

CHAPTER V

THERMAL AND MECHANICAL PROPERTIES OF PP/ORGANOCLAY NANOCOMPOSITES

5.1 Abstract

The modification of clay by ion exchange reaction with cationic surfactants plays an important role in the greater interlayer spacing of Na-bentonite. The quaternary alkyl ammonium ion, DOEM, was introduced into the clay in order to investigate the effects of intercalation of the cationic surfactants. The organobentonites were characterized by XRD, FTIR and TGA. Polypropylene and the organoclay were melt compounded through a twin screw extruder using Surlyn[®] as a reactive compatibilizer by varying the clay contents from 1 to 7 wt%. Subsequently, the nanoclay composites were as a sample sheet for the determination of thermal and mechanical properties.

5.2 Introduction

In recent years, there has been extensive study of the factors which control whether a particular organo-clay hybrid can be synthesized as an intercalated or exfoliated structure in the polymer/clay nanocomposites. Clay nanocomposites can produce dramatic improvements in a variety of properties. [1] By modifying the surface polarity of the clay, alkylammonium ions allow thermodynamically favourable penetration of polymer into the interlayer region. The ability of the alkylammonium ions to assist in delamination of the clay depends on its chemical nature such as its polarity. The loading of the alkylammonium ion on the clay is also important.

The clay is naturally a hydrophillic material, which makes it difficult to exfoliate in a non-polar polymer matrix. Therefore, the surface treatment of silicate layers is necessary to render its surface more hydrophobic, which facilitates exfoliation. Generally, this can be done by ion exchange reaction with cationic surfactants. This modification also leads to expand the basal spacing between the silicate layers due to the presence of alkyl chain intercalated in the interlayer. However, in the case of

polypropylene, it is frequently necessary to use a compatibilizer such as ethylene methacrylic acid copolymer, Surlyn[®]. There are two important factors to achieve the exfoliation of the clay layer silicates: (1) the compatibilizer should be miscible with polymer matrix, and (2) it should include a certain amount of polar functional groups in a molecule. Surlyn[®] can fulfill the two requirements and is frequently used as a compatibilizer for polypropylene nanocomposites. [2-4]

The aim of this study is to determine the effect of organoclay content in the system of polypropylene/organoclay. The polypropylene/organoclay composites were prepared by two-step compounding method using Surlyn[®] as a reactive compatibilizer through a twin screw extruder. The state of dispersion was analyzed by X-ray diffraction and the influence of this filler on thermal and mechanical properties was examined.

5.3 Experimental

A. Preparation of organomodified bentonite

350 g of Na-bentonite, (Mac-Gel[®] GRADE SAC) supplied by Thai Nippon Co., Ltd. Thailand, was swollen in water 1.05 liter for 24 hr. DOEM (Stepantex VP-850, Union Carbide Co., Ltd.) 285 g as an alkyl ammonium ion (1.5CEC) was dissolved in the mixture of water and methanol (1:1 v/v) 1500 ml. The whole swollen clay was then mixed with DOEM solution under vigorous stirring for 2 hr at 80°C. After that the mixture was homogenized for 20 min at 80°C. The sediment was filtered and washed with hot water several times to remove to excess salts. It was dried in a vacuum oven at 100 °C overnight and ground into powder using centrifugal ball mill (FRITSCH Peluerisette 6) for 20 min before being screened through a mesh #325.

The content of the organic component was determined analyzed by TGA using a Perkin-Elmer Pyris Diamond TG/DTA instrument under N₂ flow of 200 ml/min. The heating process was conducted from 30-900°C at a rate of 10°C/min.

The presence of the organo-surfactant was measured by FT-IR. Fourier transform infrared spectra were recorded using a Nicolet Nexus 670 FT-IR spectrometer over a wave number range of 4,000-400 cm^{-1} with 32 scans at a resolution of 2 cm^{-1} .

B. Preparation of PP/clay nanocomposites

Polypropylene (Meplon HP 400H, HMC Polymer Co., Ltd.), organomodified clay, and Na salt Surlyn[®] (PC350, DuPont Co., Ltd.) as a reactive compatibilizer were prepared as a two-step compounding process. First, polypropylene was blending with 6%wt of compatibilizer, Surlyn[®] using twin screw extruder as a masterbatch. Then, the organoclay was incorporated into the PP masterbatch, varying the clay contents at 1, 3, 5 and 7% by weight. After being dried, the pellets of the nanoclay composites were injection molded into test pieces for mechanical tests using an Arburg Allrounder 270M-350-90 injection molding machine. The barrel temperature profiles were 200/190/180/170/160°C with injection pressure of 1,000 bars.

The contents of the inorganic clay of the nanocomposites were measured by burning the sample in a Perkin-Elmer Pyris Diamond TG/DTA Analyzer. The crystallization and melting behaviors of the PP/organoclay nanocomposites were measured with a Perkin-Elmer DSC 7 analyzer. During the crystallization experiment, the specimens were first melted at 200°C, and then cooled to room temperature at 10°C/min rate. The specimens were subsequently heated at 10°C/min for the corresponding melting behavior investigations.

The structure of organobentonite and its nanocomposites in PP was analyzed by wide angle X-ray diffraction (WAXD) using a Rigaku Model Dmax 2002 diffractometer with Ni-filtered Cu K_{α} radiation operated at 40 kV and 30 mA. The experiment was performed in the 2θ range of 1.2-20 degrees with scan speed 2 degree/min and scan step 0.01 degree.

The crystal structures of PP/organoclay nanocomposites were also analyzed by Wide angle X-ray diffraction (WAXD) using a Rigaku Model Dmax 2002 performed in the 2θ range of 10-30 degrees with the same scan speed and scan step as performed in organoclays.

Mechanical properties test followed ASTM D 638 type I using Instron Universal Testing Machine model 4206. The dumbbell specimens prepared by injection molding machine were 3.9 mm wide and 10.4 mm thick. The tests were carried out at room temperature using crosshead speed of 50 mm/min and the load cell of 100 kN. The mean values were obtained from at least 5 separated tests.

5.4 Results and Discussion

A. Characterizations of the organobentonite

The X-ray diffraction patterns of Na-BTN, organomodified BTN and the nanocomposites are shown in Figure 5.1. The peaks correspond to the (001) diffraction of the clay. The d_{001} peak of pristine Na-BTN at $2\theta = 5.92^\circ$ corresponds to basal spacing of 1.49 nm (Figure 5.1 a). The d_{001} peak of organomodified bentonite is shown in Figure 5.1b observed at lower angle than that of pristine Na-BTN, indicating the ammonium ions intercalate into the silicate layers and expand the basal spacing of the clay. For the PP/organoclay nanocomposites with the indicator dyes, it cannot be observed the XRD patterns suggesting that the organoclay modified with cationic surfactant has a nearly exfoliated dispersion in the polymer matrix.

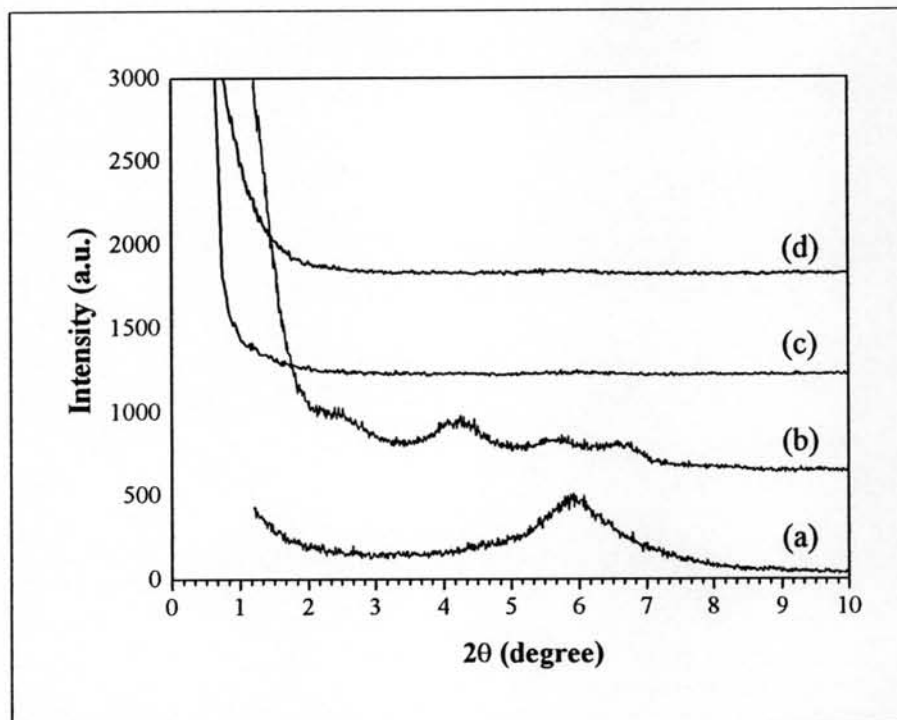


Figure 5.1 The WAXD patterns of organomodified bentonite: (a) Na-BTN, (b) DOEM-BTN, (c) PP2S6D3-BP and (d) PP2S6D3-BMB.

The results of thermogravimetric analysis of Na-bentonite and organo-bentonite were represented in Table 5.1. The content of the organic component was determined from the weight loss during TGA. For Na-bentonite, there are two main mass loss steps, the first 3% mass loss due to the dehydration is observed over temperature range of 52.0-66.5°C with 3% mass loss. Another step from 569.9 to 681.9°C is attributed to the decomposition of the structural OH units having about 3.4 % mass loss.

Table 5.1 Thermal behavior of organomodified clay

Sample	Mass Loss H ₂ O (wt%)	Mass Surfactant		Char Residual (wt%)	Desurfactant		
		wt%	mole		T _d (°C)	T _i (°C)	T _f (°C)
Na-BTN	0.7	-	-	96.0	-	-	-
BTN-DOEM	0.9	28.2	0.04	58.5	351.4	246.4	364.8

The presence of the organo-surfactant was confirmed by FT-IR. Figure 5.2 shows the FT-IR spectra of Na-BTN and organo-BTN. The bands at 1092 and 1039 cm^{-1} are the characteristic absorption bands of the clay. [5] After the treatment of DOEM, not only a pair of strong bands near 2850 and 2930 cm^{-1} at each spectrum can be assigned to the symmetric and asymmetric stretching vibration of methylene group (νCH_2) of the guest molecules but the characteristic bands of amide group at 1750 and 1470 cm^{-1} are observed as well, supporting the intercalation of the surfactant molecule between the silicate layers.

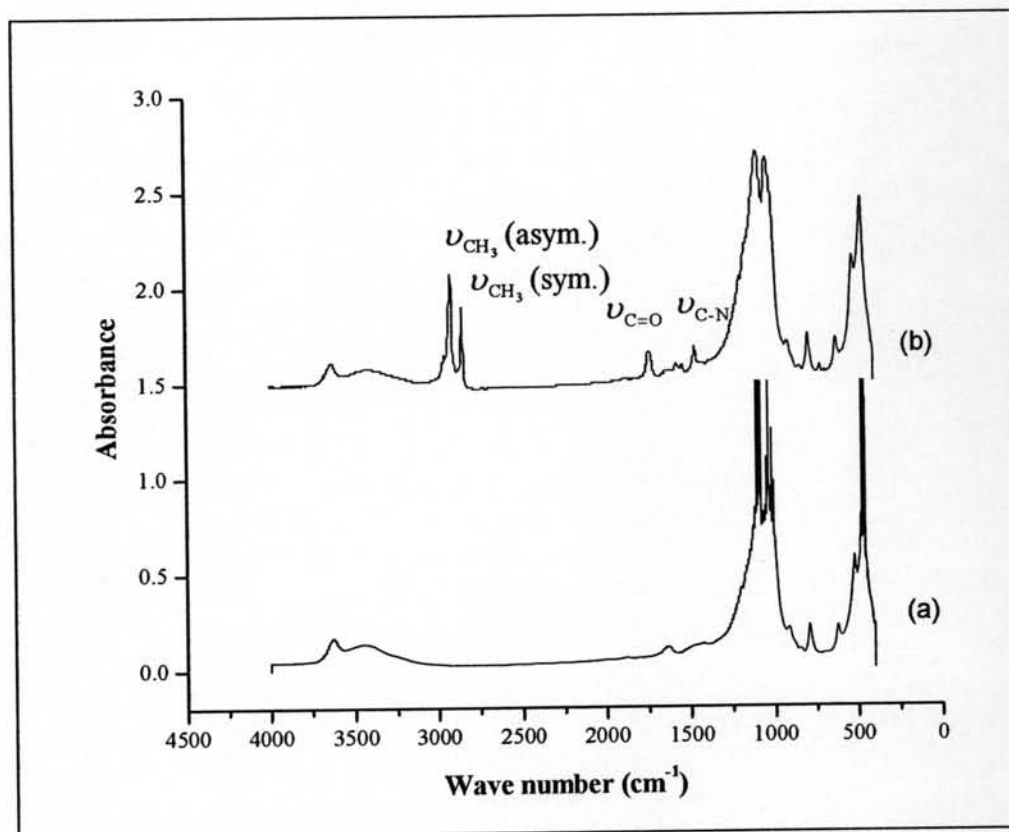


Figure 5.2 Infrared spectra of organomodified bentonite: (a) Na-BTN, (b) DOEM-BTN.

B. Thermal behavior of PP/organoclay nanocomposites

The melting and crystallization behavior, as measured by DSC, of PP and the nanoclay composites shown in Figure 5.3 are collected in Table 5.2. The peak melting temperature (T_m) and the heat of fusion (ΔH_f) were observed while the cooled sample was reheated from 30°C at 10°C/min. ΔH_f of the nanocomposites slightly decreased as the clay content increased because the organoclay firmly seized the chemically bound PP molecules, making crystallization more difficult.

From Fig. 5.3, the reduction in ΔH_f observed as increasing the clay content may simply be due to a dilution effect, caused by a reduction of crystallisable component in the systems. The melting and crystallization temperatures are slightly changed when compared with PP since the nanoscale fillers have insignificantly effect on the crystallite size of the based polymer.

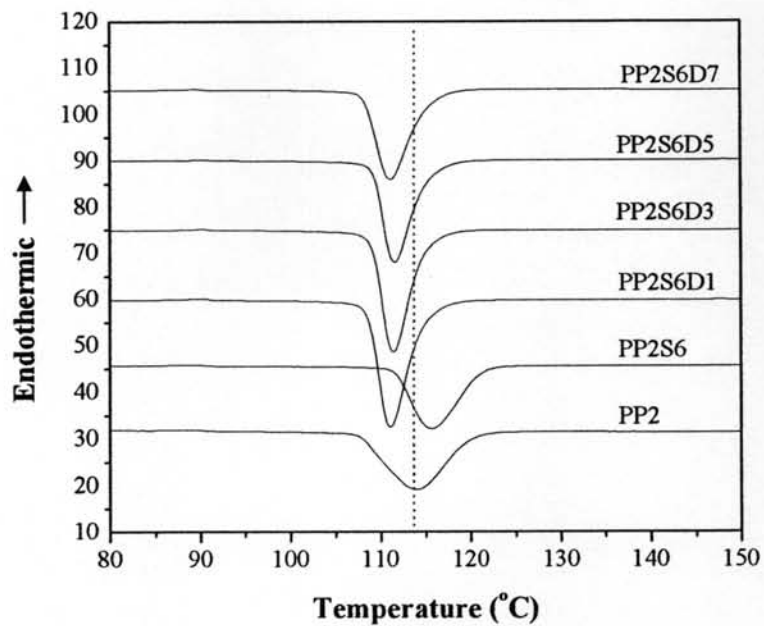
Table 5.2 Melting and crystallization behavior of PP and PP/organoclay nanocomposites

Composition	T_m (°C)	T_c (°C)	ΔH_f (J/g)	Normalized % Crystallinity
¹ PP2	161.0	113.8	62.9	100
² PP2S6	161.2	115.1	62.5	93
³ PP2S6D1	160.8	114.1	62.1	92
PP2S6D3	160.5	111.7	61.9	91
PP2S6D5	160.1	111.9	58.7	84
PP2S6D7	160.0	111.9	58.3	82

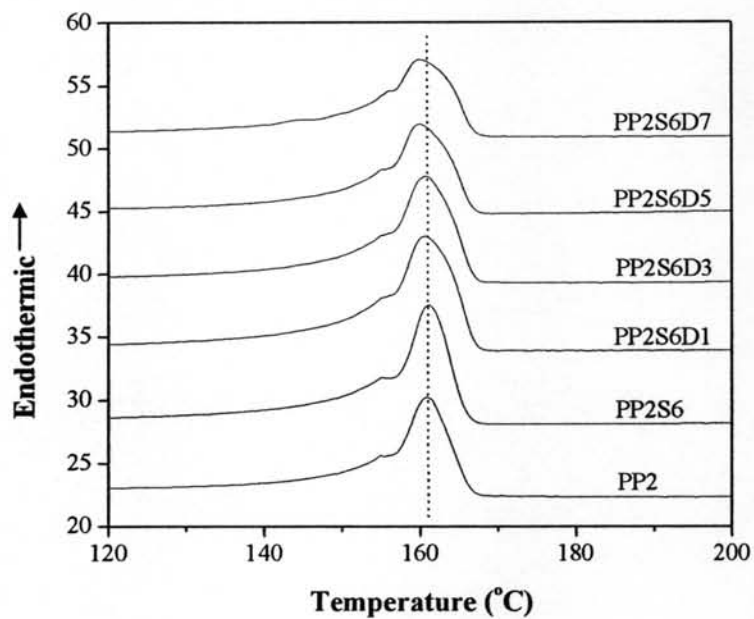
¹ PP2 = Polypropylene which has MFI of 2

² PP2S6 = Polypropylene blended with 6%wt Surlyn®

³ PP2S6Dx = Blended PP with x%wt organoclay modified by DOEM



(A)



(B)

Figure 5.3 DSC thermograms of PP/organoclay nanocomposites (A) Crystallization Temperatures, and (B) Melting Temperatures.

Table 5.3 Thermal behavior of PP and PP/organoclay nanocomposites

Sample	TGA			
	Clay Content (wt%)	T _d (°C)	T _i (°C)	T _r (°C)
PP2	-	454.8	417.9	470.3
PP2S6	-	456.0	430.7	477.1
PP2S6D1	1.1	458.9	433.0	476.1
PP2S6D3	2.6	458.4	435.4	475.1
PP2S6D5	3.6	458.3	430.9	473.8
PP2S6D7	5.4	459.9	430.2	475.0

The clay content of the nanoclay composites was determined from the residual content using TGA, as shown in Table 5.3. The actual clay content, as inorganic fraction, was found by TGA analysis in different parts of the samples. The clay percentage by weight is close to 3.6% in the samples where 5% clay was added during nanocomposite preparation. In 7% samples, the final clay content was around 5%.

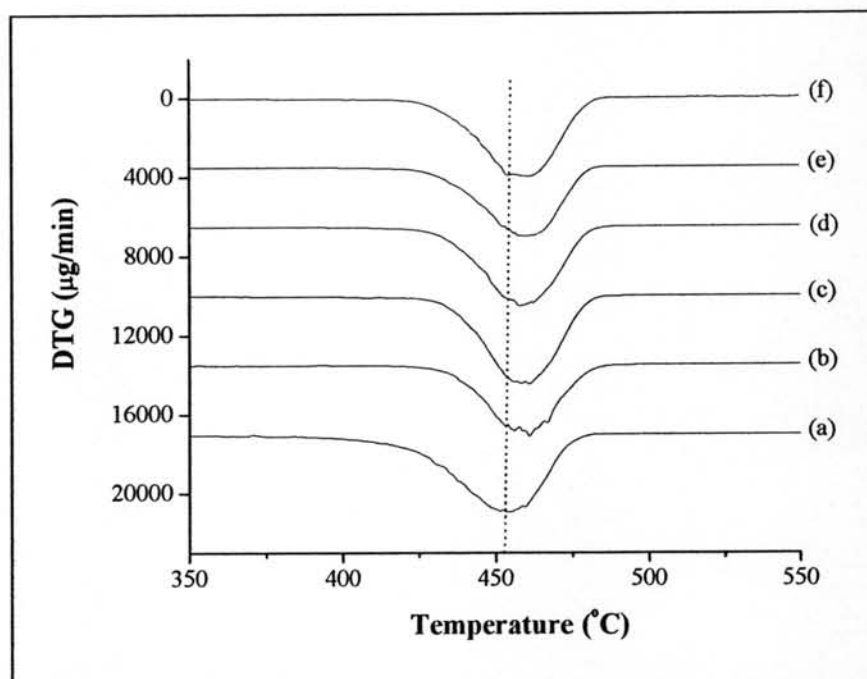


Figure 5.4 DTA curves of PP/organoclay composites (a) PP2, (b) PP2S6, (c) PP2S6D1, (d) PP2S6D3, (e) PP2S6D5, and (f) PP2S6D7.

C. Crystallization behavior of PP/organoclay nanocomposites

The structure of the nanocomposites was examined by XRD. The characteristic peaks of PP crystal peak were analyzed with the 2θ range of $10\text{-}30^\circ$, as shown in Fig. 5.5. Pristine PP shows five prominent which correspond to monoclinic α crystal-line phase: α_1 , α_2 , α_3 and α_4 belong to the (110), (040), (130) and (111, 041) crystal planar corresponding to $2\theta = 14.04, 16.86, 18.50, 21.08$ and 21.72 , respectively. The results indicate that the presence of the organoclay does **not** affect the crystal structure of PP matrix, as already observed for the PP/clay nanocomposites. [6-7]

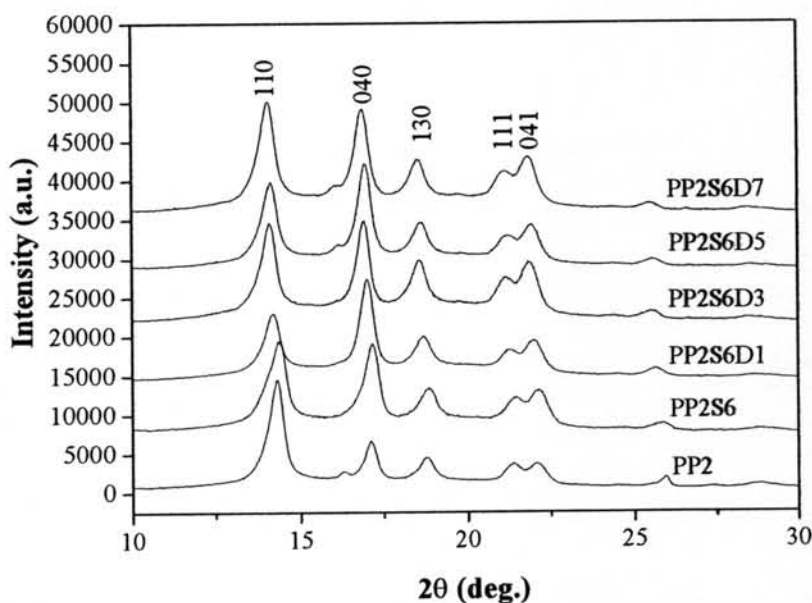


Figure 5.5 The WAXD patterns of pure PP and PP/organoclay composites varied the compositions.

D. Mechanical measurement of PP/organoclay nanocomposites

The influence of the organoclay content on the mechanical properties is shown in Figure 5.6-5.9. When the clay content is less than 3 %wt, Young's modulus, stress at break and toughness are increased with the clay content. When the clay content exceeds 3 %wt, these mechanical properties are decreased. Probably due to the aggregation of the organoclay, this leads to the loss of the features of the nanocomposites.

Another important factor is the impurity of the bentonite. The modified bentonite has many inhomogeneous aggregates, calcium content and siliceous impurities. Although many of the impurities are eliminated during modification process, due to the flocculation of the clay and the differences in specific gravity between clay and siliceous materials, and also during screening through a 44 μm sieve. They act as stress concentrators, allowing crack initiation and propagation, consequently making the inferior of the mechanical performance of the nanocomposites.

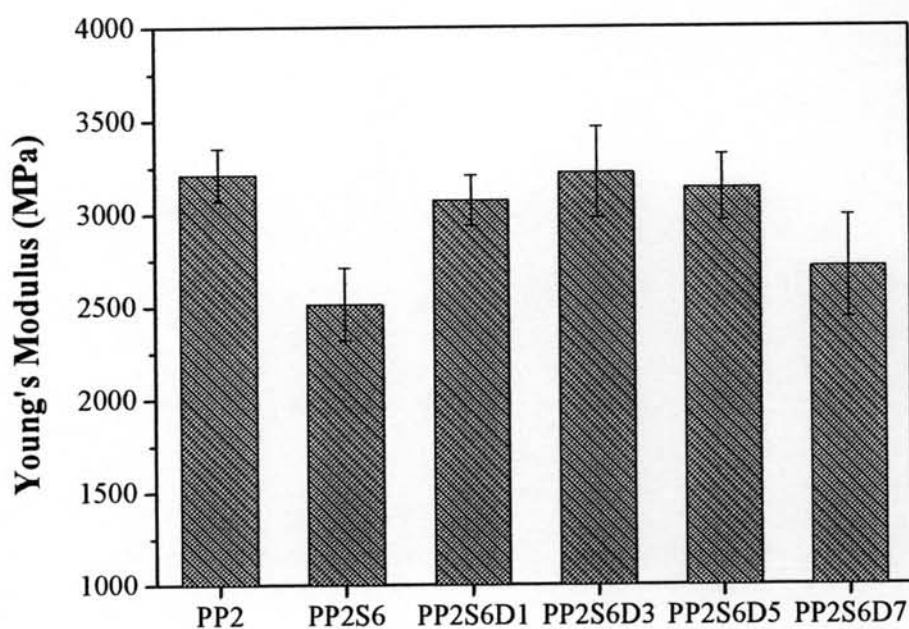


Figure 5.6 Young's modulus of PP and PP/organoclay composites with various organoclay loadings.

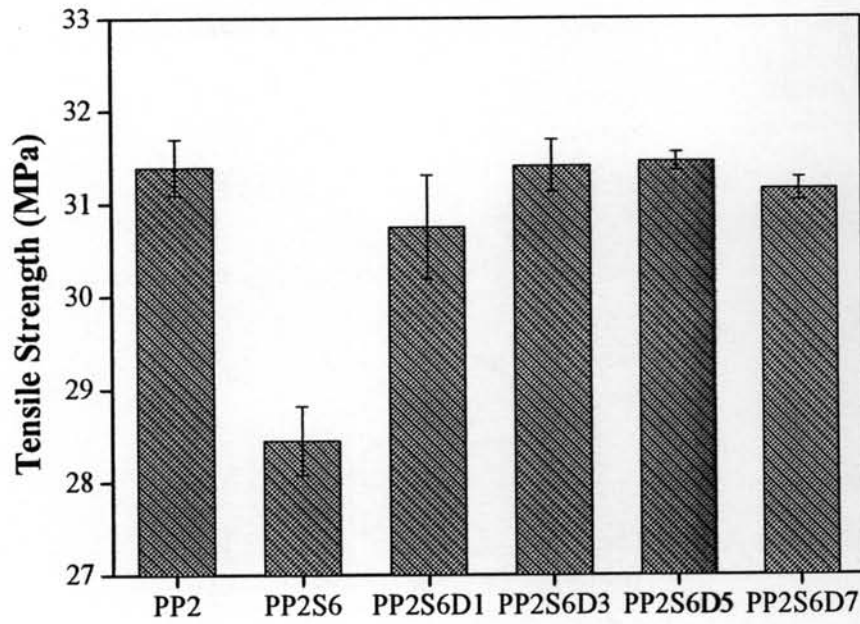


Figure 5.7 Tensile strength of PP and PP/organoclay composites with various organoclay loadings.

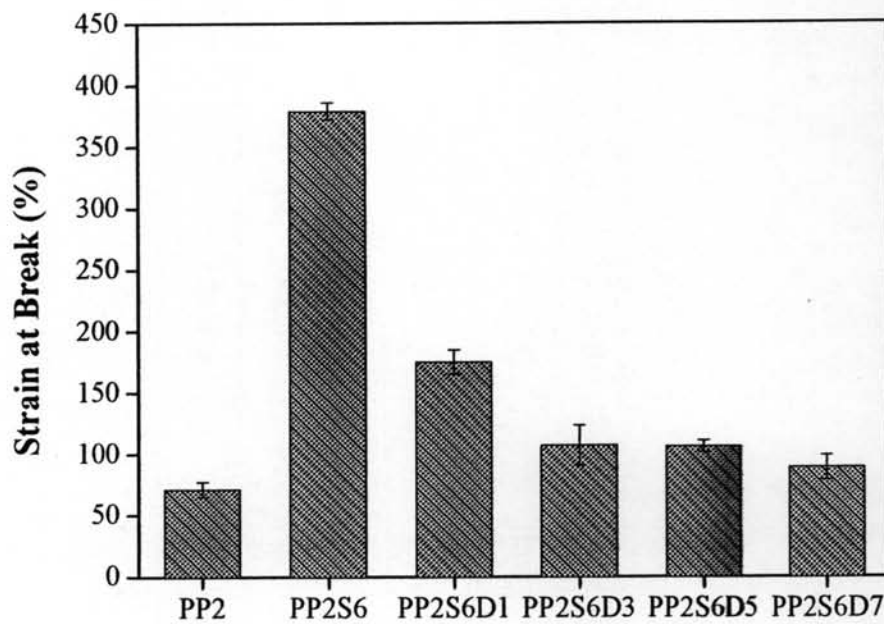


Figure 5.8 Strain at break of PP and PP/organoclay composites with various organoclay loadings.

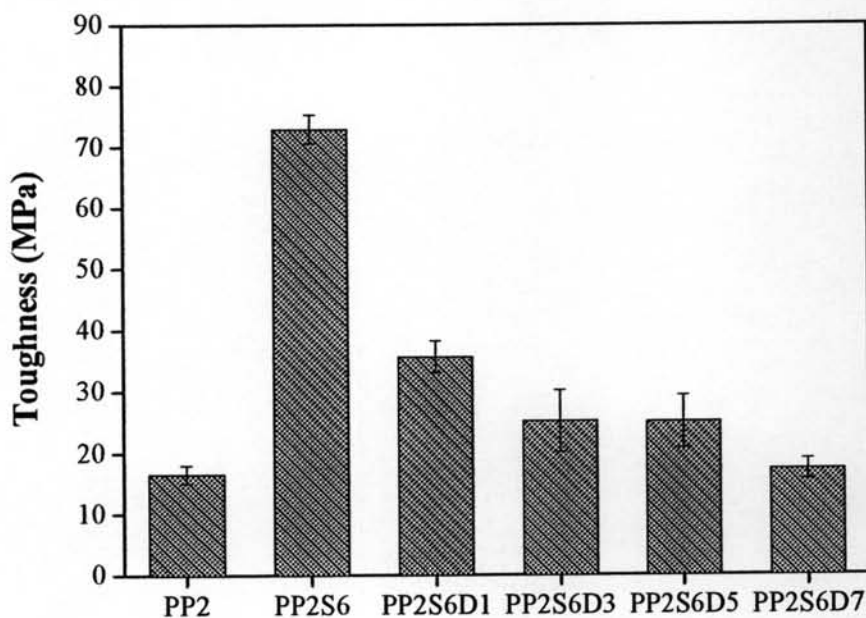


Figure 5.9 Toughness of PP and PP/organoclay composites with various organoclay loadings.

Table 5.4 Effect of organoclay loading on mechanical properties

Composition	Young's Modulus (MPa)	Stress at yield (MPa)	%Strain at break (%)	Toughness (MPa)
PP2	3157 ± 128	31.4 ± 0.3	71 ± 7	16.6 ± 1.4
PP2S6	2541 ± 169	28.5 ± 0.4	377 ± 7	72.9 ± 0.9
PP2S6D1	3069 ± 151	30.7 ± 0.4	175 ± 10	35.6 ± 2.6
PP2S6D3	3222 ± 244	31.4 ± 0.3	109 ± 17	26.0 ± 5.1
PP2S6D5	3139 ± 178	31.4 ± 0.1	106 ± 4	23.5 ± 2.1
PP2S6D7	2714 ± 240	31.2 ± 0.1	91 ± 9	17.6 ± 1.7

5.5 Conclusions

The clay content has a direct influence on the mechanical properties of the obtained nanocomposites. The improvement is marked for the samples with 1 and 3 %wt of the organoclay with the highest Young's modulus, strain at break and toughness. PP/organoclay composites start to drop in all mechanical properties, except the tensile strength, when the organoclay is incorporated more than 3%wt.

5.6 Acknowledgements

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5.7 References

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