Chemistry and Materials Research
ISSN 2224- 3224 (Print) ISSN 2225- 0956 (Online)
Vol.6 No.1, 2014

Synthesis and characterization of the PMMA/ Sio2 hybrids by sol-gel method

Seenaa Ibrahem , Harith Ibrahem
Deprtment of physics ,college of science, university of Baghdad
Sinna633@gmail.com , Harith ibrahem@yahoo.com

Abstract :-
This research describes the synthesis and characterization of the organic –inorganic hybrid materials((methyl methacrylate) (PMMA) and tetraethyl orthosilicate (TEOS)) film were fabricated using sol-gel technique T_1=20/80,T_2=50/50,T_3=80/20. the ratios of PMMA/TEOS (20\80,50/50,80/20) V/V, .The films were then characterized using FTIR, TGA ,and UV-VIS., the hybrids organic –inorganic film is devised by the assembly between silica xerogel and polymer with C=O group via hydrogen bonding .The best transmission of the ratio PMMA/TEOS is (80/20),the thermal gravimetric analysis the stable thermal with increasing PMMA content .
Keywords:-PMMA,TEOS,HYBRIS FILM,SOL-GEL

Introduction :-

PMMA has been widely used in optical devices due to its excellent optical properties and processibility [1]. These novel materials combine the excellent properties of both organic (e.g. flexibility, toughness and formability) and inorganic components (e.g. mechanical, optical properties and high thermal stability) which offer new possibility for advanced applications. These hybrids are versatile in the composition, processing and properties. [2] Hybrid organic-inorganic systems (OIS) are a new class of polymer materials, high interest to which appeared in recent years. It is explained by their peculiar structure, which includes organic and inorganic units, and, accordingly, possesses their common properties. Such combination provides the opportunity to obtain materials with predefined properties, which are regulated by variation of chemical composition of organic and inorganic components.[3] Sol-gel is a very flexible route for the synthesis of inorganic, organic-inorganic networks such as glasses, ceramics, films or powders. For a long time, sol-gel techniques have been used for manufacturing glasses and ceramics [4]. More recent studies of this process have focused on electrical applications [5], medical science [6], protection coatings , and solar energy applications [7].The combination of an inorganic material with a polymer gives the resultant hybrid properties from both constituents – the flexibility of the polymer with the strength of the inorganic. Depending on the types of interactions that occur between the constituents, better properties than either of the components could emerge. Creating these materials can be as easy as mixing them together in asol-gel process to produce a homogeneous hybrid.

Sol-gel chemistry is a wet chemical process that allows an inorganic oxide to be produced from organically modified pre-cursor materials at lower processing temperature than a traditionally created inorganic oxide[8].the preparation of the inorganic phase, tetraethoxy silane was added to a solution containing the organic polymer and hydrolysis and condensation was induced by acid catalyst. Analogous procedures have been applied by Landry et al. (1992a; 1992b)[9][10], Chan et al. (2001)[11], and Zulfikar et al. (2006a; 2006b)[12][13] to prepare organic-inorganic polymer hybrids for which the organic matrix was poly(methyl methacrylate). Polymers such as poly(methyl methacrylate), poly(vinyl acetate), poly(vinyl pyrrolidone), poly(N,N-dimethyl acrylamide) and poly(acrylicacid) are able to form hydrogen bond with silanols on the silicate network (Landry et al., 1992b; Chan et al., 2001; Zulfikar et al., 2006a, 2006b) and therefore transparent homogeneous hybrid films are usually produced. The presence of carbonyl groups in organic polymer chains helps retard ing phase separation during the vitrification of the hybrid film (Landry et al., 1992b; Chan et al., 2001; Zulfikar et al., 2006a, 2006b).

Objective :-

The goal of this project is to determine the structure hybrids ,thermal gravimetric, and optical properties for silica with pmma (20%,50%,and 80%) .

Experimental :-

Materials

All chemical materials used were of the highest purity available,the materials used in the research and their companies were listed in table (1)

Table (1) chemical materials used in this study

Raw Material	supplier	Molecular Formula	Molecular Weight (g/mol)	Density (g/cm^3)	Purity	State of Raw Material
Tetraethoxysilane (TEOS)	Sigma-Aldrich (Germany)	$Si(OC_2H_5)_4$	208.3	0.933	>98%	liquid
Deionized Water	University of Baghdad/ College of Science/Laboratory of service	H_2O	18	1	high degree of purity/empty of additional ions	Liquid
Hydrochloric Acid (HCl)	BDH	HCl	36.46	1.19	37%	Liquid
Polymethylmethacrylate (PMMA)	china	$(C_5O_2H_8)_n$	120,000	1.18		solid
chloroform	Hopkin&Williams england	CHCL3	119.38	1.48	99%	liquid
Ethanol (EtOH)	GCC/Gainland chemical company	C_2H_5OH	46.07	0.785	99.9%	Liquid

Synthesis of pure polymer film casting -:

Thermoplastic PMMA is dissolve the chloroform ($CHCL_3$) the weight of pmma (1 gm) were dissolved in (10 ml) of chloroform to give solutions of 10%$\left(\frac{wt}{vol}\right)$. The solutions were stirrer for 30 minute or more to achieve an almost homogenous content. the samples were dried in free air for 24 hour at room temperature and then kept inside an oven of temperature (50 °C) for at least 1hour to allow for the evaporation of all the residual solvent .

Synthesis of the PMMA/TEOS film :-

Tetraethoxysilane (TEOS,) was used as the inorganic precursor, poly(methyl methacrylate), PMMA,[-CH_2-C(CH_3) form as the organic precursor, chloroform($CHCL_3$) as the solvent and hydrochloric acid (HCl) as the catalyst for hydrolysis and condensation of TEOS to prepare PMMA/SiO2hybrid materials. Three PMMA/TEOS ratios by volume were prepared,namely PMMA/TEOS=20/80, 50/50 and 80/20 (v/v), which referred as T_1, T_2 and T_3 respectively.Fig. (1) is a simple schematic of the synthesis of PMMA/SiO2film , PMMA were first dissolved in at chloroform a concentration of 10 wt%. TEOS solution(TEOS+ HCl (0.15M)) was added drop by drop to the solution under continuous stirring to give three different organic/inorganic ratios (20/80, 50/50 and 80/20, v/v). provide water and to catalyze the sol-gel reaction. The H2O: TEOS molar ratio was 4:1.The solution was stirred for 1 h at room temperature and later transferred to closed glass Petri dishes. the dishes were opened to allow the solvent to slowly evaporate at room temperature. Relatively longer evaporation time was used to avoid phase separation in the hybrids, because the hybrids became less transparent when evaporated fast.

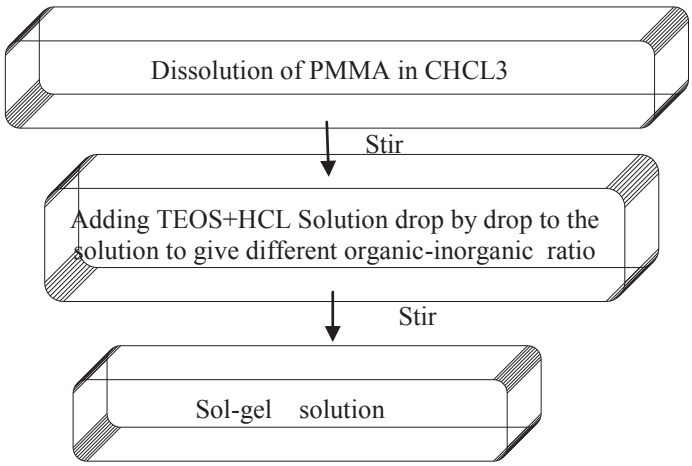


Fig. (1) The schematic of the synthesis of PMMA/SiO2sol-gel solution.

characterization techniques:-

1-Fourier transform infrared spectroscopy (FTIR)

FTIR-Spectrometer, supplied by Shimadzu(Japan) ,Mid-IR spectra, from 4000 to 400 cm^{-1}, were obtained for some pure samples and all hybrids samples using, on KBr pellets of the samples.

2-Thermogravimetric analysis (TGA)

TGA use helium as inert gas in rate 20ml/min ,at temperature range of 0 to 1000° c at a heating rate of 10° c/min. the samples were ground into fine powder .the measurements were taken using 3-5mg samples.

3-Optical Properties:-

UV spectrophotometer (UV-1800/SHIMADZU) was measured the transmission spectra of the hybrids samples ,the wavelength range of 190 nm to 1100 nm.

Results and Discussion:-

1-FTIR Study

The figure (2) shows The silica xerogel ,in this spectral range(3000-4000)cm^{-1} the bands are mainly due to overtones and combination of vibration of H2O. 3000 cm^{-1} - 1200 cm^{-1}: In this spectral range, the bands are due to the overtones and combination of vibration of organic residue, molecular water,and 1200 cm^{-1} - 400 cm^{-1} This spectral region is associated with combinations of vibration of silica network. The band at (1076-443) cm^{-1} , assign to asymmetric stretching vibrations of Si-O-Si bridging sequences.

Fig .(3) the same absorption was shown at silica xerogel because 20% percent of pmma does not effect on absorption i.e the effective absorption region may be over lap with spectra silica xerogel.

The hybrid film (50% PMMA+50% TEOS) and(80% PMMA+20% TEOS) were sketched in Figure (4,5) In hybrid film, it can be easily found that the absorption region of Si-O-Si asymmetric stretching at 472 $cm^{-1}$and 819 cm^{-1}, which was due to the formation of silica structure via sol-gel process with TEOS added with agree the paper R.K. Satvekar etal.[14] The two companion peaks in this region arise from Si–O–Si groups at 1005 and 1153 cm^{-1}.in the hybrid films partial shift in the C=O peak (1663.0cm^{-1}, 1629cm^{-1}) , this being due to the presence of hydrogen bond in the system. Simultaneously, absorption region of silanol groups (Si-OH) at 819$cm^{-1}$and 3543 cm^{-1} and 886-3560 cm^{-1} the ratio $T_2$and T_3 respectively were also found, which resulted from the existence of unreacted silanol group on TEOS to formation of silica network [15].

Figure (6)shows of pure PMMA is primarily characterized by the 1648.9 cm $^{-1}$ band assigned to free lateral C=O stretching ,Other peaks in this figure at 2875.3 cm^{-1} and 990-650 cm^{-1}correspond to CH3 symmetric stretching and bending respectively and peaks at 1375 cm^{-1} are ascribed to O-CH3 deformation, 1062 cm^{-1} to O-CH2stretching vibrations and 1196 cm-1to C-O stretching vibrations which agree with A.K.Tomara et al., [16]. hybrid organic-inorganic film is devised by the assembly between SiO2 xerogel and polymer with C=O groups via hydrogen bonding

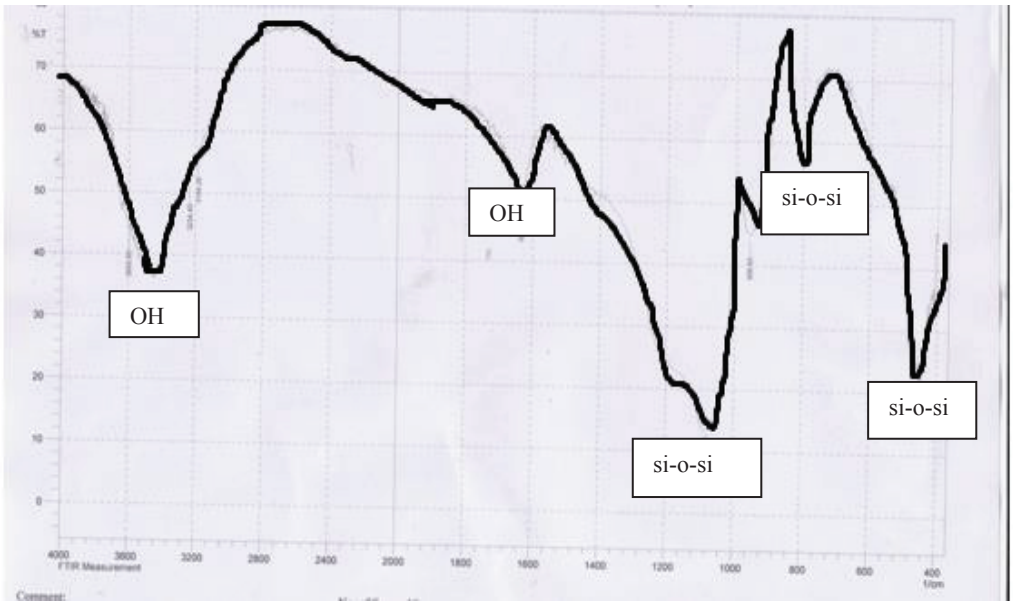


Fig.(2) FTIR of silica xerogel

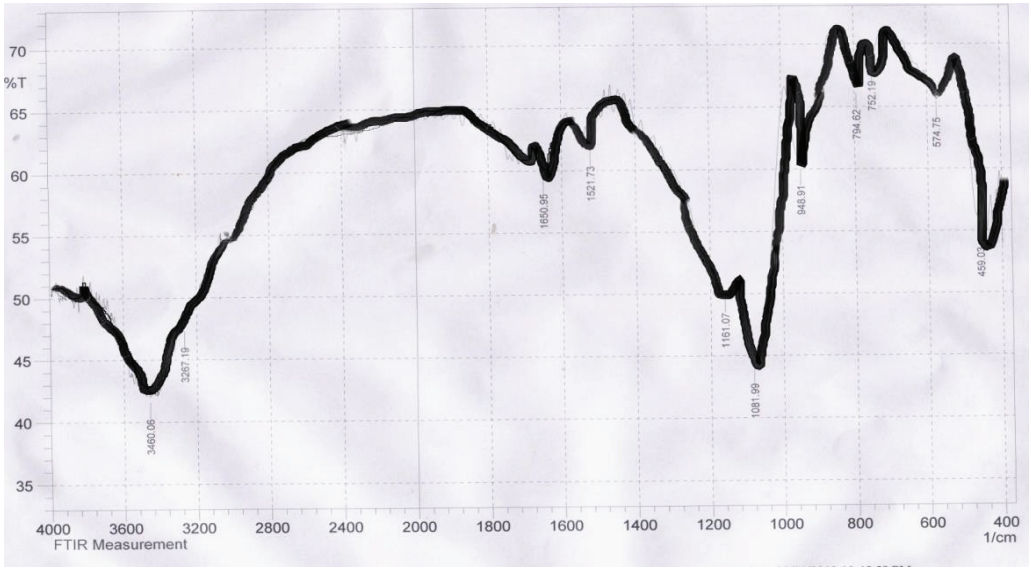


Fig.(3) FTIR of 20%PMMA+80%TEOS

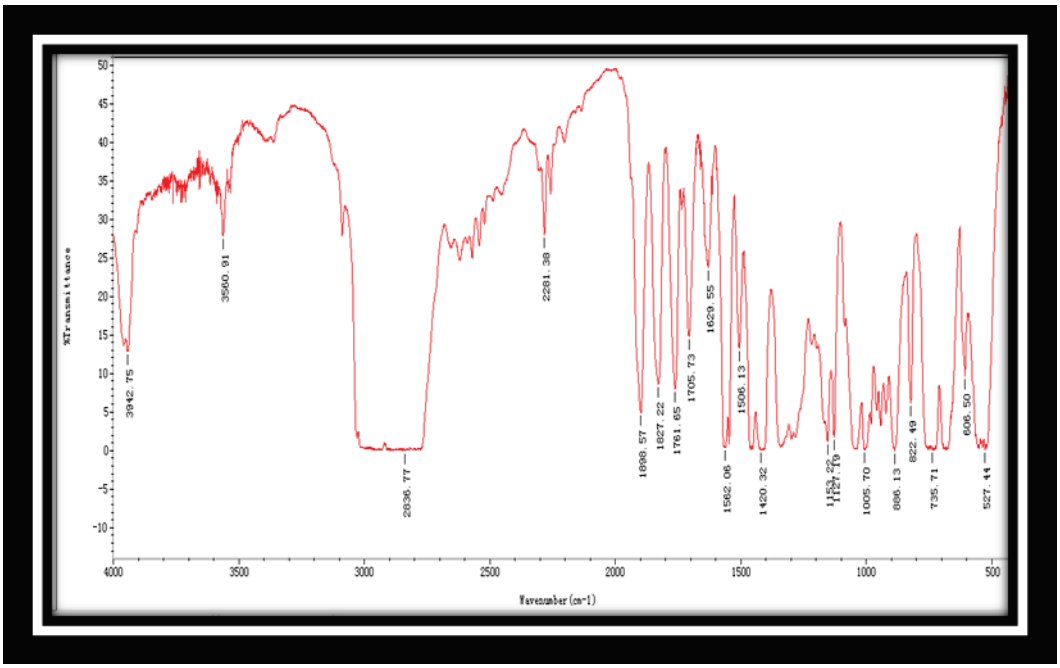


Fig.(4) FTIR of 50%PMMA+50TEOS

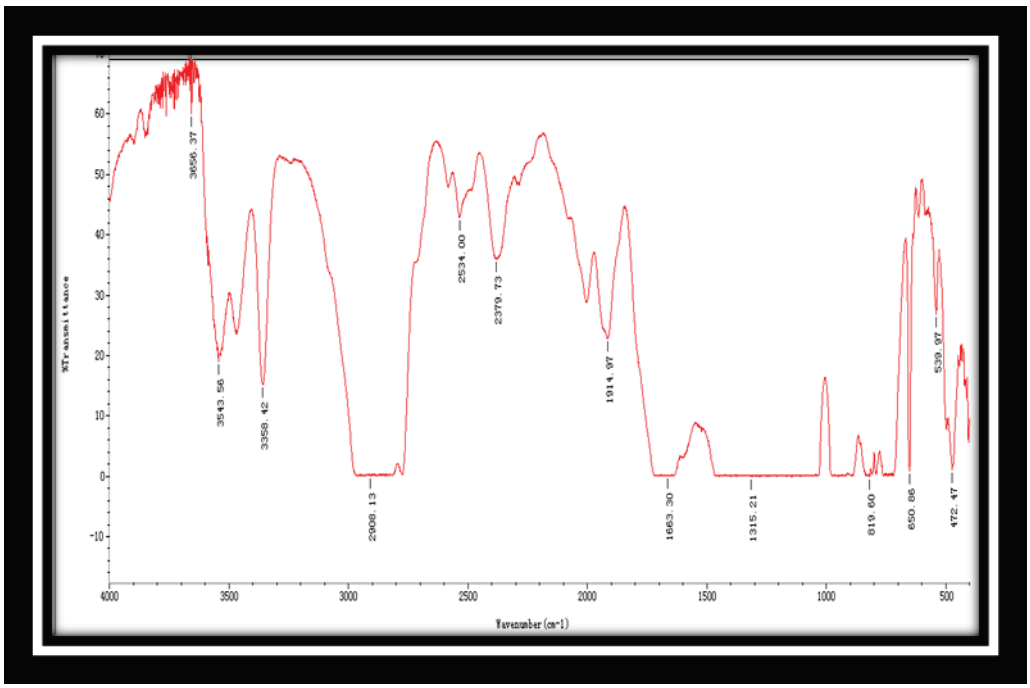


Fig.(5) FTIR 80%PMMA+20%TEOS

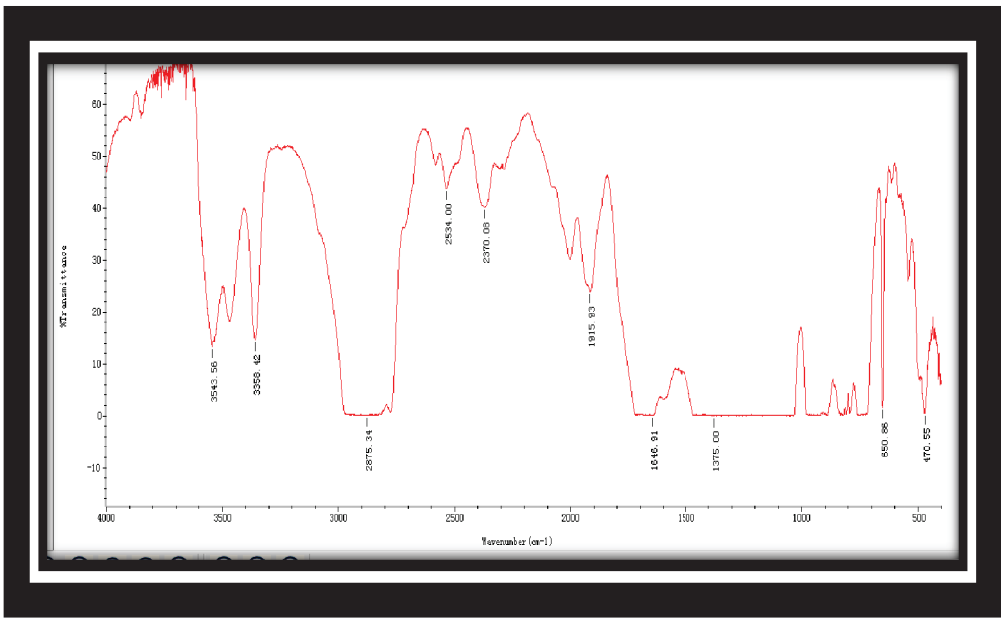


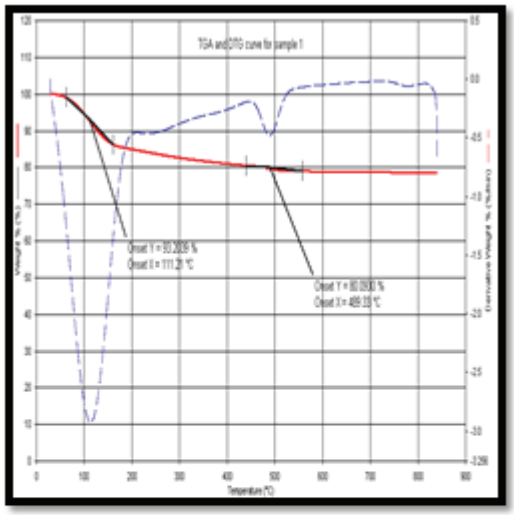
Fig.(6) FTIR spectra of PMMA pure

2-TGA study

Figure (7)TGA curves of Silica xerogel ,decrease the weight with increasing the temperature ,the lower curve at 100 ºC represent the amount of water and the lower curve at 489.3 ºC represent degradation of some organic in the sample.

Figure(8) at 20% percent as show the area under the curve for second decease on lower and the same behavior observed for 50%,80%,and PMMA.

Figure (8,9,10) represent ,First, the weight percent at 182 ºC,177 ºC, and 172 ºC the monoliths hybrids T_1, T_2 andT_3 ,were 97.3%, 97.1% , 98.2%, and respectively, indicating little water or solvent content left in the hybrids for the TGA measurements. This is due to the fact that these hybrids were left in hood at room temperature for 2 weeks to evaporate water and $CHCL_3$ solvent . Therefore, the evaporated samples can be used for the measurements and characterization. Second, the residue at 800 ºC increased with increasing TEOS content, from 15 wt% for T_3, to 23 wt% for T_2, and to 48 wt% for T_1. The residue reflected the SiO2content in the hybrids, because essentially only inorganic components are present at 800 ºC. Comparing the experimental and calculated values of residue in TGA data, the similar trend suggested the successful formation of SiO2in the monoliths. The lower experimental values are probably due to TEOS evaporation during synthesis, incomplete on version of TEOS to SiO2 and residual $CHCL_3$ Third, the main weight loss of the hybrids took place at 190-375 ºC, corresponding to the random scission of PMMA main chains[17]. Furthermore, it was found that all the three hybrid monoliths have higher decomposition temperatures (~385 ºC) than that of pure PMMA (~375 ºC). The slightly improved thermal stability for the hybrids compared to the pure PMMA may be caused by the interactions between the polymer chains and SiO2, and hydrogen bonding should be the main source of such interactions.



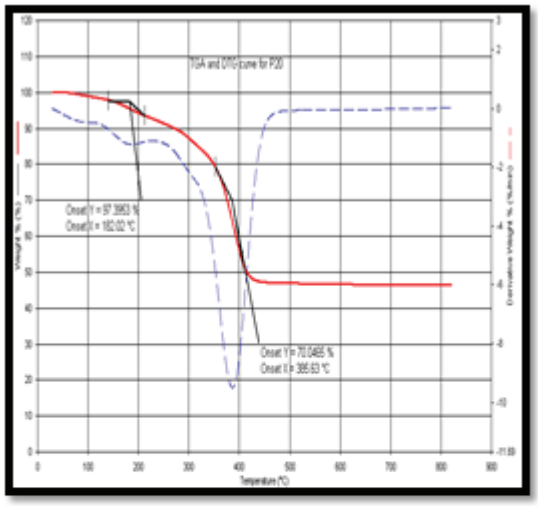
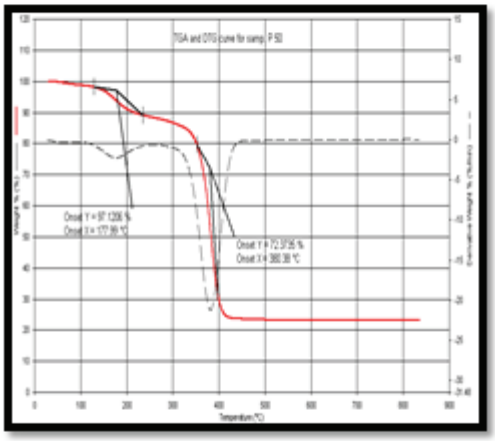


fig.(7) TGA+DTG of silica xerogel fig.(8)TGA+DTG of 20%PMMA



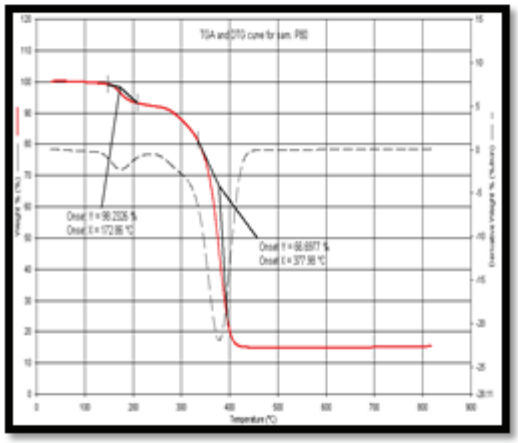


Fig.(9)TGA+DTG of 50%PMMA fig.(10)TGA+DTG of 80%PMMA

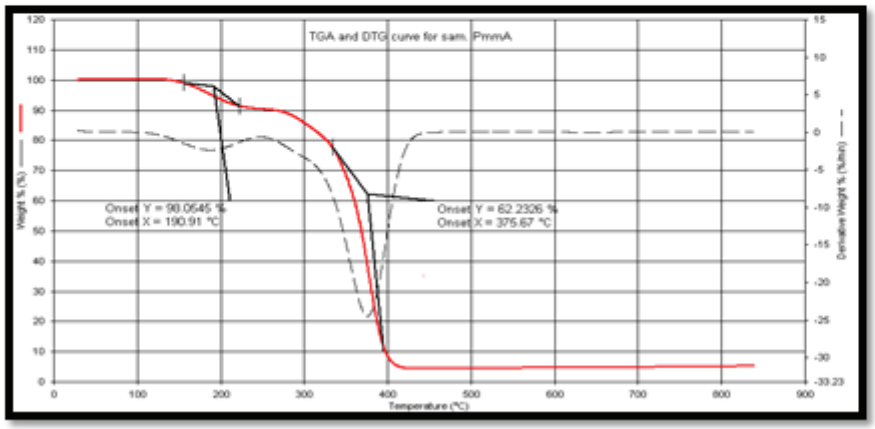


fig.(11) TGA+DTG of PMMA

3- optical properties :-

Transparency :-

The transparency of the PMMA and monoliths after evaporation are shown in Fig. (12). The T_3 sample was transparent compared with T_1 ,sample T_2 was opaque .Furthermore, the better transparency for the monoliths T_3 indicated there was strong interfacial reaction between organic and inorganic components.

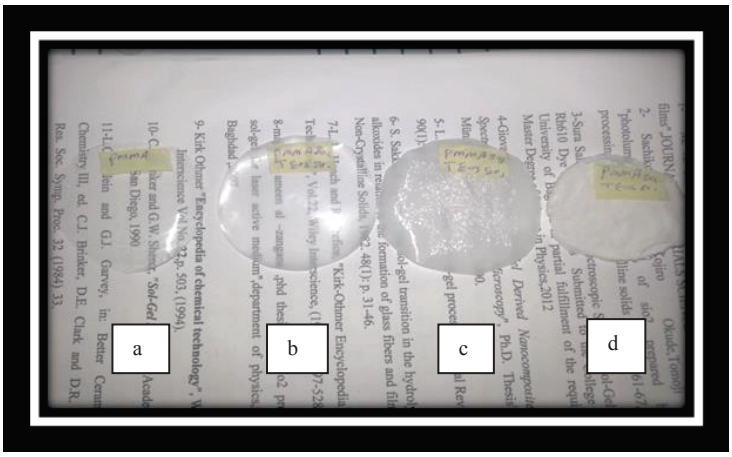
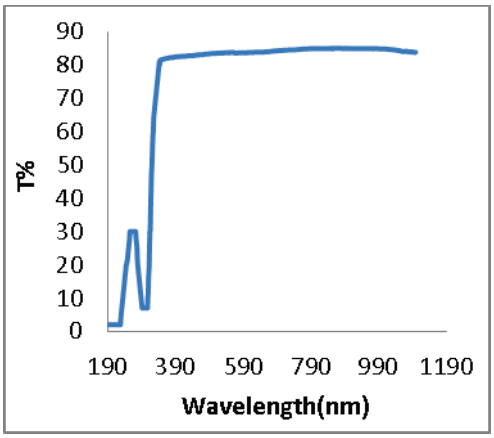
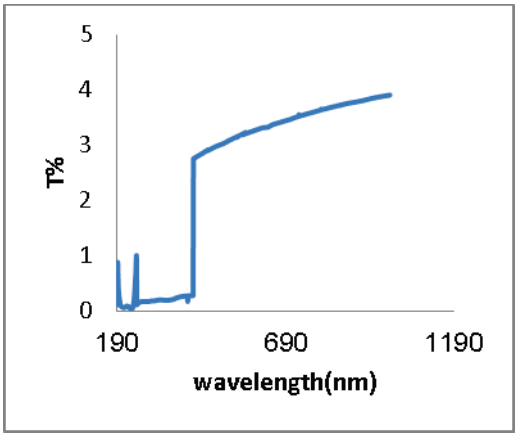


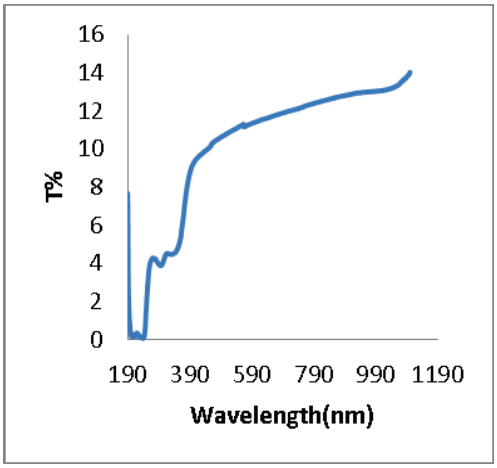
Fig. (12) The pictures of the three PMMA/SiO2hybrids and pure PMMA
a-PMMA b- 80%PMMA+20%TEOS c-50%PMMA+20%TEOS
d- 20%PMMA+80%TEOS



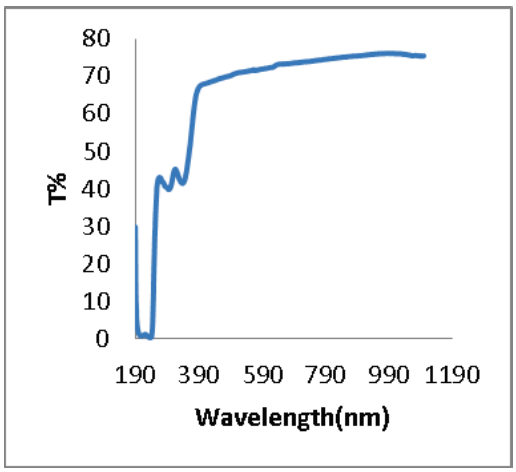
(a)



(b)



(c)



(d)

Fig.(13)transmittance curves of the three ratio PMMA/ Sio_2 hybrids and pure PMMA
a-PMMA b- 80%PMMA+20%TEOS c-50%PMMA+20%TEOS
d- 20%PMMA+80%TEOS

Conclusion:-

1-The TGA curves of Silica xerogel ,decrease the weight with increasing the temperature.

2- The slightly improved thermal stability for the hybrids compared to the pure PMMA may be caused by the interactions between the polymer chains and SiO2, and hydrogen bonding should be the main source of such interactions.

3-The ratio 80%pmma+20%TEOS(T_3) the better transparency compared with other ratio.

References:-

[1] Yu, Y. Y., Chen, C.Y and Chen, W.C., (2003)" Synthesis and characterization of organic-inorganic hybrid thin films frompoly(acrylic) and monodispersed colloidal silica, Polymer", 44, pp.593-601.

[2] Jinging Sun(2010) " Micropen direct-write thchnique for fabrication of advanced electroceramic and optical materials " Doctor of Philosophy Graduate Program in Material Science and Engineering Rutgers, The State University of New Jersey.

[3] M. Maksym Iurzhenko(2009)"Electrical, thermomechanical and sorption properties of hybrid organic-inorganic systems based on urethane oligomers and silicates",Polymers and composites materials ,Defence of the thesis will be held on 25 November .

[4] C.A. Milea ,C. Bogatu,A. Duta (2011)"The influence of parameters in silica sol-gel process",Engineering Sciences • Vol. 4 (53) No. 1 .

[5] He, Z.W., Zhen, C.M., et al.(2004)" Micro-structural Characterization of Low Dielectric Silica Xerogel Film". In: Thin Solid Films 462-463, p. 168-171.

[6] Coradin, T., Boissière, M., Livage,(2006) J.: Sol-Gel Chemistry in Medicinal Science. In: Current Medicinal Chemistry 13(2006).

[7] Wang, D., Bierwagen, G.P.(2009)" Sol-Gel Coatings on Metals for Corrosion Protection"In: Progress in Organic Coatings 64, p. 327-338.

[8] Morgan L. Ferguson,(2011)"Preparation and Characterization of Polymer-SiO2 Hybrids"in partial fulfillment ofthe requirements for thedegree of Doctor of Philosophy , Oregon State University.

[9] Landry, C.J.T., B. K. Coltrain, and B. K. Brady,(1992a) "In situPolymerization of Tetraethoxysilane inPoly(methyl methacrylate)": Morphology and Dynamic echanical Properties, Polymer, 33:7, 1486.

[10]Landry, C. J. T., B. K. Coltrain, J. A. Wesson, and J. L. Lippert,(1992b) " In situPolymerization of Tetraethoxysilane in Polymers": Chemical Nature of The Interactions, Polymer, 33:7, 1496.

[11] Chan, C. K., S. L. Peng, I. M. Chu, and S. C. Ni,(2001) " Effects of Heat Treatment on the Properties of Poly(methyl methacrylate)/silica Hybrid Materials Prepared by Sol-gel Process",Polymer, 42, 4189.

[12] Zulfikar, M. A., A. W. Mohammad, A. A. Khadum,and N. Hilal,(2006a)"Synthesis and Charac-terization of Poly(methyl methacrylate)/SiO2Hybrid Membranes: Effect of Solvents on Structural and Thermal Properties", J. App. Polym. Sci., 99, 3163.

[13]Zulfikar, M. A., A. W. Mohammad, A. A. Khadum, and N. Hilal,(2006b) " Synthesis and Charac-terization of Novel Porous PMMA/SiO2Hybrid Organic-Inorganic membranes" Desalination, 192, 262-270.

[14] R.K. Satvekar, M.R. Phadatare, V.A. Karande, R.N. Patil, B.M. Tiwale and S.H. Pawar,(2012) "Influence of Silane Content on the Optical Properties of Sol Gel Derived Spin Coated Silica Thin Films",International Journal of Basic and Applied Sciences, 1 (4) ,pp. 468-476.

[15]Muhammad Ali Zulfikar, Abdul Wahab Mohammad",(2004)Synthesis and characterization of poly(methyl methacrylate)/SiO2 hybrid membrane",Department of Chemical and Process Engineering, Universiti Kebangsaan Malaysia.

[16] A. K. Tomara, b. Suman Mahendiaa and Shyam Kumaraa,(2011)" Structural characterization of PMMA blended with chemically synthesized PAni ",Department of Physics, Kurukshetra University, Kurukshetra, INDIA, Advances in Applied Science Research, 2 (3): PP.327-333.

[17] H. Wang, P. Xu, W. Zhong, L. Shen, Q. Du, (2005)"Transparent poly(methyl methacrylate) /silica/zirconia nanocomposites with excellentthermal stabilities", Polym. Degrad. Stab., 87, p319.