

# IV. Conclusion

A different series of polyurethane-organoclay nanocomposites were synthesized by two ways. The first way is the in-situ polymerization which includes intercalation of tyramine or 12-aminododecanoic acid onto montmorillonite clay followed by addition of diol, diamine and toluene diisocyanate. The second way is free radical polymerization of vinyl-groups-endcapped polyurethane with vinyl-monomer-clay. The infrared (IR) spectroscopy confirms the interaction between the polymer and silicate layers. The XRD illustrates that the d-spacing which increased to more than 44 Å since there is no peak corresponding to  $d_{001}$  with small ratios of organoclay ( $\cong 5$  wt-%) leading to exfoliation. While exfoliation/intercalation was found with the higher ratios of organoclay (7-20 wt-%), since a low intensity and broad peaks were observed. The morphological structure of the materials was investigated. The SEM images which confirmed the dispersion of nanometer silicate layers in the polyurethane matrix.

The presence of organoclay has led to an improvement in the mechanical properties. Since, the tensile strength increased by 194 % with increasing the organoclay contents up to 20% compared to the PU with 0% organoclay. The results of tensile strength of PU/SMA/ALA-MMT nanocomposites are higher than the corresponding PU/Tyr-MMT and PU/vinyl monomer-MMT by 6-7 times. Also, it was found that the elongation decreases with increasing the organoclay contents in case of the two series PU/SMA/ALA-MMT and PU/Tyr-MMT, due to stiffness of the film samples. While in case of the third series (PU/vinyl monomer-MMT) the elongation was increased with increasing the organoclay contents, which can be attributed to both complete exfoliation of MMT in the polymer matrix and flexibility.

# Summary

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This thesis contains three main parts includes the introduction, experimental part, and results discussion. In addition, it contains the conclusion, references, english summary and arabic summary.

***The first part, Introduction:*** it includes background, chemistry, structure and uses of polyurethane. Also, it contains the types and preparation of composite materials, and some details about PU-clay nanocomposites which have been reported.

***The second part, Experimental:*** it contains a complete description of the materials, instruments, measurements and the preparation methods of the intercalation of surfactant or vinyl monomer salts onto montmorillonite clay. The preparations of PU-clay nanocomposites by in-situ polymerization of different modified-clay with different diols and/or diamine and styrene-co-maleic anhydride have been described. Also, PU-clay nanocomposites were prepared via solution polymerization of vinyl monomer-MMT and acrylate terminated PU. The formation PU-clay hybrid films and measurement of IR, TGA, SEM, tensile strength and elongation were also, described.

***The third part, Results & Discussion:*** it includes the data obtained from the characterization methods that have been reported for all polymer-clay hybrids. The characterization of the prepared materials was investigated by different testing methods that confirm the intercalation of modifiers within the clay interlayers as illustrated by IR spectra. The TGA of the incorporated polymer within clay layers shows higher thermal stability than virgin polymers. The swelling measurements in different organic solvents and water show highly decrease or disappearance the swelling properties of PU-clay hybrids. This may reflect the improvement in the solvent resistance of the prepared materials. The X-ray diffraction illustrates that grafted

polyurethane-organoclay gave completely exfoliated nanocomposites with all modified-clay. The SEM results confirm the homogenous dispersion of nanometer silicate layers in the polyurethane matrix, i.e. the clay was completely exfoliated in the polyurethane matrix. It was also found that the presence of organoclay leads to an improvement in the mechanical properties. Since, the tensile strength is increased with increasing the organoclay contents up to 20% by the ratio 194% in compared to the PU with 0% organoclay. The results show that the tensile strength of PU/SMA/ALA-MMT nanocomposites was high by 6-7 times than the corresponding PU/Tyr-MMT and PU/vinyl monomer-MMT. Also, the elongation is decreased with increasing the organoclay contents in case of the two series PU/SMA/ALA-MMT and PU/Tyr-MMT.

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# VI. APPENDIX

# 1. ABBREVIATIONS

## USED IN THIS THESIS

<b>PU</b>	Polyurethane
<b>PUU</b>	Poly(urethane urea)
<b>SPUU</b>	Segmented polyurethane urea
<b>CEC</b>	Cation exchange capacity
<b>CMC</b>	Critical micelle concentration
<b>PP</b>	Polypropylene
<b>PMMA</b>	Poly(methyl methacrylate)
<b>MMT</b>	Montmorillonite clay
<b>VDAC</b>	Vinyl benzyl diethyl dodecyl ammonium chloride
<b>OMMT</b>	Organophilic montmorillonite clay
<b>DSC</b>	Dynamic scanning calorimeter
<b>DMAC</b>	Dimethyl acetamide
<b>SDS</b>	Sodium dodecyl sulfate
<b>SBRS</b>	Styrene butadiene rubber
<b>PUI</b>	Polyurethane interpenetrating network
<b>UPR</b>	Unsaturated polyester resin
<b>CTAB</b>	Cetyltrimethyl ammonium bromide
<b>PEG</b>	Poly(ethylene glycol)
<b>PPG</b>	Poly(propylene glycol)
<b>EPU</b>	Electrometric polyurethane
<b>TDI</b>	Toluene diisocyanate
<b>DMF</b>	Dimethyl formamide
<b>THF</b>	Tetra hydrofuran

<b>HEMA</b>	2-Hydroxyethyl methacrylate
<b>PHEMA</b>	Poly(2-hydroxy ethyl methacrylate)
<b>TGA</b>	Thermogravimetric Analysis
<b>SEM</b>	Scanning Electron Micrograph
<b>DTG</b>	Derivation thermogravimetric

## **2. DOCUMENTS**

### **Papers published from the thesis**

- 1) Preparation and Characterization of PU-Clay Nanocomposites**  
[*Polymer Composites*, 28, 108, 2007]
  
- 2) PU-Nanocomposites Material via *in situ* Polymerization into Organoclay Interlayers** [*Polymer for Advanced Technology*, 2007, in press]

# Preparation and Characterization of Polyurethane–Organoclay Nanocomposites

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Nanocomposite polyurethane (PU)–organoclay materials have been synthesized via in-situ polymerization. The organoclay is first prepared by intercalation of tyramine into montmorillonite (MMT)-clay through ion exchange process. The syntheses of polyurethane–organoclay hybrid films containing different ratios of clay were carried out by swelling the organoclay into diol and diamine followed by addition of diisocyanate and then cured. The nanocomposites with dispersed and exfoliated structure of MMT were obtained as evidenced by X-ray diffraction and scanning electron microscope. X-ray diffraction showed that there is no peak corresponding to  $d_{001}$  spacing in organoclay with the ratios up to 20 wt%. SEM images confirmed the dispersion of nanometer silicate layers in the polyurethane matrix. Also, it was found that the presence of organoclay leads to improvement in the mechanical properties. The tensile strength was increased with increasing the organoclay contents to 20 wt% by 221% in comparison to the PU with 0% organoclay. POLYM. COMPOS., 28:108–115, 2007. © 2007 Society of Plastics Engineers

## INTRODUCTION

Introducing the promising nanocomposite, which is described as the next great new frontier of materials science, recognized the technological development of this century. Nanocomposites are a class of composite materials having more than one solid phase with a dimension in the 1–20 nm ranges in which the reinforcing phase dimensions are in the order of nanometers [1]. Layered materials are potentially well suited for the design of hybrid nanocomposites, because their lamellar elements have high in-plane strength, stiffness, and a high aspect ratio.

Polymer-nanocomposites are a class of polymers reinforced with a small quantity (1–10% by weight) of particles with nanometric size. The polymer-layered silicate nanocomposites with polymer chain intercalating galleries of adjacent silicate layers to form exfoliated or intercalated,

which represent improved or new properties compared with bulk polymer, have attracted much interest. The significant improvement in the properties in comparison to the unmodified resin or conventional polymer-composite with inorganic fillers were observed. These properties include mechanical (modulus, strength, fracture toughness, and surface hardness) [2], barrier performance [3], thermal [4], flammability resistance [5], and solvent (or water) uptake [6]. To achieve equivalent physical properties, the conventional polymer composite must mix with more than 30–40 wt% of inorganic fillers such as talc, mica, silica, and carbon black, whereas a nanocomposite only requires the addition of a few percent if 1-nm thick layered silicate is well dispersed on a nanoscale (exfoliation).

The smectic clays [e.g. montmorillonite (MMT)] and related layered silicates are the preferred inorganic reinforcing materials for polymer nanocomposites for two important reasons: The first reason is they occur ubiquitously in nature and can be obtained in mineralogically pure form at low cost. The second reason is they exhibit a very rich intercalation chemistry, which allows them to be chemically modified and made compatible with organic polymers for dispersal on a nanometer length scale. The layered clay-polymer nanocomposites can be prepared by replacing the hydrophilic  $\text{Na}^+$  and  $\text{Ca}^+$  exchange cations of the native clay with more hydrophobic onium ion to form a polymer-clay hybrid through two ways. The first way is the intercalation of a monomer into the clay interlayer and subsequent heat treatment for polymerization (*in-situ*) [7]. The second way is the direct intercalation of a preformed polymer into the layered clay [8].

Since the development of nylon-6/clay nanocomposite by Toyota researchers [9], extensive studies on polymer-clay nanocomposites have been investigated to obtain new organic–inorganic nanocomposites with enhanced properties. The use of clay or organically modified clay as precursors for preparation of nanocomposites has been studied into various types of polymer systems including polyamide 6 [10], poly(oligooxyethylene methacrylate) [11], epoxy [12], polypropylene [13], polyacrylamide [14], polypyrrol [15], polystyrene [16], poly(*p*-phenylene vinylene) [17],

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poly(ethylene oxide) [18], polycaprolactone [19], and poly(methyl methacrylate) [20].

Polyurethanes (PUs) are one of the most interesting classes of synthetic elastomers that have unique properties. PU's elastomers are a family of segmented polymers with soft segments derived from polyols and hard segments from isocyanates and chain extenders. They are very versatile polymer materials and their properties can be modified by varying the PU microstructure and by dispersing inorganic fillers in PU matrix [21]. PUs have the advantages such as the best abrasion resistance, outstanding oil resistance, and excellent low-temperature flexibility. They also exhibit the widest variety of hardness and elastic moduli that just fill in the gap between plastics and rubbers. However, they show poor thermal stability and barrier property, which can be modified by clay [22].

In recent years, much attention has been focused on PU-clay nanocomposites, which represent greatly improved performance properties compared to the pristine PU [23–33]. However, there also exist some disadvantages concerning with thermal stability and solvent resistance properties. So, the present work will discuss our efforts to synthesis a new PU-MMT nanocomposites with improved thermal, mechanical, and solvent resistant PU-clay nanocomposites.

## EXPERIMENTAL PART

### Materials

Kunipia-F, sodium montmorillonite clay ( $\text{Na}^+$  O-MMT) with cation exchange capacity (CEC) of 119 mequiv./100 g, was supplied by Kunimine Industry (Japan). Styrene was supplied from Aldrich and used after purification by washing with 1 M NaOH, then dried over anhydrous sodium sulphate followed by distillation under vacuum. Toluene-2,4-diisocyanate (TDI) was provided by Fluka, Germany, and having 99.5% of purity for 2,4-isomer with an m.p. of 21°C, was used as received. Jeffamine D-400 (Jf-400) [poly(oxypropylene-diamine)] was supplied from Huntsman (Denmark) and used after dehydrating by evacuation at 80°C for about 6 h just before use. Tyramine hydrochloride (Tyr) was used as obtained from Tokyo kasei. Poly(ethylene glycol) (PEG-1540) with average molecular weight of 1540 was purchased from Kock-Light Laboratories, England and was dried under vacuum at 80°C for 6 h just before use. Dimethylformamide (DMF) from Adwic (Egypt) was used after distillation and drying over A4 molecular sieve. Ethanol (from Adwic, Egypt) was used as obtained without further purification.

### Preparation of Tyramine/Montmorillonite Organoclay I

The montmorillonite (10 g,  $\approx 11.9$  mequiv.) was swelled in 350 ml distilled water overnight with slow stirring. The tyramine hydrochloride (2.05 g, 11.82 mequiv.) dissolved in 50 ml distilled water was added slowly to the swelled

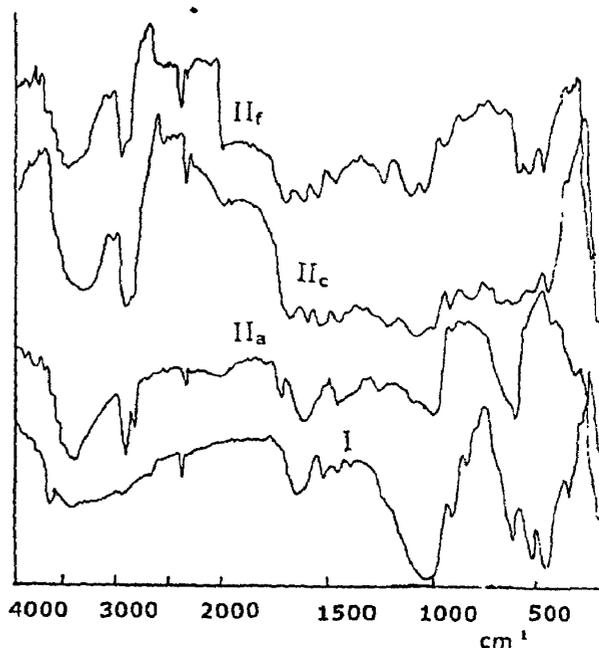


FIG. 1. IR spectra for organoclay I and PU-Tyr-MMT II<sub>a,c,r</sub>.

suspended clay with vigorous stirring at 60°C. The resultant suspension was stirred overnight. The suspension was allowed to stand for a few hours followed by filtration through sintered glass (G4) and finally washed by distilled water until no white precipitate was detected on addition of  $\text{AgNO}_3$  solution to the filtrate. The product was dried at  $\sim 50^\circ\text{C}$  under vacuum to yield 11.18 g of MMT-tyramine intercalate product. The product was re-treated with tyramine by swelling in mixture of 200 ml DMF and 200 ml water followed by addition 1 g of tyramine hydrochloride solution in 10 ml distilled water, and the procedure was repeated as previously to give 11.39 g of MMT-tyramine intercalate I.

The characteristic properties were investigated by infrared (IR) (Fig. 1); thermogravimetric analysis (TGA) (Fig. 2); calcination; elemental microanalysis, swelling data Table 1; and X-ray diffraction (XRD) (Fig. 3).

### Synthesis of PU-Tyr-MMT Nanocomposites II<sub>a,c</sub>

A 16 g of dry diol (PEG-1540, 10.34 mmol) and 8.3 g of the diamine (Jf-400, 20.75 mmol) were mixed at molar ratio of 1:2, respectively and dissolved in 24.3 g of the dried DMF to give a solution (50% w/w of monomers/solvent) and it was kept as stock solution.

A 0.2105 g of the organoclay I was mixed with 8 g of the previous stock diol/diamine solution (i.e. 4 g diol/diamine) and stirred for 6 h till the mixture becomes homogenous and the organoclay completely swelled. Using the dropping funnel, 0.6 g (0.5 ml, 3.448 mmol) of TDI was added dropwise with vigorous stirring at room temperature. The reaction mixture was stirred for 8 h to give nanocomposite with 5 wt% organoclay by in-situ polymerization technique. After removing the

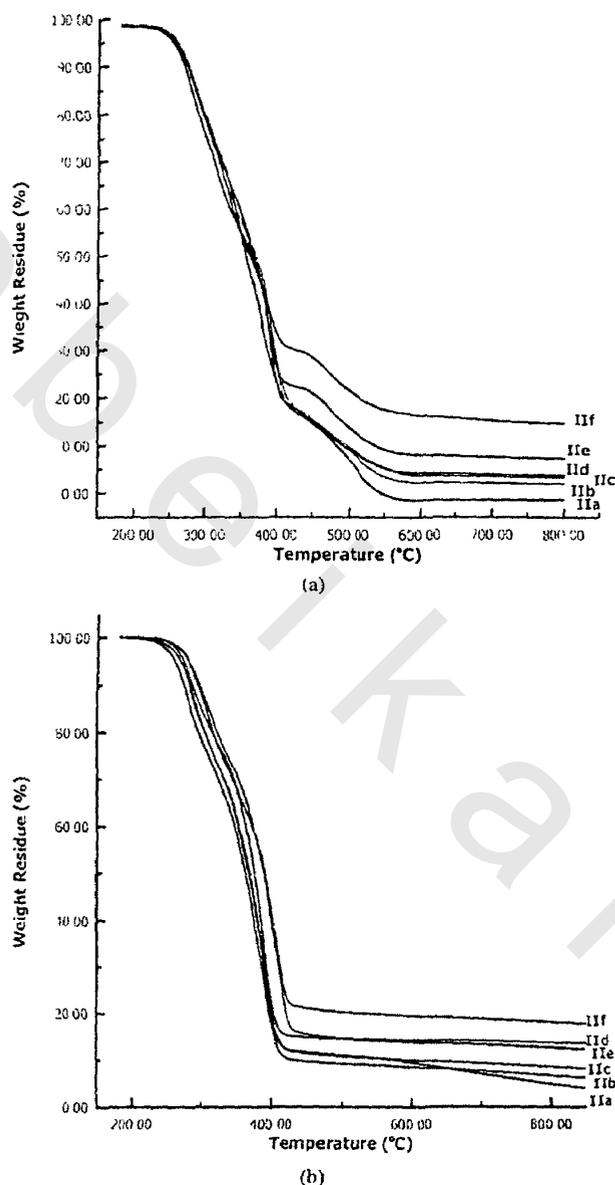


FIG. 2. (a) TGA thermograms for PU-organoclay samples (from down to top II<sub>a</sub>, II<sub>b</sub>, II<sub>c</sub>, II<sub>d</sub>, II<sub>e</sub>, and II<sub>f</sub>) in air. (b) TGA thermograms under argon atmosphere for PU-organoclay composites II<sub>a-f</sub>.

adsorbed gases from the polymerization mixture, the PU-clay nanocomposite film II<sub>c</sub> was formed by casting the solution in a mold and then removing the solvent at 80°C in a vacuum oven for 12 h to give elastic films.

A series of composite samples (II<sub>a-f</sub>) containing different amounts (0, 3, 5, 7, 10, and 20%) of modified clay (I) were prepared by the same procedure using the same diol, diamine, and the same diisocyanate to give elastic films and the data relevant were illustrated in Table 1.

#### Measurements

Infrared spectra (IR) were carried out on a Perkin-Elmer 1430 ratio-recording infrared spectrophotometer using the

potassium bromide disc technique in the wavenumber range of 4000–400 cm<sup>-1</sup>.

Thermogravimetric analyses (TGA) were determined with a Rigaku Thermo Plus 2 TG-DTA TG8120. The heating rate was 5°C/min in all cases in the temperature range ~30–800°C in air and under argon flow.

Calcination Measurements. A definite weight of the sample was introduced into a porcelain crucible and dried in an electric oven at 120°C overnight, then introduced into an ignition oven and the temperature was increased to 1000°C and adjusted at this temperature for 5 h. The loading of each sample was expressed as the weight loss by ignition per 100 g of the dry sample. The data of all prepared samples are listed in Table 1.

X-ray diffraction (XRD) measurements were carried out using a Rigaku RINT2000 Powder-Diffractometer equipped with a Ni-filtered Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$  at scanning rate 0.05°/sec, divergent slit 0.3°). Measurements were made for the dried product to examine the interlayer activity in the composite as prepared.

Morphology of the composite was examined by a Joel JXA-840 scanning electron microscopy (SEM) equipped with an energy dispersive X-ray detector to examine the morphology and particle size of MMT in the polymer-MMT composites. Specimen was deposited on double-sided scotch tape and examined at their fracture surface.

Mechanical properties of the samples were tested with an Instron mechanical tester [model LR5K plus (LLOYD)] at crosshead speed of 500 mm/min. The I-shaped specimens were prepared with 5 cm ( $5 \times 10^{-2} \text{ m}$ ) in length, 1 cm ( $1 \times 10^{-2} \text{ m}$ ) in width, and 330–450  $\mu\text{m}$  ( $0.33\text{--}0.45 \times 10^{-3} \text{ m}$ ) in thickness. For each datum point, five samples were tested, and the average value was recorded.

The swelling degree was determined by taking a definite weight (about 0.15 g) of the dry sample and introduced into a small sintered glass and allowed to imbibe in different solvents, such as distilled water, benzene, and acetone, for 24 h. The excess solvent was removed by gentle centrifugation. The swelled sample was weighed and resuspended in the solvent. This procedure was repeated until obtaining on a constant weight for the swelled sample. The swelling degree of each sample is expressed as the amount of sorbed solvent per 100 g of dry sample.

## RESULTS AND DISCUSSION

### Synthesis and Structure

The synthesis of PU-organoclay nanocomposites was carried out through the following steps as illustrated in Scheme 1: the first step involves the modification of hydrophilic clay to become organophilic and promote the absorption of organic materials used in formation of PU and improve the particle-matrix interactions. This step was achieved through ion exchange process between sodium

TABLE 1. Thermal analysis and swelling data of PU-tvI-MMT nanocomposites II<sub>a-f</sub>

Run	Organoclay I (wt%)	TGA analysis data						Calcination <sup>a</sup>		Swelling data <sup>b</sup>		
		In air			Under argon			Clay content (%)	Organic content (%)	Water (%)	Acetone (%)	Benzene (%)
		Temperature at d-5%	Temperature at d-10%	Char yield (%)	Temperature at d-5%	Temperature at d-10%	Char yield (%)					
II <sub>a</sub>	0	—	—	0.0	271	287	7.90	0.0	100	0.98	0.58	0.13
II <sub>b</sub>	3	265	279	3.38	286	301	3.22	2.62	97.38	0.84	0.57	0.10
II <sub>c</sub>	5	262	278	4.64	295	311	10.92	4.37	95.63	0.76	0.48	Nil
II <sub>d</sub>	7	264	277	5.32	283	300	12.45	5.28	94.72	0.79	0.43	Nil
II <sub>e</sub>	10	275	272	8.42	297	314	13.16	8.35	91.65	1.58	0.26	Nil
II <sub>f</sub>	20	264	279	16.04	280	293	17.97	16.01	83.99	1.67	0.22	Nil

<sup>a</sup>At 1,000°C for 8 h.

<sup>b</sup>Swelling (%) = (weight of absorbed solvent/weight of dry sample) × 100.

cation in MMT and ammonium groups in tyramine hydrochloride I, which contains functional group that can react with diisocyanate. The calcination indicates that the functionalization was achieved with a high degree of conversion (88%). The second step is the formation of PU nanocomposites. This step is achieved by solvation of the organoclay with the diol as PEG[b]-1540 and diamine as amine-terminated poly(oxypropylene) JF-400. It was found that the modified clay was first swelled in the diol and diamine at room temperature, and followed by addition of the diisocyanate to produce the intercalated PUs II<sub>a-f</sub>. The previous mixture was then casted in films to produce the intercalated PUs II<sub>a-f</sub> films with different organoclay contents. The structural composition and properties of the prepared composite materials were determined by several analytical techniques.

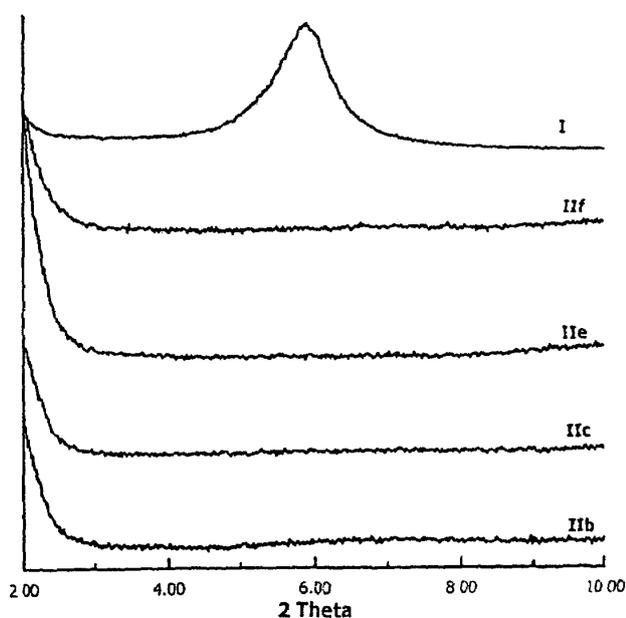
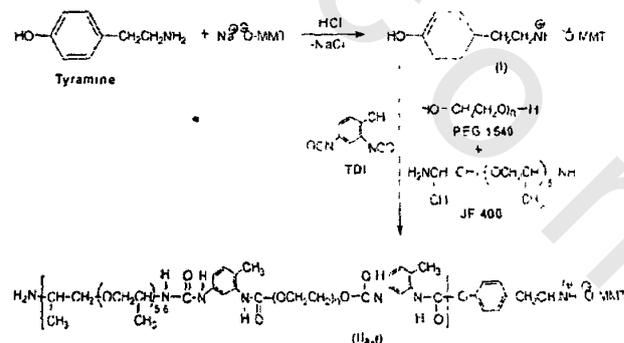


FIG. 3. XRD pattern for organoclay I and PU-organoclay II<sub>a-f</sub>.

The swelling data in Table 1 indicated that the swelling degrees in the polar solvents such as water and acetone are very small or there is no swelling in the nonpolar solvent such as benzene. These data reflect that there is improvement in the barrier properties of the produced materials. It was found that the materials adsorb very small quantity of the polar solvents such as water and acetone in comparison with the nonpolar solvent such as benzene, the swelling degree followed the order water ≥ acetone > benzene. Also, the data show a very small increase in the water uptake with increasing ratio of clay, which can be attributed to the higher hydrophilic characters of clay.

The IR spectra of the samples were illustrated in Fig. 1. The spectra of modified clay I shows that the reported NH stretch band near 3400 cm<sup>-1</sup> and NH bend band near 1645 cm<sup>-1</sup> are shifted quite substantially to regions associated with <sup>+</sup>NH<sub>3</sub> vibration, which facilitate the ion exchange with MMT. A characteristic band appears at 1039, 523, and 462 cm<sup>-1</sup> for Si—O and at 3629 cm<sup>-1</sup> for OH group. The quaternary ammonium group (—N<sup>+</sup>≡) shows a characteristic band at 1518 cm<sup>-1</sup>.

The free OH band at 3629 cm<sup>-1</sup> in organoclay I disappeared in nanocomposites indicating that the strong interaction are occurring between OH group in organoclay and



SCHEME 1. Preparation of modified clay and PU-modified clay composites.

the isocyanate forming the isocyanate linkage. It is clear that the  $\text{NH}_2$  band near  $1630\text{ cm}^{-1}$  in organoclay was shifted to higher wavelength near  $1690\text{ cm}^{-1}$  with nanocomposite, which indicate that an interaction occurs between organoclay and the polymer. The spectra of PU  $\text{II}_a$  shows that the absorbance that appeared at  $1729\text{ cm}^{-1}$  were assigned to hydrogen-bonded urethane carbonyl ( $\text{C}=\text{O}$ ) and the one that appeared at  $1453\text{ cm}^{-1}$  were assigned to a secondary urethane amide ( $\text{C}-\text{NH}$ ). The spectra of the PU-organoclay  $\text{II}_{c-f}$  shows peaks at  $1728\text{ cm}^{-1}$  due to the stretching of urethane carbonyl group ( $\text{C}=\text{O}$ ), and at  $2919$  and  $2864\text{ cm}^{-1}$  due to the asymmetric and symmetric  $\text{C}-\text{H}$  stretching vibration. The  $3309\text{ cm}^{-1}$  peak resulted from the  $\text{N}-\text{H}$  group in hydrogen bonding; the main features of various bond vibrations and hydrogen bonding of these PU-modified clay nanocomposites remained the same as that of neat PU. These results deduce that there were no major chemical structural changes in PU, owing to the presence of organoclay.

### Thermal Analysis

Thermal properties of PU-modified clay materials were determined by both calcination and TGA in atmospheric air and under inert condition (argon atmosphere). The data are summarized and listed in Table 1 and Fig. 2a and 2b. The data and the figures show the weight loss encountered during heating; the PU-modified clay materials were found in the range from 84 to 97% as determined by both TGA and calcination. It is clear that the weight loss evident in TGA curves is nearly compatible with the calcination measurements.

The TGA thermograms for the samples  $\text{II}_{a-f}$  in Fig. 2a indicate that there are two stages of decomposition. The first stage is the sharp and major, which involve the thermal decomposition of the polymers present on the surfaces of the clay layers and intercalated polymers into the clay. The decomposition temperature in this stage started at  $\approx 260^\circ\text{C}$  and took place until  $\approx 400^\circ\text{C}$ , with the corresponding weight loss ranging from  $\approx 65$  to 80%. In this stage, the difference between the samples is very small with no order can be mentioned. The second stage is broad, in which the weight loss was ranging from  $\approx 17$  to 22% in the temperature range  $\approx 400^\circ\text{C}$  to  $\approx 570^\circ\text{C}$ . In this stage, the composites displayed higher thermal resistance than pure polymers. This stage was attributed to further decomposition of the rest intercalated polymers, especially the polymers present in the interlayers of the clay or some salts in the interlayer of the clay or interval the clay mineral loses OH groups and the crystallographic structure collapsed [4]. Generally, the first stage appear that the composite samples were degraded nearly at the same temperature range and slightly faster than pure PU. This may be due to the presence of organic residues. However, in the second stage, after complete decomposition of the small organic molecules, all the nanocomposites show higher thermal resistance than pure PU matrices [28].

It was found that there are differences in the TGA analysis under argon than in air. This was explained for two reasons: the first is the presence of oxygen in air help in increasing the rates of decomposition. The second is higher thermal conductivity of air than argon, which leads to the slower decomposition rates under argon than in air as illustrated in Table 1 and Fig. 2b. The data in the Table show that the temperature at which the samples losses 5 and 10% of its weight is higher under argon than in air for all the samples. The derivation thermogravimetric (DTG) under argon for the samples  $\text{II}_c$  and  $\text{II}_d$  illustrate that the maximum rate of pyrolysis was 21.15 and 20.38% per minute at  $426$  and  $418^\circ\text{C}$ , respectively. These results indicate that the thermal properties were improved with increasing the contents of clay up to 10 wt% organoclay as illustrated in Fig. 2b in comparison with the sample with 0% clay.

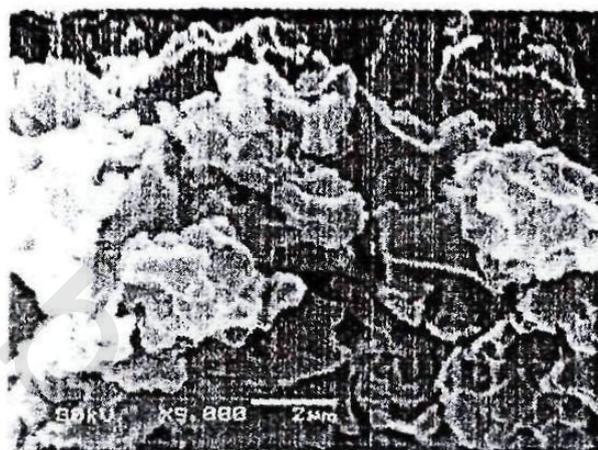
### XRD Analysis

The crystal structure of MMT consists of two-dimensional layers formed by fusing two silica tetrahedral sheets to an edge-shared octahedral sheet of aluminum hydroxide. Stacking of layers of clay particles are held by weak dipolar or van der Waals forces [34]. XRD is a powerful technique to observe the extent of silicate dispersion, ordered or disordered structure in the PU nanocomposites.

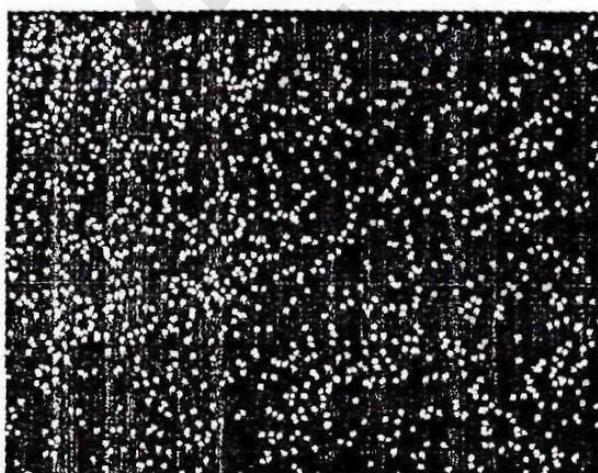
Figure 3 show typical XRD for the  $\text{Na}^+\text{-O-MMT}$ , organoclay I, and PU-organoclay  $\text{II}_{a-f}$ . The 001 reflection has sharp intense peak at  $2\theta = 5.82^\circ$  for I. The  $d_{001}$  spacing was calculated from peak position using Bragg's law  $d = \lambda/(2 \sin \theta)$ . It is clear that the  $d$ -spacing for  $\text{Na}^+\text{-O-MMT}$  ( $2\theta = 7.18^\circ$ ,  $d$ -spacing =  $12.34\text{ \AA}$ ) was increased to  $15.20\text{ \AA}$ , since onium group in tyramine through an ion exchange process exchanges the small inorganic  $\text{Na}^+$  cation. Figure 3 presents XRD pattern for organoclay I and a series  $\text{II}_{a-f}$  of PU clay nanocomposites with different ratios of organoclay. The figure showed the disappearance of the peak corresponding to intercalated organoclay with all the ratios (0, 3, 5, 7, 10, and 20 wt%). This indicated that the clay was homogeneously dispersed and completely exfoliated in the PU matrix. These results confirm that modified MMT with different percentages of organoclay leads to various degree of the dispersion in the polymer matrix. These results are similar to the one described using another structures in PU nanocomposites [35].

### SEM Examination

The examination of the surface of the deposition-molded samples was investigated by scanning electron microscope (SEM). Figures 4a and 5a shows micrographs of the surface at 9000 magnifications for the samples  $\text{II}_b$  and  $\text{II}_c$  as examples. The micrographs showed a homogenous dispersion of MMT in the PU matrix. The micrographs do not show the MMT particles on the micron level. The absence of MMT particles indicates that the agglomerate did not reveal the inorganic domains at the possible magnification. Also, the



(a)



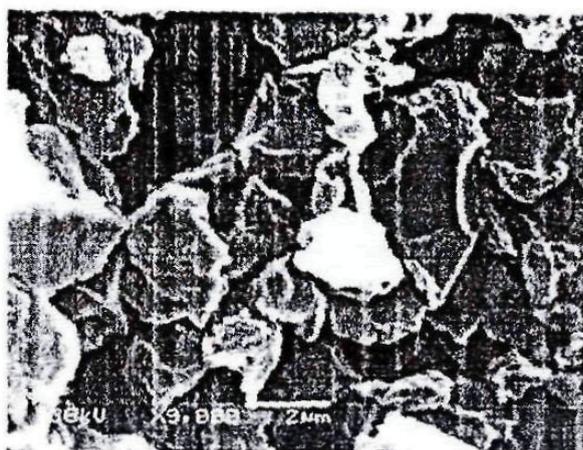
(b)

FIG. 4. (a) SEM micrograph for PU-organoclay nanocomposite II<sub>a</sub>. (b) Elemental mapping for Si of PU-organoclay nanocomposite II<sub>a</sub>.

absence of MMT aggregates was confirmed by an energy dispersion X-ray probe. An image for elemental mapping for Si was shown in Figs. 4b and 5b, in which the white dots represent uniformity dispersion of Si element. The silicon mapping shows that the mineral domains are homogeneously dispersed in the polymer matrix.

#### The Mechanical Behavior

The mechanical behavior of PU-organoclay nanocomposites was investigated by measuring the tensile strength and elongation at  $PK_{max}$  and at break and the results are shown in Table 2 and Fig. 6. The data in the table show increasing tensile strength with increasing clay contents. The tensile strength of II<sub>a</sub>, which contain zero percent clay, was found to be 114 kg/cm<sup>2</sup> at  $PK_{max}$ . These values were increased to 194 kg/cm<sup>2</sup> with 5% organoclay, 215 kg/cm<sup>2</sup> with 10% organoclay, and 221 kg/cm<sup>2</sup> with 20% organoclay. Figure 6a illustrates that the tensile strength highly



(a)



(b)

FIG. 5. (a) SEM micrograph for PU-organoclay nanocomposite II<sub>b</sub>. (b) Elemental mapping for Si of PU-organoclay nanocomposite II<sub>b</sub>.

affected by the clay contents especially with the small ratios of clay. The figure shows that the increasing rate of tensile strength at  $PK_{max}$  is large with small contents (3–5%) of organoclay than with the high contents. Also, the data in tables and figures show that tensile strength at break increased with the same manner as at  $PK_{max}$  with the small quantity of organoclay (3%) followed by gradual decrease with increasing the organoclay quantities. This is due to increasing brittleness and the materials start losing their mechanical properties after the point of  $PK_{max}$ .

In contrast, the data in table illustrate that the elongation at  $PK_{max}$  and at break (Fig. 6b) was decreased with increasing clay contents, due to increasing film strength. It was found that the elongation is nearly the same at  $PK_{max}$  and at break. Also, the figure show the elongation rate is large with small contents (3–5%) of organoclay than with the high contents. These data were compatible with the data obtained in our work on PU-aminolauric acid-montmorillonite nanocomposites [24].

TABLE 2 Mechanical properties data for PU-organoclay nanocomposites films II<sub>n-r</sub>.

Sample	Organoclay I (wt%)	Thickness (μm)	Load cell (MPa)		Tensile strength (kg/cm <sup>2</sup> )		Elongation (%)	
			At PK <sub>max</sub>	At break	At PK <sub>max</sub>	At break	At PK <sub>max</sub>	At break
II <sub>a</sub>	0	430	0.49	0.46	114	107.0	416.5	466.2
II <sub>b</sub>	3	390	0.71	0.70	182.1	179.5	318.8	339.9
II <sub>c</sub>	5	420	0.82	0.75	194.2	177.5	306.2	321.4
II <sub>d</sub>	7	450	0.906	0.757	201.3	168.2	273.4	280.3
II <sub>e</sub>	10	400	0.86	0.63	215.0	157.5	110.2	115.6
II <sub>f</sub>	20	380	0.84	0.55	221.1	144.7	23.2	25.4

\*Calculated from the relation  $\text{Tensile Strength (kg/cm}^2\text{)} = \frac{\text{Force}}{\text{Area (}w \times t\text{)}} = \frac{\text{MPa} \times 10}{\text{cm}^2}$  where  $w$  is width and  $t$  is thickness of the film under test

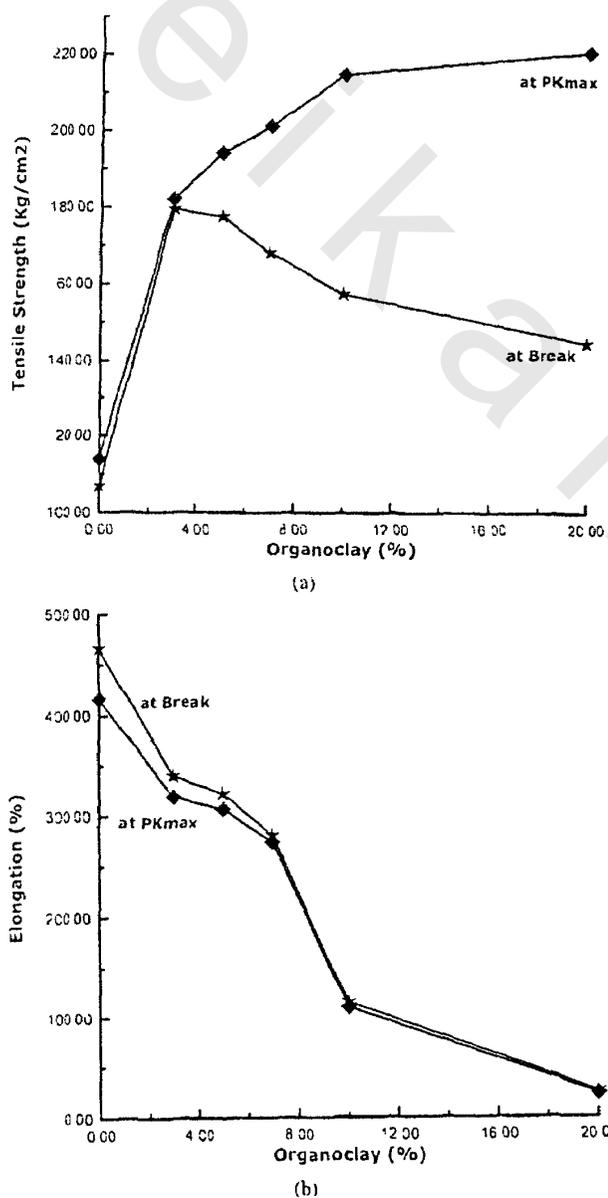


FIG. 6 (a) Tensile strength for PU-tyr-MMT nanocomposites II<sub>n-r</sub> at PK<sub>max</sub> and at break. (b) Elongation for PU-tyr-MMT nanocomposites II<sub>n-r</sub> at PK<sub>max</sub> and at break.

## CONCLUSION

A series of PU-organoclay nanocomposites were synthesized by *in situ* polymerization using diol, diamine, and toluene diisocyanate in the presence of montmorillonite clay modified with tyramine. The infrared (IR) spectroscopy confirms the interaction between the polymer and silicate layers. The swelling studies show that the swelling degrees in the polar solvents such as water and acetone are very small or there is no swelling in the nonpolar solvent such as benzene. These data of swelling reflect that there is improvement in the solvent resistance property of the prepared materials. X-ray analysis showed that the *d*-spacing increased to more than 44 Å, since there is no peak corresponding to *d*<sub>001</sub> due to the homogeneously dispersed and exfoliated clay in the PU matrix. The SEM results confirm the dispersion of nanometer silicate layers in the PU matrix. Also, it was found that the mechanical properties were improved due to the presence of organoclay. The tensile strength increased with increasing the organoclay contents to 20 wt% by the ratio 221% relative to the PU with 0 wt% organoclay. Also, the elongation is decreased by increasing the organoclay contents due to increasing the stiffness of the films.

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# Polyurethane-nanocomposite materials via *in situ* polymerization into organoclay interlayers

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New nanocomposite materials based on polyurethane intercalated into organoclay layers have been synthesized via *in situ* polymerization. The syntheses of polyurethane–organoclay hybrid films were carried out by swelling the organoclay [12-aminododecanoic acid montmorillonite] into different kinds of diols followed by addition of diisocyanate then casting in a film. The homogeneous dispersion of MMT in the polymer matrix is evidenced by scanning electron microscope and x-ray diffraction, which showed the disappearance of the peak characteristic to  $d_{001}$  spacing. It was found that the presence of organoclay has improved the thermal, solvent resistance and mechanical properties. Also, the tensile strength is increased with increasing the organoclay contents to 20% by the ratio 182% related to the PU with 0% organoclay. On the contrary, the elongation has decreased with increasing the organoclay contents. Copyright © 2007 John Wiley & Sons, Ltd.

**KEYWORDS:** polymer composites; polyurethane-clay nanocomposites; polymer-layered silicates nanocomposite; polyurethane-organoclay hybrids; intercalated polymers

## INTRODUCTION

Nanocomposites are a class of materials, which are described as the next great new frontier of materials science. These materials have the solid reinforcing phase with a dimension ranging in the order of nanometers range 1–20 nm.<sup>1</sup> The layered silicates as montmorillonite are the preferred inorganic materials for the design of hybrid polymer nanocomposites. This, because they can be obtained in mineralogically pure form at low cost and occur ubiquitously in nature. Also, they exhibit a very rich intercalation chemistry, which allows them to be chemically modified and made compatible with organic polymers for dispersal on a nanometer length scale.

Since the development of nylon-6/clay nanocomposite by Toyota researchers,<sup>2</sup> extensive studies on polymer/clay nanocomposites have been investigated in order to obtain new organic–inorganic nanocomposites with enhanced properties. The use of clay or organically modified clay as precursors for preparation of nanocomposites has been studied in various types of polymer systems.<sup>3–12</sup>

The polymer-layered silicate nanocomposites with polymer chain intercalating galleries of adjacent silicate layers to form intercalated or exfoliated have attracted much interest. It was found as a significant improvement in the physical and mechanical properties,<sup>13</sup> barrier performance,<sup>14</sup> thermal,<sup>15</sup> flammability resistance,<sup>16</sup> solvent uptake,<sup>17</sup> compared to the

unmodified resin or polymer with inorganic fillers. The polymer-MMT nanocomposites can be prepared by replacing the  $\text{Na}^+$  or  $\text{Ca}^+$  cations of the native clay with a hydrophobic onium ion to form organo-MMT, followed by monomer polymerization (*in situ*)<sup>18</sup> or by direct intercalation of a preformed polymer into the organo-silicate materials.<sup>19</sup>

Polyurethanes (PUs) elastomer is one of the most interesting classes of synthetic elastomers that have unique properties. PUs elastomers are a family of segmented polymers with soft segments derived from polyols and hard segments from isocyanates and chain extenders. PUs have the advantages, such as the best abrasion resistance, outstanding oil resistance, and excellent low-temperature flexibility. They also exhibit the widest variety of hardness and elastic moduli that just fill in the gap between plastics and rubbers. However, they show poor thermal stability and barrier property, which can be modified by clay.<sup>20</sup> They are very versatile polymer materials and their properties can be modified by dispersing inorganic fillers in polyurethane matrix,<sup>21</sup> to meet the demands of modern technologies such as coatings; adhesives; reaction injection molding fibers, foams, rubbers, thermoplastic elastomers, and composites.

Recently, much attention has been focused on the improved performance properties on PU-clay nanocomposites compared to the pristine PU polymer.<sup>22–30</sup> The present work discusses the synthesis of PU-organoclay nanocomposites with improved physical and mechanical properties.

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## EXPERIMENTAL PART

## Materials

Sodium montmorillonite clay ( $\text{Na}^+\text{-O-MMT}$ ), with cation exchange capacity (CEC) of 119 mEq/100 g, was supplied by Coniine Industry Co (Japan) under trade name Kunipia-F. Styrene was supplied from Aldrich and used after purification by washing with 1 M NaOH then dried over anhydrous sodium sulfate followed by distillation under vacuum. Maleic Anhydride (from Merck-Schuchardt, Germany); 12-Aminododecanoic Acid, from Aldrich; tetrahydrofuran (THF) (from Fluka) and ethanol (from Adwic, Egypt) were used as obtained without further purification. Toluene-2,4-diisocyanate (TDI) was provided by Fluka, Germany, and having 99.5% of purity for 2,4-isomer with an m.p. 21°C, was used as received. Poly(ethylene glycol), PEG-400, with average molecular weight 400 was obtained from WINLAB laboratory chemicals, UK, was used dried under vacuum at 80°C for 6 hr just before use. Poly(ethylene glycol), PEG-1540, with average molecular weight 1540 was purchase from Cock-Light laboratories Ltd, England, was used dried under vacuum at 80°C for 6 hr just before use. Dimethylformamide (DMF) from Adwic (Egypt) was used after distillation and drying over A4 molecular sieve.

## Preparation of 12-aminododecanoic acid-montmorillonite organoclay I

A 2.73 g of 12-Aminododecanoic acid (11.9 mEq.) was dissolved in 500 ml of 0.02 N HCl and added portionwise to the swelled suspension of 10 g ( $\approx 11.9$  mEq) montmorillonite in distilled water with vigorous stirring at 60°C. The resultant suspension was stirred for overnight. The suspension was allowed to stand for a few hours followed by filtration through sintered glass (G4) and washed with distilled water until no white precipitate was detected on addition of  $\text{AgNO}_3$  solution to the filtrate. The product was dried at  $\sim 50^\circ\text{C}$  under vacuum to give 12.17 g of MMT-12-Aminododecanoic intercalate I. The characteristic properties were investigated by infrared (IR), thermogravimetric analysis (TGA), calcination; swelling data and x-ray diffraction (XRD).

## Preparation of poly(styrene-co-maleic anhydride), PSM, II

A 10 g of pure styrene (96.2 mmol) and 9.42 g of maleic anhydride (96.2 mmol) were mixed and dissolved in 3 ml of tetrahydrofuran with stirring then 0.2 g of benzoyl peroxide was added as initiator. The solution mixture was heated at 80°C with stirring for 2 hr. The product was dissolved in 1,4-dioxane and precipitated in ethanol. The white polymer was filtered, washed with ethanol and finally dried under reduced pressure at 50°C for 12 hr to give 18.7 g of copolymer II.

IR (KBr disc):  $\nu = 3447$  (C-H aromatic, stretching), 2938  $\text{CH}_2$  aliphatic, stretching), 1777, 1725 (C=O), 1449, 1396 ( $\text{CH}_2$  bending), 1219 (C-O anhydride), 953, 922, 762, 703  $\text{cm}^{-1}$  (C-H aromatic, bending, out of plane)

Synthesis of PU-PSM-12-aminododecanoic-MMT nanocomposites III<sub>a-e</sub>

A mixture of 20 g (12.987 mmol) of dry PEG-1540, 10.39 g (25.975 mmol) of PEG-400 and 3.38 g (10% by weight) of PSM II was dissolved in 33.77 g dry DMF to give solution (50% w/w of monomers/solvent).

A 0.2392 g of organoclay I was mixed with 8.9 g of the previous mixture (contains 4 g PEG-1540/PEG-400 with mole ratio 1:2) and stirred for 8 hr until the organoclay become completely swelled. To the mixture a 0.6 g (3.448 mmol) of TDI was added dropwise at room temperature with vigorous stirring. The stirring was continued for 8 hr to give nanocomposite by *in situ* polymerization technique with 5 wt % organoclay. The PU-clay nanocomposite film III<sub>c</sub> was formed by casting the free air (gases) solution mixture in a mold and then removing the solvent under reduced pressure 80°C for 12 hr.

The other samples III<sub>a-e</sub> were prepared by the same procedure and conditions with different amount (0, 1, 10% and 20%) of modified clay I and the same diols, and diisocyanate to give elastic films

## Analytical procedures

Infrared spectra (IR) were carried out on a Perkin-Elmer 1430 Ratio-recording infrared spectrophotometer using the potassium bromide disc technique in the wave number range of 4000–400  $\text{cm}^{-1}$ .

Thermogravimetric analyses (TGA) were determined with Rigaku Thermo Plus 2 TG-DTA TG8120. The heating rate was 5–10°C/min. under air and argon atmosphere in the temperature range  $\sim 30$ –900°C.

X-ray diffraction (XRD) was observed from an X-ray diffractometer, Rigaku RINT2000 equipped with a Ni-filtered Cu-K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at scanning rate of 0.3 degree per minute.

Morphology of the composite was examined by a Joel JXA-840 Scanning Electron Microscopy (SEM) equipped with an energy dispersive x-ray detector to examine the morphology and particle size of MMT in the polymer-MMT composites. Specimen was deposited on double-sided scotch tape and examined at their surface.

Mechanical properties of the samples were tested with an Instron mechanical tester [model DL-35/ LR5K plus (LLOYD)] at crosshead speed of 500  $\text{mm min}^{-1}$ . The I-shaped specimens were prepared with 5 cm ( $5 \times 10^{-2}$  m) in length, 1 cm ( $1 \times 10^{-2}$  m) in width, and 330–450  $\mu\text{m}$  ( $0.33$ – $0.45 \times 10^{-3}$  m) in thickness. For each datum point, five samples were tested, and the average value was recorded.

Calcination Measurements: A definite weight of the sample was introduced into a porcelain crucible and dried in an electric oven at 120°C overnight, then introduced into an ignition oven and the temperature was increased to 1000 C and adjusted at this temperature for 5 hr. The loading of each sample expressed as the weight loss by ignition per 100 g of the dry sample. The data of all prepared samples are listed in Table 1.

The swelling degree was determined by taking a definite weight (about 0.15 g) of the dry sample and introduced into a small sintered glass and allowed to imbibe in different solvents (distilled water, benzene and acetone) for 24 hr. The

Table 1. Swelling and thermal analyses data of PU(SMA/LA)-MMT nanocomposites (III<sub>a-e</sub>)

Sample	I (%)	Swelling <sup>1</sup>					TGA analysis data						Calcination <sup>2</sup>
		Water (%)	Acetone (%)	Benz. (%)	Under Air		Under Argon		Clay contents (%)	Organic contents (%)			
					Temp. at d-5%	Temp. at d-10%	Temp. at d-5%	Temp. at d-10%			Chair Yield (%)	Chair Yield (%)	
III <sub>a</sub>	00	0.93	0.67	0.15	268	286	286	298	286	3.21	9.10	0.00	100.00
III <sub>b</sub>	1	0.71	0.62	Nil	—	—	294	311	294	—	13.09	0.76	99.24
III <sub>c</sub>	5	1.25	0.57	Nil	271	290	290	309	290	8.40	15.55	3.80	96.20
III <sub>d</sub>	10	1.46	0.5	Nil	292	312	296	315	296	11.37	21.75	7.30	92.70
III <sub>e</sub>	20	1.68	0.24	Nil	268	287	280	300	280	13.95	22.25	13.81	96.19

<sup>1</sup>Calculated by (adsorbed solvent (g) × 100/dry sample (g)).

<sup>2</sup>At 1000°C for 8 hr.

excess solvent was removed by gentle centrifugation. The swelled sample was weighed and re-suspended in the solvent. This procedure was repeated until obtaining on a constant weight for the swelled sample. The swelling degree of each sample is expressed as the amount of sorbed solvent per 100 g of dry sample.

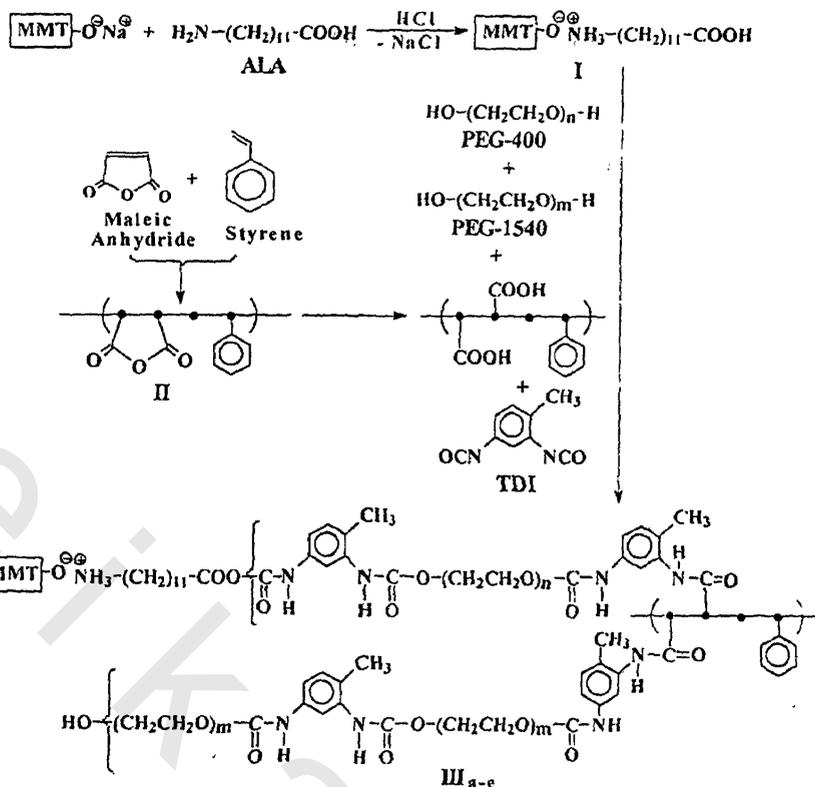
## RESULTS AND DISCUSSION

### Synthesis and structure

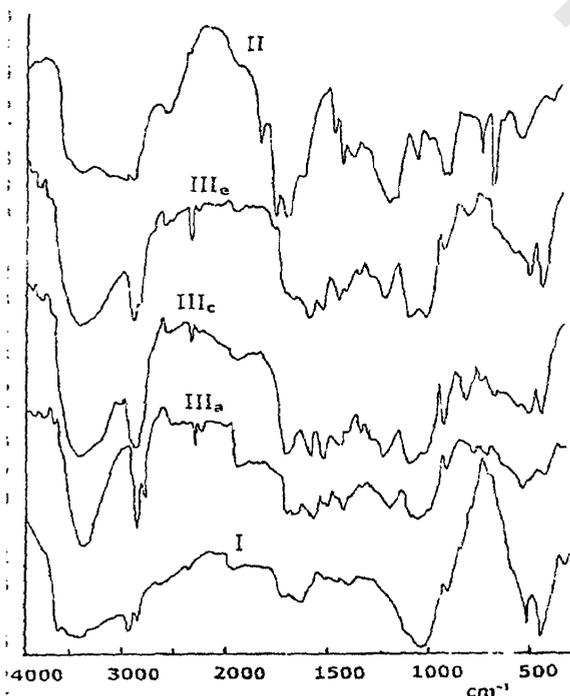
The synthesis of new organic-inorganic nanocomposite materials was achieved by the intercalation of polyurethane onto functionalized montmorillonite clay through *in situ* condensation polymerization technique. The synthesis was carried out through two steps as illustrated in Scheme 1: the first step is the ion exchange process between sodium cation in MMT and ammonium salt of 12-aminododecanoic acid which to organophilic-MMT I. This organophilic-MMT contains carboxylic group to react with diisocyanate and hence promote the interaction of organic materials used in formation of PU and improve the particle-matrix interactions. The calcination indicates the functionalization was achieved with a high degree of conversion (86%). The second step is the solvation of the organoclay with the diols and a solution of preformed poly(styrene-co-maleic anhydride) PSM. This solvation was followed by the addition of the TDI, then casted in films to produce the intercalated polyurethanes III<sub>a-e</sub> films with different organoclay contents. The structural composition and properties of the product materials was determined by several analytical techniques.

PU-organoclay samples III<sub>a-e</sub> showed very small swelling in the polar solvents (water and acetone), but they showed no swelling in nonpolar solvents (benzene). The affinity to water shows very small increase with increasing the ratio of clay, which may be attributed to the higher hydrophilic characters of clay. The swelling degree in water (0.7–1.7%), acetone (0.2–0.7%) and benzene (0.0–0.15%) illustrates that there are improvement in the solvent resistance property of the prepared materials.

The IR spectra of the samples were illustrated in Figure 1. The spectra of modified clay I show that the NH stretch band at 3430 cm<sup>-1</sup> and NH bend band at 1631 cm<sup>-1</sup> are shifted quite substantially to regions associated with <sup>-</sup>NH<sub>3</sub> vibration which facilitate the ion exchange with MMT. A characteristic band appears at 1040, 522, and 460 cm<sup>-1</sup> for Si-O; 2928, 2852 cm<sup>-1</sup> for CH aliphatic and at 3608 cm<sup>-1</sup> for acidic OH group for I. The quaternary ammonium group (<sup>-</sup>N<sup>+</sup>) shows a characteristic band at 1499 cm<sup>-1</sup>. The free acidic OH band at 3608 cm<sup>-1</sup> in organoclay I is disappeared in nanocomposites indicating the strong interaction is occurred between OH group in organoclay and the isocyanate forming the isocyanate linkage. Comparing the <sup>+</sup>NH<sub>3</sub> band at 1631 cm<sup>-1</sup> in organoclay with nanocomposite it is clear that this band is shifted to higher wavelength at 1721 cm<sup>-1</sup> indicating that an interaction occurred between organoclay and the polymer. The spectra of polyurethane III<sub>a</sub> shows the absorbance appeared at 1728 cm<sup>-1</sup> that was assigned to hydrogen-bonded urethane carbonyl (C=O), 1418 cm<sup>-1</sup> to a secondary urethane amide (C-NH). The spectra of the



**Scheme 1.** Preparation of modified clay I, poly(styrene-co-maleic anhydride) PSM II and PU-modified clay nanocomposites III<sub>a-e</sub>.



**Figure 1.** IR spectra for organoclay I, copolymer II and PU-organoclay III<sub>a,e</sub>.

synthesized PU/modified clay show III<sub>c</sub> peaks at  $1719\text{ cm}^{-1}$  that caused by the stretching of urethane carbonyl group ( $\text{C}=\text{O}$ ), and  $2921$  and  $2862\text{ cm}^{-1}$  that attributed to the asymmetric and symmetric C-H stretching vibration. The peak at  $3425\text{ cm}^{-1}$  resulted from the N-H group in H-bonding. The main features of various bond vibration and H-bonding of these PU-clay nanocomposites are remained near as in the pure PU. These results confirm that there were no major changes in the chemical structural of PU with the dispersion of organoclay in the polymer matrix.

### Thermal analysis

Thermal properties of polyurethane-organoclay compounds were determined by TGA under argon atmosphere, in air and calcination. The data are summarized and listed in Table 1. The data TGA show the weight loss encountered during heating the PU-clay materials in the range 86%–97% in air and 91%–78% under argon atmosphere. While, the calcination measurements show that the weight loss ranged from 100% to 86%. It is clearly that the weight loss evident in the calcination measurements is nearly compatible with the TGA data.

The thermograms of the samples III<sub>a-e</sub> were illustrated Figure 2, which indicate that the thermal decomposition takes place in two stages. The first stage is the sharp and major, which involve the thermal decomposition of the polymers present on the surfaces of the layers of the clay. The

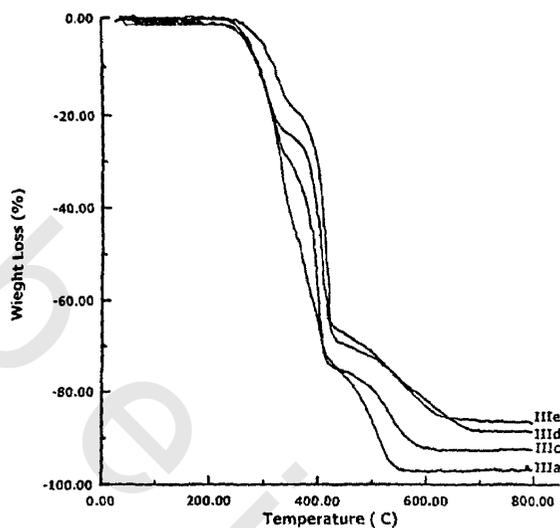


Figure 2. TGA thermograms for the PU-organoclay samples III<sub>a-e</sub> in air.

decomposition temperature in this stage was started at  $\approx 270^{\circ}\text{C}$  and take place to  $\approx 400^{\circ}\text{C}$ , which corresponding the weight loss ranged from  $\approx 65\%$  to  $\approx 75\%$ . In this stage, there is no order can be mentioned between the samples since the difference is small. The *second stage* is a broad, in which the weight losses ranging from  $\approx 20\%$  to  $\approx 25\%$  in the temperature range  $\approx 400^{\circ}\text{C}$  to  $\approx 650^{\circ}\text{C}$ . In this stage, the samples displayed higher thermal resistance than pure polymers. This stage is attributed to the further decomposition of the rest intercalated polymers present in the interlayer of the clay, or to the losses of OH groups of the clay mineral and the crystallographic structure collapsed or to the losses of some salts in the interlayer of the clay.<sup>4</sup> The thermal decomposition of samples III<sub>a-e</sub> under argon atmosphere, Figure 3, is occurred in one step and sharp. The decom-

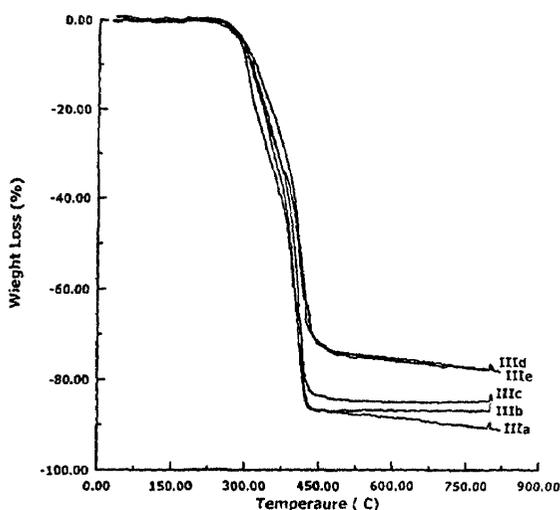


Figure 3. TGA thermograms for the PU-organoclay samples III<sub>a-e</sub> under argon atmosphere.

position temperature in this step started from  $\approx 290^{\circ}\text{C}$  to  $\approx 425^{\circ}\text{C}$  due to the thermal decomposition of the polymers present on the surfaces and the intercalated in the layers of the clay. This step followed by a gradually and very smooth and very low weight loss, which may be due to the losses of OH groups of the clay mineral and the crystallographic structure collapsed, or to the further decomposition of some salts in the interlayer of the clay.<sup>4</sup> The difference in the TGA analysis under argon than in air can be explained for two reasons: (a) the presence of oxygen in air help in the decomposition fast; (b) the higher thermal conductivity in air than in argon leads to the slower decomposition rates under argon than in air as illustrated in Table 1. The temperature at which the samples losses 5% and 10% of its weight is higher under argon than in air for all the samples. These results indicate that the thermal property was improved with increasing the contents of clay in air and under argon

**XRD analysis**

XRD is powerful technique to observe the extent of silicate dispersion, ordered or disordered structure in the polyurethane nanocomposites. Since, the crystal structure of MMT consists of two-dimensional layers formed by fusing two silica tetrahedral sheets to an edge-shared octahedral sheet of aluminum hydroxide. Stacking of layers of clay particles are held by weak dipolar or Vander Waals forces<sup>31</sup>. Figure 4 shows typical XRD for the organoclay I and PU-organoclay III<sub>c-d</sub>. The  $d_{001}$  spacing was calculated from peak positions using Bragg's law  $d = \lambda / (2 \sin \theta)$ . The d-spacing for Na-MMT is increased from  $12.34 \text{ \AA}$  ( $2\theta = 7.18^{\circ}$ ) to  $18.24 \text{ \AA}$  ( $2\theta = 4.85^{\circ}$ ) since the small inorganic  $\text{Na}^+$  cation is exchanged by the ammonium group

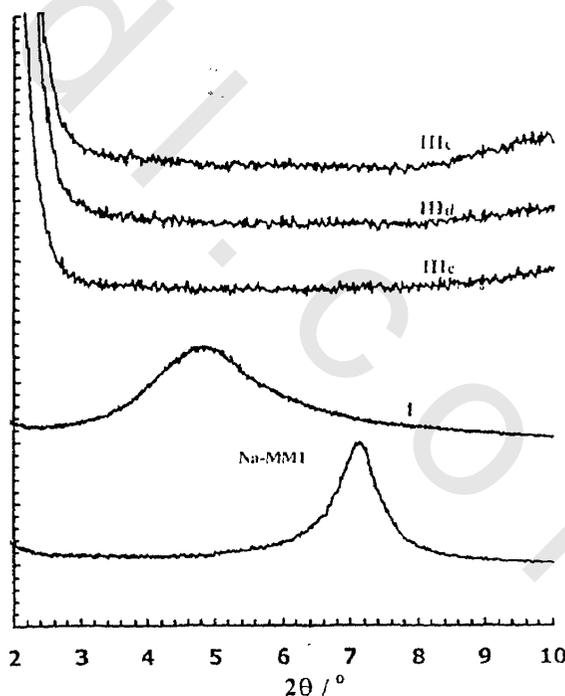


Figure 4. XRD pattern for Na-MMT, organoclay I and PU-organoclay samples III<sub>c-e</sub>.

of 12-aminododecanoic acid through an ion exchange process. Figure 3, also presents a series of XRD pattern corresponding to polyurethane-clay nanocomposites III<sub>c,d</sub> with ratios 5%, 10%, and 20% of organoclay I. This figure showed the disappearance of the peak corresponding to intercalated organoclay with all the ratios, which corroborate that the clay was homogeneous dispersion and completely exfoliated in the matrix of polyurethanes. Also, these results confirm that the different percentage of organoclay leads to

high degree of the dispersion in the polymer matrix, as described by another author.<sup>32</sup>

#### SEM examination

The microstructure of the nanocomposites was examined by studying the change in the morphology of the MMT with scanning electron microscope (SEM). The examination of the surface of the deposited samples did not reveal the inorganic domains at the possible magnification. Figures 5a and

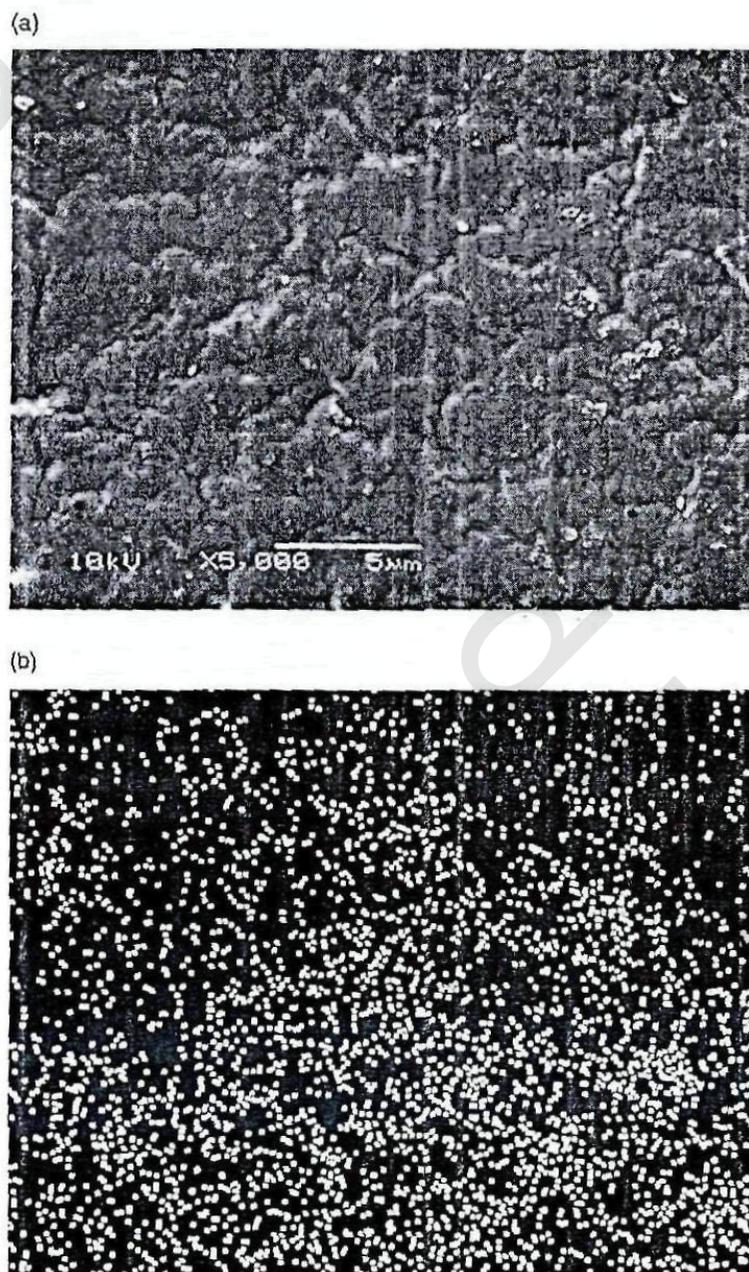


Figure 5. a: SEM image of PU-organoclay sample III<sub>c</sub>. b: Elemental mapping for SI of PU-organoclay nanocomposite III<sub>c</sub>.

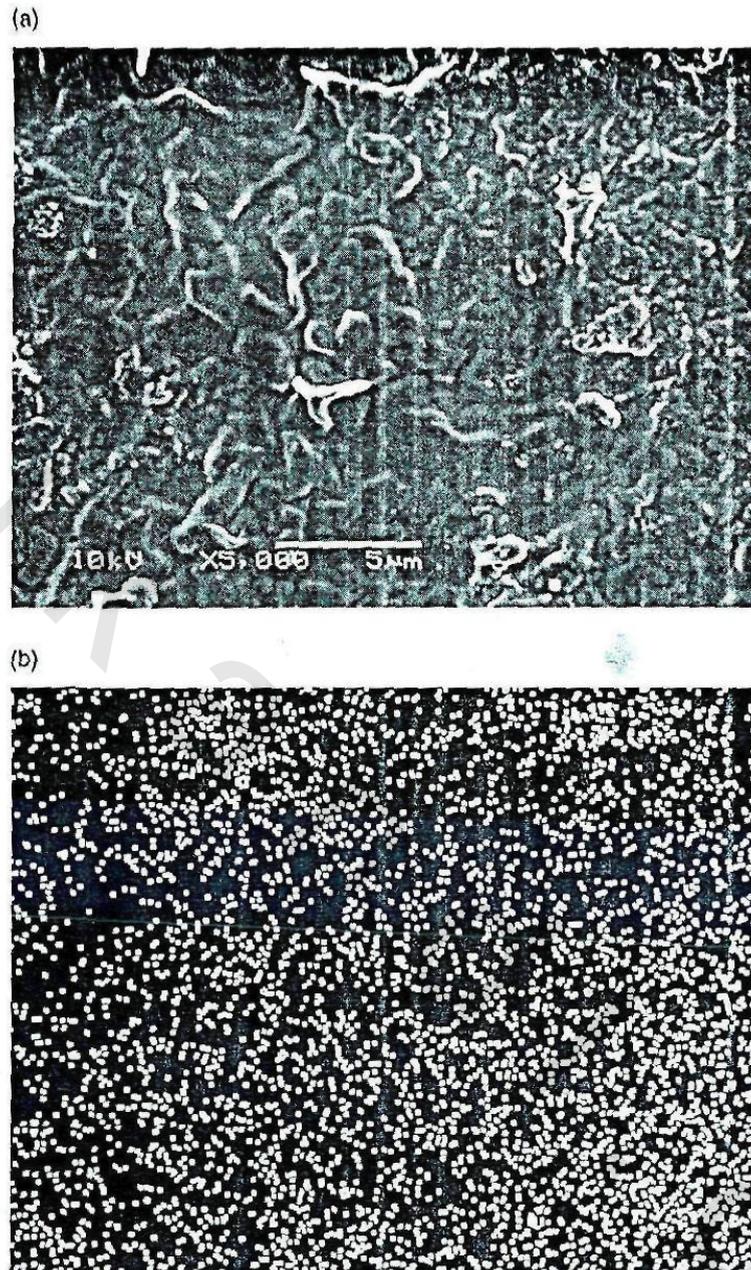


Figure 6. a: SEM image of PU-organoclay sample III<sub>c</sub>. b: Elemental mapping for Si of PU-organoclay nanocomposite III<sub>c</sub>.

Figure 6a show the micrograph of the samples III<sub>c</sub> at 5000 magnifications, which indicates that, the ionic bonding leads to adherence between the polymer and clay, and there is no mineral domains could be seen. This indicates that the agglomerates of mineral domains are broken down to the elementary particles and are homogeneously dispersed in the polymer matrix to produce intercalated and/or exfoliated nanocomposites. Also, the absence of MMT aggregates was confirmed by an energy dispersion x-ray

probe. An image for elemental mapping for Silicon (Si) was shown in Figures 5b and 6b, in which the white dots represent uniformity dispersion of Si element. The Silicon mapping shows that the mineral domains are homogeneously dispersed in the polymer matrix.

#### The mechanical behavior

The mechanical behavior of PU-organoclay nanocomposites was investigated by measuring the tensile strength and

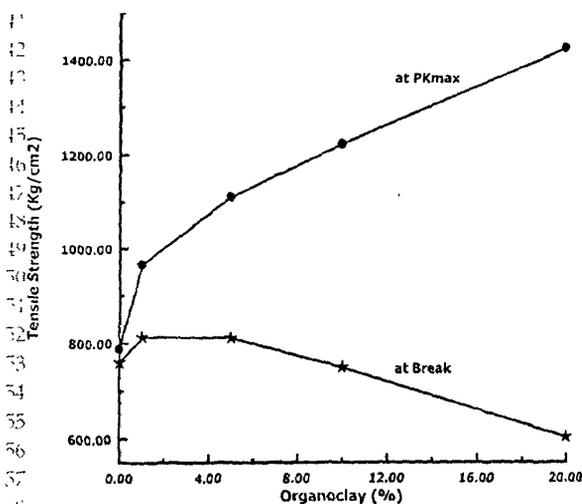
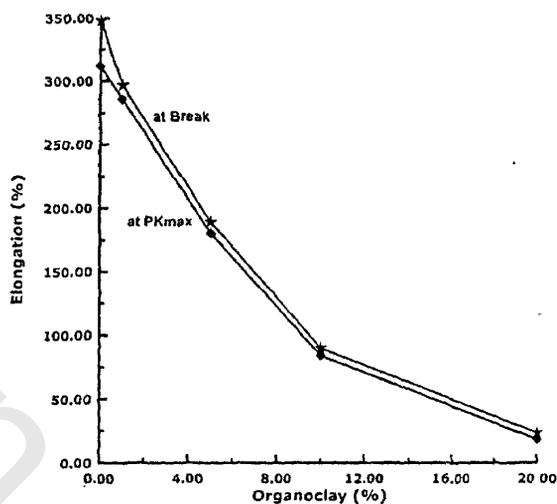
**Table 2.** Mechanical properties data for PU-PSM-ALA-MMT nanocomposites films IV<sub>a-e</sub>

Sample	Organoclay Contents (%)	Film Thickness ( $\mu\text{m}$ )	Load cell (M. Pa)		Tensile strength ( $\text{Kg}/\text{cm}^2$ ) <sup>a</sup>		Elongation (%)	
			At PK <sub>max</sub>	At break	At PK <sub>max</sub>	At break	At PK <sub>max</sub>	At break
III <sub>a</sub>	00	450	3.54	3.42	787	760	311.8	348.0
III <sub>b</sub>	1	380	3.67	3.09	966	813	285.6	296.5
III <sub>c</sub>	5	360	4.00	2.92	1111	811	180.0	189.0
III <sub>d</sub>	10	440	5.38	3.30	1223	750	84.1	90.0
III <sub>e</sub>	20	330	4.71	1.99	1427	603	18.2	23.5

<sup>a</sup> Calculated from the relation Tensile Strength ( $\text{Kg}/\text{cm}^2$ ) =  $\frac{\text{Force}}{\text{Area}(wt)}$  =  $\frac{M \cdot P_{\text{max}} \cdot 10}{\text{cm}^2}$   
 Where  $w$  is width and  $t$  is thickness of the film under test.

elongation at PK<sub>max</sub> and break as illustrated in Table 2. The data show increasing the tensile strength with increasing the clay contents. Since the tensile strength of III<sub>a</sub>, (787  $\text{Kg}/\text{cm}^2$  at PK<sub>max</sub>) was increased to 1111  $\text{Kg}/\text{cm}^2$  for III<sub>c</sub> with 5% organoclay; and to 1223  $\text{Kg}/\text{cm}^2$  for III<sub>d</sub> with 10% organoclay; and to 1427  $\text{Kg}/\text{cm}^2$  for III<sub>e</sub> with 20% organoclay. Figure 7 shows that the tensile strength is highly affected by the contents of the clay, the rate of tensile strength at PK<sub>max</sub> is largely increased at the small contents (1–5%) of organoclay than at the higher contents. Thus, the tensile strength at break is increased at small quantity of organoclay ( $\approx 5\%$ ) followed by gradual decrease with increasing the organoclay quantities. This may be due to increasing the hardness and the materials start to loose the mechanical properties after the points of PK<sub>max</sub>.

The data of elongation in Table 2 illustrate decreasing the elongation at PK<sub>max</sub> and at break with increasing the clay contents, due to increasing the film strength. Figure 8 shows also that the decreasing rate of elongation is higher with small contents (1–5%) than with the high contents of organoclay. These results are similar to the data obtained in the PU-tyramine-clay nanocomposites,<sup>23</sup> which indicate that the tensile strength of PU/SMA/ALA-MMT nanocomposites is higher 6–7 times than the corresponding to PU/Tyr-MMT.

**Figure 7.** Tensile strength for PU-SMA-ALA-MMT samples.**Figure 8.** Elongation for PU-SMA-ALA-MMT samples.

## CONCLUSIONS

A series of polyurethane-clay nanocomposites were prepared by *in situ* polymerization using different kinds of diols and toluene diisocyanate in the presence of montmorillonite clay modified with 12-aminododecanoic acid. The infrared (IR) spectroscopy confirms the interaction between the polymer and silicate layers. X-ray analysis showed that the d-spacing was increased to exfoliated layers, since there are no peaks corresponding to  $d_{001}$ . The morphology of the prepared samples was investigated by SEM, which confirms the dispersion of nanometer silicate layers in the polyurethane matrix. It was found that the presence of organoclay leads to improvement in the mechanical properties, since the tensile strength is increased by the ratio 181% with increasing the organoclay contents to 20%. The elongation was also decreased with increasing the organoclay contents, which is attributed to increasing the stiffness of the film samples. The swelling measurements show that there are improvements in the solvent resistance of the prepared materials. The tensile strength is higher 6–7 times of PU/SMA/ALA-MMT nanocomposites more than the corresponding PU/Tyr-MMT.<sup>21</sup>

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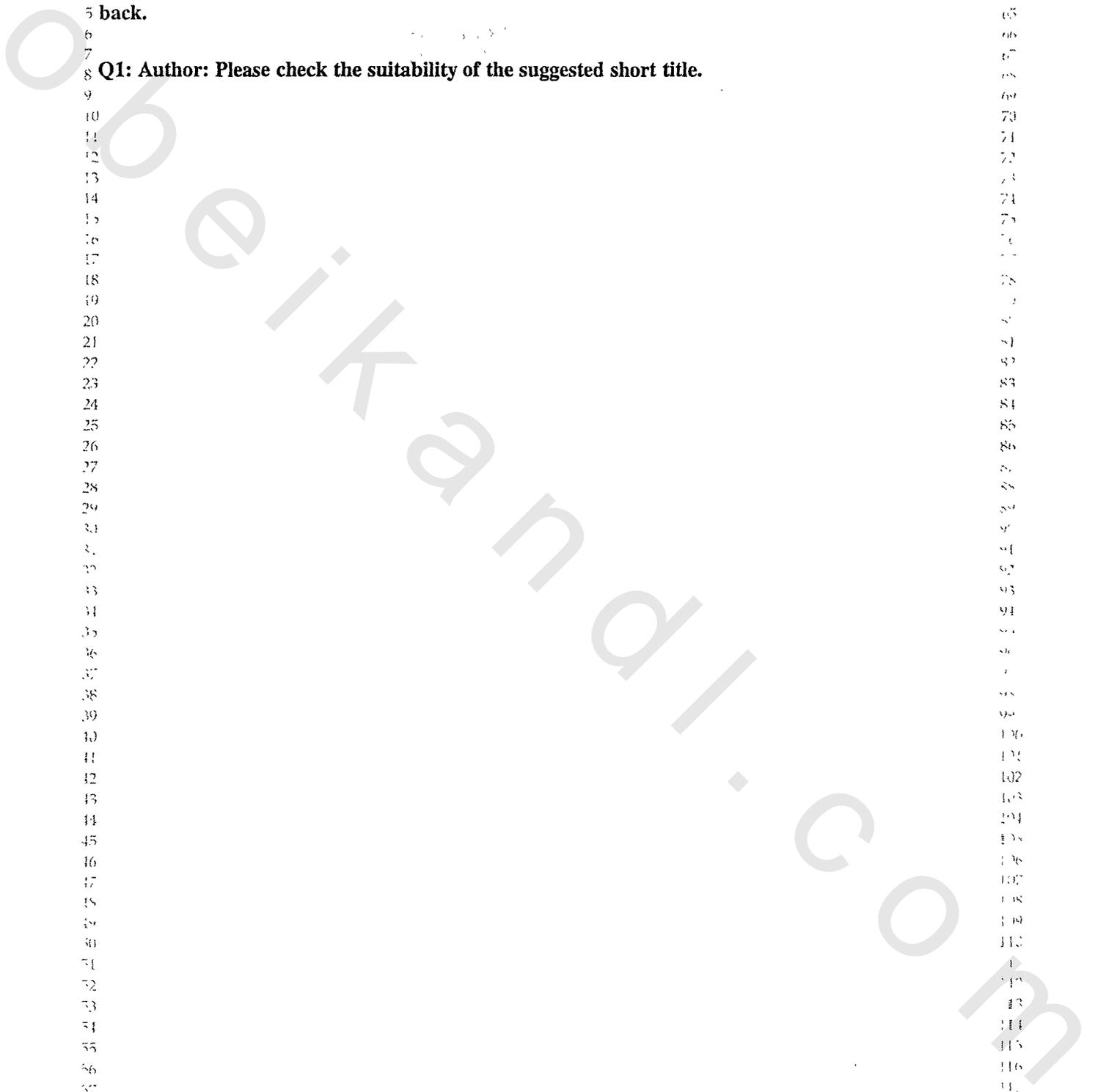
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جامعة طنطا  
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# دراسات علي بعض المتراكبات النانومترية المستحدثة للبولي يوريثان مع الطفلة

## رسالة

كجزء متمم للحصول على درجة الماجستير فى العلوم  
(فى الكيمياء)

مقدمة من

**ناصر حلمى صالح شلبى**

بكالوريوس علوم- كيمياء

جامعة القاهرة

١٩٨٨

تحت إشراف

الأستاذ الدكتور / أحمد محمد إسماعيل عكيه

الدكتور / أحمد فتح الله رحاب

الدكتور / طارق عبد الرحمن عجاج

٢٠٠٧ م

## بِسْمِ اللّٰهِ الرَّحْمٰنِ الرَّحِیْمِ

رب أوزعني أن أشكر نعمتك التي أنعمت  
عليّ وعلى والديّ  
و أن أعمل صالحاً ترضاه وأدخلني برحمتك في عبادك الصالحين  
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# الملخص العربي

## ملخص الرسالة

تحتوى هذه الرسالة على ثلاث اجزاء اساسية هي المقدمة و التجارب العملية و النتائج المناقشة. هذا بالاضافة الى ملخص الرسالة باللغة العربية والانجليزية والاستنتاجات و المراجع التي تم الاستعانة بها فى كتابة الرسالة.

### الجزء الأول:

يشتمل على مقدمة عن كيمياء و تركيب و استخدامات البولى يوريثان، و يشتمل أيضا على مكونات و انواع المتراكبات و بعض استخدامات متراكبات البولىمير / طفله النانومترية و على المتراكبات النانومترية للبولى يوريثان / طفلة.

### الجزء الثانى:

ويشتمل على وصف تفصيلى لكل من المواد المستخدمة و اجهزة القياس التي استخدمت و على طريقة التحضير للمتراكبات الوارده فى الرسالة.

### الجزء الثالث:

ويشتمل على استعراض و مناقشة النتائج التي تم الحصول عليها. حيث تم التعرف على المواد المحضرة و خواصها التركيبية و الحرارية و الميكانيكية بالطرق التحليلية المختلفة. وقد أثبتت التحاليل بالأشعة تحت الحمراء تداخل المعدلات السطحية المختلفة و البولىميرات بين طبقات

الطفلة. كما أوضحت دراسة التحليل الحراري الوزني أن المتراكبات المحضرة لها ثبات حراري أعلى من البوليمرات الغير متراكبة مع الطفلة. كذلك أوضحت دراسة خاصة تشرب المذيبات (الانتفاخ) أن المتراكبات المحضرة لها مقاومة واضحة لهذه المذيبات.

أما التركيب البنائي لتلك المتراكبات فقد تم التحقق منه بواسطة الأشعة السينية التي أوضحت أنه قد حدث تفكك كامل لطبقات الطفلة في البوليمر لتعطي متراكبات نانومترية حيث زادت المسافات البينية بين الطبقات الى أكبر من ٤٤ أنجستروم. كما أوضحت دراسة الشكل الظاهري للمتراكبات بواسطة الميكروسكوب الاليكتروني الماسح أن الطفلة منتشرة بتجانس في مادة البوليمر، حيث أنه لا تظهر التجمعات الطبقيه للطفلة واثبتت ذلك صورة عنصر السيليكون والتي توضح توزيع متجانس لهذا العنصر وهو المكون الأساسي للطفلة. و تبين تفكك كامل لطبقات الطفلة في حالة احتواء المتراكب علي ٣% من الطفلة المعدلة و تفكك جزئي في حالة احتوائه علي ٧% او ١٠%.

هذا وقد تمت دراسة الخواص الميكانيكية والتي أوضحت تحسن لوجود الطفلة المعدلة، حيث زادت قوة الشد بمقدار ١٧٧ - ١٩٤ % للمتراكبات المحتوية علي ٢٠% طفلة معدلة مقارنة بالبولي يوريثان الذي لا يحتوي علي الطفلة المعدلة. هذا وقد دلت النتائج علي زيادة قوة الشد للمتراكبات المحتوية على الطفلة المعدلة بحامض الأمينولويوريك في وجود البوليمر الثنائي المكون من (ستيرين-ماليك أنهايديرين) بمقدار ٦-٧

مرات عن المتراكبات المحتوية على الطفلة المعدلة بالتيرامين أو المعدلة بمركب داي ميثيل اوكتاديسيل-(٤- فينيل بنزيل) أمونيوم كلوريد.

وأما نسبة الاستطالة فقد وجد أنها قلت مع زيادة نسبة الطفلة المعدلة بالتيرامين أو حامض الأمينولويوريك. أما في حالة الطفلة المعدلة بمركب داي ميثيل اوكتاديسيل-(٤- فينيل بنزيل) أمونيوم كلوريد فقد لوحظ زيادة الاستطالة مع زيادة نسبة الطفلة المعدلة.

الى جانب ما سبق يوجد ملخص للاستنتاجات التي تم التوصل اليها من هذه الدراسة واستعراض للمراجع التي تم الاستعانة بها.