

II. Experimental Part

1. Materials:

Na^+ montmorillonite clay (MMT) with cation exchange capacity (CEC) of 119 mEq/100 g was supplied by Kunimine industry Co Japan under trade name Kunipia-F. *Styrene* (St) was supplied from Aldrich and used after purification by washing with 1M NaOH to remove the inhibitors followed by drying over anhydrous sodium sulphate.

4-Vinylbenzylchloride was used as received from Fluka. *2-Hydroxyethyl-methacrylate* (HEMA) and *benzoylperoxide* (BPO) were obtained from Fluka (Switzerland) and were used as received. *N,N-dimethyl-n-octadecylamine*, *hydroquinone*, and 12-aminolauric acid were supplied from Aldrich and were used as received. *Maleic anhydride* was obtained from Merck-Schuchardt, Germany. *Tyramine hydrochloride* (Tyr) was used as obtained from Tokyo kasei. *Toluene-2,4-diisocyanate* (TDI) of 99.5% purity was provided by Fluka, Germany, with m.p. 21 °C, and was used as received. *Jeffamine D-400* [poly(oxypropylene) diamine] was supplied from Huntsman, Denmark. *Poly(ethylene glycol)* (PEG-1540) with average molecular weight 1540 was purchase from Kock-Light laboratories Ltd, UK. *Poly(ethylene glycol)l* (PEG-400) with average molecular weight 400 was obtained from WINLAB laboratory chemicals, UK. *Poly(ethylene glycol)* (PEG-1000) with average molecular weight 1000 was obtained from Tokyo-Kasei, Japan. Diols and diamine were dried in vacuum oven for 8 h just before use. *Dimethylformamide* (DMF) from Adwic (Egypt) was used after distillation and drying over A4 molecular sieve. *Ethyl acetate*, *Methanol* and *Ethanol* were used as obtained from ADWIC, Egypt without further purification. *Tetrahydrofuran* (THF) was obtained from Fluka and used without further purification.

2. Preparation of Organoclays:

2.1. Preparation of Tyramine- Montmorillonite Intercalate (I_a):

The sodium-montmorillonite (10g, ≈11.9 mEq) was dispersed in 350 ml distilled water with slow stirring overnight. Tyramine hydrochloride (2.05g, 11.82 mEq) dissolved in 50 ml distilled water was added slowly to clay suspension with vigorous stirring at 60°C. The stirring was continued for 24 h. The suspension was allowed to stand for a few hours followed by filtration through sintered glass (G4). The precipitate was repeatedly washed by distilled water till no white precipitate of chloride ions was detected on addition of AgNO₃ solution to the filtrate. The product was dried at ~50°C under vacuum to yield 11.2 g of Tyramine-MMT (Tyr-MMT) intercalate. The product was retreated with tyramine hydrochloride by dispersion of Tyr-MMT in 400 ml DMF/H₂O (1:1) followed by addition 1 g of tyramine hydrochloride dissolved in 10 ml distilled water. The procedure was repeated as previously mentioned to give 11.39 g of Tyr-MMT intercalate (I_a).

The characteristic properties of Tyr-MMT were investigated by IR, (Fig.7), calcinations; and swelling study (Table 1) and XRD, (Fig. 24).

2.2. Preparation of 12-Ammonium-dodecanoic Acid -Montmorillonite Intercalate (I_b):

12-aminododecanoic acid (2.73 g, 11.9 mEq.) was dissolved in 500 ml of 0.02N HCl. The solution was added dropwise to a suspension of montmorillonite (10g, 11.9mEq) in distilled water with vigorous stirring at 60°C. The procedure was completed as previously mentioned for I_a. The product was dried at ~50°C under vacuum to give 12.17g of MMT-12-ammoniumdodecanoic acid intercalate (I_b). The characteristic

properties were investigated by IR (Fig.8), calcinations and swelling study (Table 2) and XRD (Fig.25).

2.3. Preparation of Vinyl Monomer-Montmorillonite Intercalate (I_c):

The preparation of this organoclay was carried out through two steps as following:

A) Synthesis of *N,N*-dimethyl-*N*-(*p*-vinyl benzyl)-*n*-octadecyl ammonium chloride (II):

The ammonium salt, II was prepared by mixing of *N,N*-dimethyl-*n*-octadecylamine (10.0 g, 34.36 mmol) dissolved in 10 ml THF, *p*-vinyl benzyl chloride (5.24 g, 34.36 mmol) and hydroquinone (0.03 g) as radical inhibitor. The mixture was stirred for 4 h at room temperature, followed by adding diethyl ether (200 ml) with stirring for additional 1 h. The precipitate was filtered off, and re-crystallized from ethyl acetate at 45 °C, to give 13.8 g of II (yield = 91%).

B) Preparation of *N,N*-dimethyl-*N*-(*p*-vinylbenzyl)-*n*-octadecyl ammonium -MMT (I_c)

To a homogenous suspension of sodium montmorillonite (10 g, 11.9 mEq.) in 300 ml of distilled water and 30 ml of methanol, a solution of ammonium salts II (5.27 g, 11.9 mmol) dissolved in 100 ml of water/methanol (70:30 V/V) was added dropwise. After stirring for 8 h, the white precipitate was filtered, washed repeatedly with distilled water till no chloride ion was detected by an addition of AgNO₃ solution to the filtrate. Finally the precipitate was washed twice with 80/20 (v/v) ethanol/water,

followed by drying in a vacuum oven at room temperature for 2 days to give 13.9 g of vinyl monomer-MMT.

3. Synthesis of PU-Organoclay Nanocomposites

3.1. Synthesis of PU/Tyr-MMT Nanocomposites (III_{a-f})

PEG-1540(16 g, 10.34 mmol) and Jeffamine-400 (8.3 g, 20.75 mmol) were mixed at molar ratio 1:2 respectively and dissolved in 24.3g DMF to give a solution of 50% w/w of monomers/solvent as stock a solution.

Tyr-MMT intercalate (0.21 g) **I_a** was mixed with 8g of diol/diamine solution (i.e. 4g net diol/diamine) and stirred for 6h till a complete dispersion of organoclay. TDI (0.6 g, 3.448 mmol) was added dropwise with vigorous stirring at room temperature. The reaction mixture was stirred for 8h to give nanocomposite with 5 wt-% organoclay. After removing the evolved gases from the reaction mixture, the solution was cast on glass plate in the film form, followed by removing the solvent at 80 °C in a vacuum oven for 12h to give elastic films (see **Scheme 2**).

A series of hybrids (**III_{a-f}**) containing different amount (3, 5, 7, 10 and 20%) of modified clay (**I_a**) were prepared by the same procedure. The characteristic properties of PU/ Tyr-MMT nanocomposites were investigated by different methods as listed in **Tables 1, 3, 6** and shown in **Figures 7, 10, 15, 16, 19, 24, 26, 29, 30, 31**.

3.2. Synthesis of PU-SMA/ MMT-12-Ammonium-dodecanoicacid Nanocomposites

The synthesis of this series of hybrids was achieved through several steps as following:

A) Preparation of Poly(styrene-co-maleic anhydride) (PSMA) (IV)

Styrene (10 g, 96.2 mmol) and maleic anhydride (9.42 g, 96.2 mmol) were dissolved in 3 ml of THF then 0.2g of benzoyl peroxide was added as

initiator. The solution mixture was heated at 80°C with stirring for 2h. The solid product was dissolved in 1, 4-dioxane and precipitated in ethanol. The resulted polymer was filtered, washed with ethanol and finally dried in a vacuum oven at 50 °C for 12h to give 18.7 g of copolymer IV (see **Scheme 3**).

IR (KBr disc): $\nu = 3447$ (C-H aromatic, stretching), 2938 (CH₂ aliphatic, stretching), 1777, 1725 (C=O), 1449, 1396 (CH₂ bending), 1219 (C-O anhydride), 953, 922, 762, 703 cm⁻¹ (C-H aromatic, bending, out of plane).

B) Synthesis of PU-PSMA/MMT-12-Ammonium-dodecanoic acid

Nanocomposites (V_{a-e}):

PEG-1540 (20 g, 12.987 mmol), PEG-400 (10.39 g, 25.975 mmol) and PSMA IV (3.38g, 10 wt %) were dissolved in DMF (33.77 g) to give 50% monomer solution (w/w).

A 0.2392g of organoclay I_b was mixed with stirring with 8.9g of the previous mixture till the organoclay become completely dispersed. To this suspension, TDI (0.6 g, 3.448 mmol) was added dropwise at room temperature with vigorous stirring. The stirring was continued for 8h to give a hybrid blend containing 5 wt % organoclay. The blend was cast in the film form in a glass mold followed by removing the solvent under reduced pressure at 80°C for 12h (see **Scheme 4**). Other nanocomposite samples (V_{a-e}) were prepared by the same procedure using (0, 1, 10 & 20 %) of organoclay (I_b) content, to give hybrid films.

The characteristic properties of PU/ SMA-ALA-MMT nanocomposites were investigated by different methods listed in **Tables 2, 4, 7** and shown in **Figures 8, 12, 13, 20, 27, 33, 34**.

3.3. Synthesis of PU/Vinyl Monomer-MMT Nanocomposites

A series of PU- organoclay nanocomposites were prepared as illustrated in Schemes 3, 5 , 8 through the following steps.

A) Synthesis of Acrylate-Terminated PU Prepolymer VII

A mixture of 15g (15 mmol) of dry PEG-1000 and 5.22g (30 mmol) of TDI were stirred under nitrogen atmosphere at 50 °C for 2h to give OCN-terminated PU-prepolymer (VI). 2-Hydroxyethylmethacrylate (HEMA) (3.9g, 30 mmol) was added dropwise with stirring to the pre-polymer (VI) at room temperature. The stirring was continued for 2h to give PU end-capped with acrylate group (VII) (see Scheme 6).

B) Preparation of PU-Organoclay Nanocomposites (VIII_{a-d})

A series of nanocomposites were prepared by mixing 4g of PU (VII), 0.1238 g of vinyl monomer-MMT intercalate I_c dispersed in 30 ml THF and 0.085 g benzoyl peroxide as initiator. The mixture was stirred at room temperature for 4h, then casted on pre-treated glass plate followed by drying at 50 °C under vacuum for 15h. The hybrid films were gradually cured at 100 °C, 160 °C, and 180 °C for 2h to produce a transparent film of PU-MMT nanocomposite containing 3 wt-% organoclay (see Schemes 6, 7 and 8). Other samples were prepared by the same procedure using (0, 7 and 10 wt-%) of vinyl monomer/ MMT intercalate I_c. The characteristic properties were investigated by different methods listed in Tables 5, 8 and Figures 9, 14, 21, 28, 35, 36.

4. Testing Procedures

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

$^1\text{H-NMR}$ spectra for *N,N*-dimethyl-*N*-(*p*-vinylbenzyl)-*n*-octadecylamine ammonium chloride (II) were carried out in CDCl_3 on an lambda, Jole NM300, Japan instrument.

Thermogravimetric analyses (TGA) were determined with Rigaku Thermo Plus 2 TG-DTA TG8120. The heating rate was 10 $^\circ\text{C}/\text{min}$. under air and argon atmosphere in the temperature range ~ 30 -900 $^\circ\text{C}$.

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

Morphology of the composite was examined by a Joel JSM-5300 *Scanning Electron Microscopy* (SEM). Also, 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 was used. The specimen was deposited on double-sided scotch tape and examined at their surface in all samples

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

Calcination Measurements: A definite weight of the sample was introduced into a porcelain crucible and dried in an electric oven at 120 $^\circ\text{C}$ overnight, then introduced into an ignition oven. The temperature was

increased to 1000 °C and kept at this temperature for 8 h. The loading of each sample is expressed as the weight loss by ignition per 100 g of the dry sample.

Swelling Measurement: The swelling degree was determined by taking a definite weight 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 24h. The excess solvent was removed by gentle centrifugation. The swelled sample was weighed and resuspended in the solvent. This procedure was repeated till obtaining on a constant weight for the sample. The swelling degree of each sample is expressed as the amount of sorbed solvent per 100 g of dry sample.