surface, the tensile strength of treated PP composites was higher compared to untreated ones. It is worth

noting that the hydrophilic character of chitosan was decreased due to the formation of ester-linkage between hydroxyl group of chitosan and ester group of methyl methacrylate through trans-esterification reaction, leading to enhanced interfacial adhesion with PP matrix.

Fig. 3 shows the Young's modulus of PP/chitosan composites at different filler loading. Increasing filler loading significantly improved the Young's modulus of PP/chitosan composites. The incorporation of chitosan into PP matrix decreased the deformability of PP composites as a result of constricted molecular motion of PP chain, subsequently improved the rigidity. As the filler loading increased, the PP/chitosan composites became more rigid and the Young's modulus increased. This result confirmed that Young's modulus was less sensitive to changes in interfacial interactions than properties measured at larger deformations. Otherwise, Young's modulus of treated PP/chitosan composites was significantly higher than untreated composites. This was due to the better dispersion of treated chitosan in PP composites inducing stiffening effect.
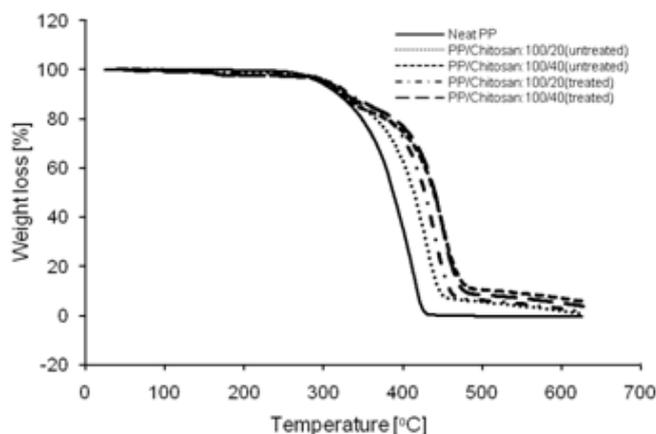
Fig 5. TGA curve of untreated and treated PP/chitosan composites
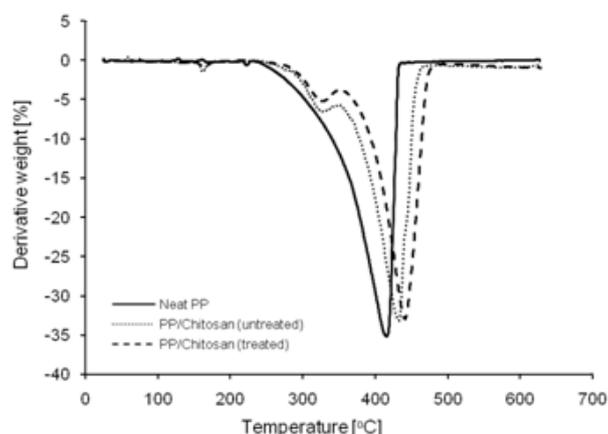
Fig 6. DTG curve of untreated and treated PP/chitosan composites

Table 2. Percentage of weight loss of neat PP and PP/chitosan composites at different temperature

Temperature (°C)	Weight loss of neat PP	Weight loss of PP/chitosan Composites (untreated)		Weight loss of PP/chitosan Composites (treated)	
		100/20 (php)	100/40 (php)	100/20 (php)	100/40 (php)
100 – 150	0.002	0.039	0.277	0.560	0.534
150 – 200	0.016	0.271	0.555	0.653	0.569
200 – 250	0.150	1.017	1.894	1.803	1.075
250 – 300	0.476	0.157	0.212	0.238	0.193
300 – 350	4.993	0.495	1.262	0.399	2.016
350 – 400	14.813	4.540	5.080	4.176	4.388
400 – 450	43.150	13.539	13.105	12.123	11.987
450 – 500	36.400	40.499	36.512	39.742	35.825
500 – 550	0	33.153	32.855	33.060	31.904
550 – 600	0	1.494	1.428	1.429	1.403
600 – 630	0	1.886	1.692	1.043	1.922
Total	100	97.090	94.872	95.226	91.816

php = part per-hundred polymer

SEM Study of PP/Chitosan Composites

Fig. 4 shows SEM micrographs of tensile fractured surface of PP/chitosan composites. The micrographs of untreated PP/chitosan composites (Fig. 4(a) and 4(b)) show the appearance of voids indicating detached filler from the matrix. This is mainly due to poor wetting of the filler by the matrix. The fracture occurred at the interface between chitosan and PP matrix. The different polarities between filler and matrix lead to lack interaction on the interface especially at higher filler loading. However, the less voids are observed on the tensile surface of treated PP/chitosan composites (Fig. 4(c) and 4(d)). A good wetting of the filler by the matrix is related to the presence of methyl methacrylate, which hydrophobically modifies the chitosan, leading to enhanced interfacial adhesion with PP matrix.

Thermal Properties of PP/Chitosan Composites

Fig. 5 and 6 demonstrate TGA and DTG curve of neat PP, untreated and treated PP/chitosan composites. The increase of temperature has dramatically increased the weight loss of neat PP, untreated and treated composites, and the results are summarized in Table 2. The thermal degradation of PP occurred in one-stage from 300 to 415 °C resulting gaseous products. It pointed out that PP is composed from carbon–carbon bonds chain and the degradation/depolymerization taking place at the weak sites of PP chain. Meanwhile, the thermal degradation of PP/chitosan composites occurred in two-stage; from 50 to 300 °C corresponded to the release of typical strong hydrogen-bonded water and the breakage of chemical bonds; and from 300 to 450 °C might be associated to decomposition and depolymerization of chitosan filler. There was another degradation stage occurring from 470 to 600 °C that attributable to the decomposition of char residue formed from the second stage. At a similar loading, the thermal stability of treated PP/chitosan composites was better than untreated ones, remarkably accompanied by the formation of ester-bond between hydroxyl group of chitosan filler and ester group of methyl methacrylate that suppressing the weight loss. Overall, the

observation clearly exhibits that neither the presence of chitosan filler at higher loading nor the presence of methyl methacrylate did alter the thermal degradation mechanism of PP/chitosan composites.

Fig. 7 shows DSC curves of neat PP, untreated and treated PP/chitosan composites at 20 php filler loading. Table 3 summarizes the melting temperature (T_m), fusion enthalpy (ΔH_f) and degree of crystallinity (X_c) of neat PP, untreated and treated PP/chitosan composites. As can be seen, the addition of chitosan filler did not significantly change the T_m of PP composites, but, decreased the degree of crystallinity (X_c). This indicates that the presence of chitosan in PP composites apparently become barrier on nuclei-growth of PP chain and delayed the crystallization process. Furthermore, the addition of natural filler into PP matrix obstructed the mobilization of the PP macromolecular chain and prevented the macromolecular segment from obtaining ordered alignment of the crystal lattice [26]. On the other hand, the treated PP/chitosan composites were obtained to have higher crystallinity than untreated PP/chitosan composites, remarkably due to enhanced interfacial bonding between chitosan and PP matrix. It is worth noting that methyl methacrylate favors the enhanced chitosan-PP matrix interfacial interaction, leading to increased crystallinity of PP composites. The treated chitosan surfaces were indicated as nuclei–growth sites for promoting the crystallization process in PP composites. However, the T_m did not significantly change when compared with untreated composites, possibly due to the non- uniformity of crystal shape and lattice resulting from different types of nucleation sites [27].

FTIR Study of Untreated and Treated Chitosan

Fig. 8 presents the FTIR spectra of untreated and treated chitosan. As can be seen, the infrared (IR) spectrum of untreated chitosan, the main characteristic
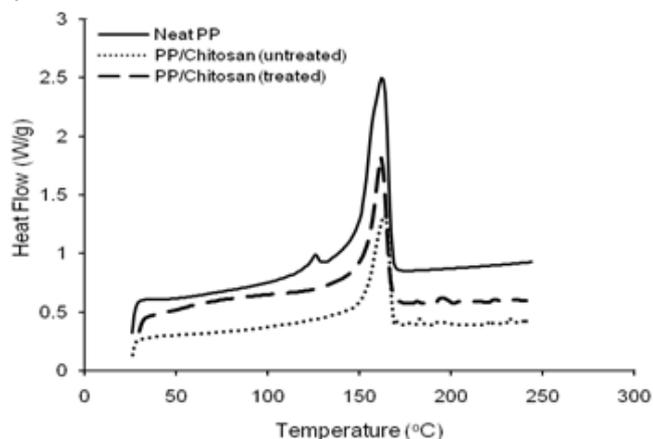
Fig 7. DSC curve of untreated and treated PP/chitosan composites containing filler loading of 20 php

Table 3. Summary of T_m and X_c of neat PP and PP/chitosan composites

Composites	T_m (°C)	X_c(%)
Neat PP	162(0.2)	38.74(0.3)
PP/chitosan: 100/20 (untreated)	163(0.3)	24.13(0.2)
PP/chitosan: 100/40 (untreated)	163(0.1)	19.81(1.0)
PP/chitosan: 100/20 (treated)	164(0.5)	28.59(0.5)
PP/chitosan: 100/40 (treated)	164(0.3)	22.76(0.4)

php = part per-hundred polymer; T_m = melting temperature; X_c = crystallinity degree
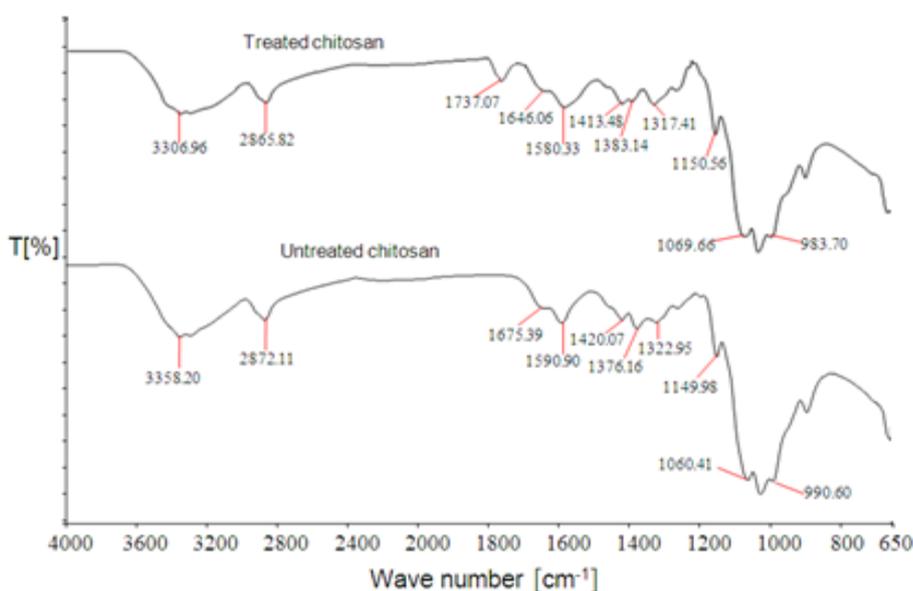
Fig 8. Infrared (IR) spectra of untreated and treated chitosan

peaks of chitosan, are at 3358 cm^{-1} (O–H stretch), 2872 cm^{-1} (C–H stretch), 1675 cm^{-1} (N–H bend) and 1590 cm^{-1} (C=O stretch). The IR spectrum of treated chitosan exhibits a significant absorption on the band of -OH group from 3358 to 3306 cm^{-1}, indicating the reduction in hydrophilic character of chitosan. This is attributed to the presence of ester-bridge as a result of trans-esterification reaction between ester group of methyl methacrylate and hydroxyl group of chitosan as identified by the presence of the absorption band at 1737 cm^{-1}. The formation of this bonding is also supported by the reduction of the bands at 1675 cm^{-1} to 1646 cm^{-1} and 1590 cm^{-1} to 1580 cm^{-1}, indicating N–H bending vibration and amide I (C=O) stretching vibration of chitosan chain.

CONCLUSION

Chitosan, a kind of natural filler was incorporated into PP matrix to produce composite materials. Methyl methacrylate was employed as chemical treating agent to reduce the polar character of the chitosan filler. Tensile test results showed that the incorporation of chitosan filler into PP matrix reduced the tensile strength, but increased the Young's modulus. The treated PP/chitosan composites were observed to have higher tensile strength and Young's modulus than untreated PP/chitosan composites. The thermal analysis results showed that the treated PP/chitosan composites had higher thermal stability and crystallinity than untreated ones. Additionally, it was found that chemical treatment did not alter the thermal degradation mechanism of treated PP/chitosan composites when compared with untreated ones. FTIR spectra and SEM micrographs revealed that methyl methacrylate was successfully bonded onto the chitosan surface, leading to enhanced interfacial adhesion with PP matrix.

ACKNOWLEDGEMENT

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