EFFECT OF MOLAR RATIO (R) ON OPTICAL AND MECHANICAL PROPERTIES OF EPOXY/SILICA HYBRIDS

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ABSTRACT: *New hybrids Silica/epoxy materials were prepared using sol-gel method for their use as a high transparent,good mechanical properties, and thermostablity. The effect of the molar ratio (R) on the properties of the silica /EP hybrid films and rods, such as transmittance, mechanical strength. A strong chemical interaction between silica and epoxy is indicated by the bond of the Si-O-C. This excellent compatibility between EP and silica leads to a 93%in visible light transmittance as compared with epoxy. The density of the hybrids material, hardnessand compression strength increased with increase in molar ratio (R) whereas, the wear rate decreased with increase in molar ratio and increased with increased applied load.*

Key words :-epoxy ;silica; new hybrids ;optical; mechanical.

1-INTRODUCTION

Organic–inorganic hybrids obtained via the solution–gelation (sol–gel) inorganic polymerization process have become with various applications as monoliths, powders, tubes and fibers[1].

Sol–gel method is based on by hydrolysis of liquid precursors to form colloid as sols and their subsequent condensation to obtain the gel [2] .

Epoxy (Ep) is a highly adhesive polymer and excellent forming properties [3]. It has been proven that silica/Ep hybrid materials have great potential in applications such as coatings, inorganic adhesives and other silica-based materials with enhanced thermal stability, mechanical and tensile strength [4].Epoxy nanocomposites are materials consisting of two phases, a nanoparticles inorganic domain, well-dispersed in a cross-linked epoxy matrix [5].

Hybrids materials, usually containing Si oxide particles. They have been applied in a great number of applications, such as stone restorations, coatings, adhesives, mechanical materials [6-7].

2-Sol-Gel Method:-

The silicon-based sol–gel process is probably the one that has been most investigated; therefore the fundamental reaction principles are discussed using this process as a model system. There are several silicon

Alkoxides(alkoxysilanes) commercially available, but the most frequently used is tetraethoxysilane (TEOS). The starting sol-gel mixtures of TEOS typically consist of the alkoxide, water and a solvent, often ethanol. To the aim to control the hydrolysis and condensation reactions rates, either an acid or a base must be used as catalyst [8]. Si—C bonds have enhanced stability against hydrolysis in the aqueous . Therefore, in addition to tetralkoxysilanes, other categories of sol-gel precursors include organofunctionalalkoxysilanes. Alkyl-substituted alkoxysilanes or organoalkoxysilanes [8] are useful to modify the polymer network because of the presence of the non-hydrolysable groups. They are also used when the introduction of organic matter within the inorganic network is required. These silanes, known as coupling agents, were originally introduced as connectors between organic resin matrices and mineral reinforcement, namely fibers and particulates, to improve bond strength and chemical resistance [9].Large number of variables influence the amount of hydrolyzed and condensed species and then the structural evolution of silicate polymers: water content, reaction time, nature of the alkoxide, solvent, pH and thermal history. As a matter of fact, the choice of process parameters affects the microstructure of the produced gels. sol-gel method involves many stages: Hydrolysis ,Condensation, Gelation, Ageing , Drying , and Densification [9].

3- Factors Affecting Hydrolysis/Condensation Reactions

3.1 Nature of catalyst :-

The nature of the catalyst determines the relative rates of hydrolysis and condensation reactions and affects the of gel in terms of open network structure or dense network structure. Aelion*et al* [10] reported that the rate and extent of alkoxide hydrolysis are greatly influenced by the dissociation constant and concentration of the acid or base catalyst.

3.2 PH of solution :-

The silanols {($OR)_3$ SIOH} obtained replacing the alkoxy groups on the silicon with hydroxyl group are more acidic and so more prone to be attacked by hydroxide ions [11]. The basic catalysis is an aggregation (monomer-cluster) of highly cross-linked sol particles to form gels with large pores between the interconnected particles. [12].

3.3 Water:-

an increase in water content leads to a corresponding increase in hydrolysis and condensation rate. McDonagh *et at*. [13], for obtaining SIO_2 films, R = 2 is insufficient for complete hydrolysis and higher R-values are required. It is also showed by Butler *et. Al.* [14], that under low R-value, a matrix with a more open structure is produced due to incomplete hydrolysis .

3.4 Solvent :-

The solvent , An important factor in sol-gel reactions . It affects the rates of hydrolysis and condensation. many types of solvents have also been used H_2O, methanol and formamide), (DMF, THF and acetonitrile), and non-polar aprotic, (dioxane) [15].

Non-polar aprotic solvents, cannot impede the condensation process because they offer no possibilities of either [15]

4- Epoxy/silica Hybrids :-

The polymer/silica hybrids materials, can be prepared by using epoxy resin and alkoxysilane and by progressing the sol-gel reaction of the alkoxysilanes during the progress of epoxy curing. By following this route of hybrid preparation, a contemporaneous growth of the two networks are allowed [16].

5- EXPERIMENTAL DETAILS PROCEDURES:-

5-1 materials

Tetraethoxysilane (TEOS>98%) and epoxy (PE) with density 1.2 g/cm^3 were supplied by Sigma-Aldrich ,Hydrochloric acid (HCl, AR grade, 36 wt%), deionized , and ethyl alcohol .

5-2preparationsol A (silica solution) & sol B (epoxy pure)

To prepare silica solution using tetraethylorthosilicate (TEOS, ≥98%) ethanol, water and HCl. volumes of tetraethylorthosilicate (TEOS) , water and ethanol were mixed and stirred for 60min at 60 °C , water by TEOS molar ratio(R=1,2 and 3) in Table (1).

5-3 preparation sol B (epoxy pure)

The solution of epoxy and hardener was formed with ratio of 3:1.The hardener liquid was added slowly to epoxy resin at room temperature, this mixture was stirred manually for 5 min, and the composition was left at room temperature for 24 hours to dry.

5-4 preparation epoxy / silica hybrid :-

Sol A(silica solution) to add the epoxy resin and stirred at 60 min at 60° c after cooled solution added the hardener and stirred at 3 min. figure 1(a,b) sample of preparation for rods and thin films

Table (1):- volumes used in sol preparation

Samples	TEOS(ml)	ETOH(ml)	H2O(ml)	R(molar ratio)
A	5	2.5	5	1
B	5	2.5	10	2
C	5	2.5	15	3

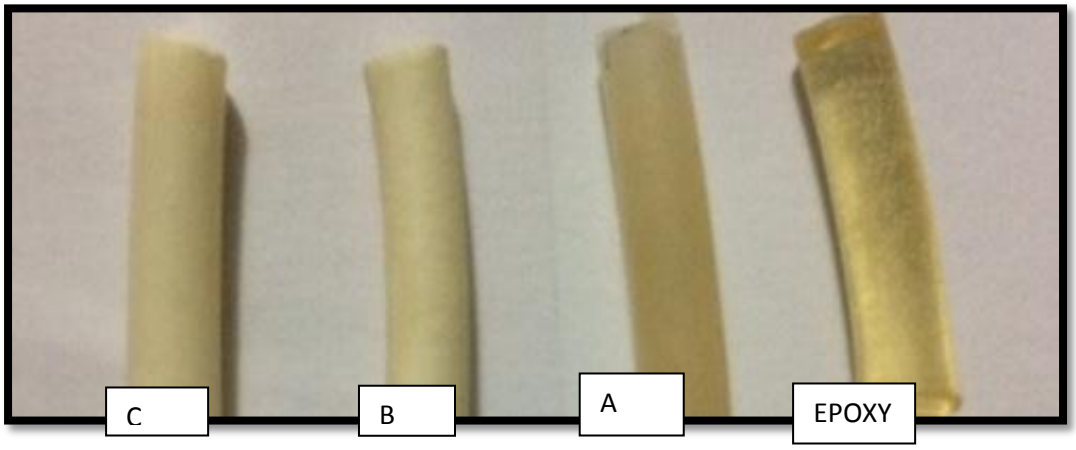

Figure (1a) samples of rods

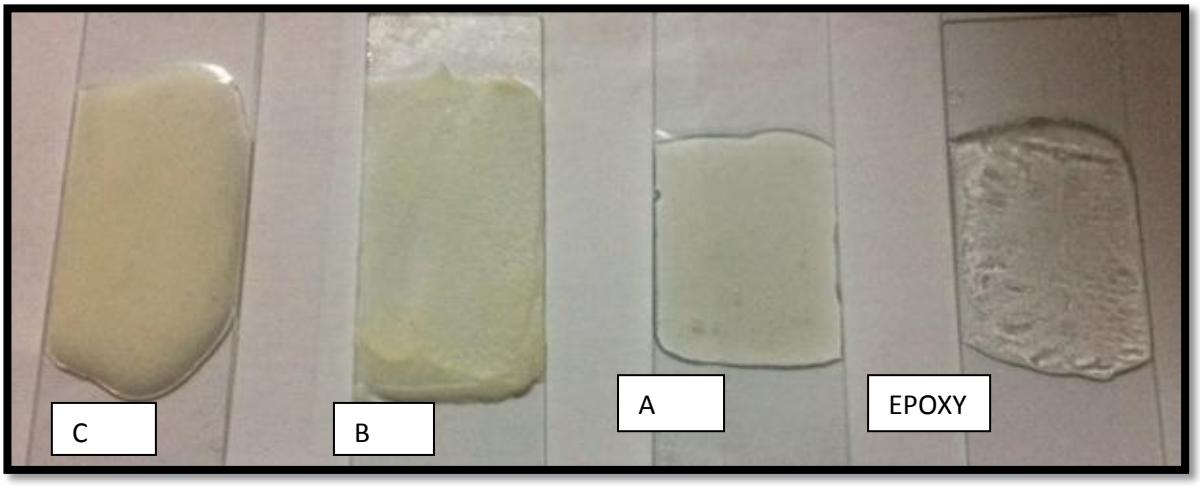

Figure (1b) samples of thin films

5-4 Characterization :-

UV-vis spectrometer in the range from 400nm-800nm , the physical properties (density, micro hardness, wear rate, and Brazilian compressive strength).

Density :-

The density of materials was evaluated as per relationship between weight and its volume

Density = $\frac{weight}{volume}$……..(1)

1.2**Micro hardness:-**

Micro hardness tester, the samples made of (Adolph I Buehler Inc. USA) was used in this work for Vickers hardness (HV), the measurements were achieved by micro indentation under (500 g) load and with load application times of 45 sec.

$Hv=2L \sin(\theta/2)/ d^2$ ……..(3)

d: is the diagonal of the impression , L : Load

θ: is the angle between opposite face of the diamond=136°

1.3**Wear test :-**

The wear machine consists of metal disk rotating motor connecting power .A plate as an arm containing specimen holder .The a Speed of disc (500cycles /min.), and the hardness of disc is 9269 HB[17].The rate of wear :

Wear rate = $\Delta W/D_S$ …… (4) (gm./cm)ΔW :- where the mass sample before and after test (gm)

ΔW=W1-W2……..(5)

Is calculated from the following relationship, distance Slide(S_D)(cm)

$S_D=2\pi rnt$…….(6)

Note that:

r:- radius the specimen to Center of the disc(cm)n:- Number of sessions of the disk (r / min).

t:- Testing time (min).

1.4 Brazilian disk fracture test :-

One of the most interesting mechanical tests for materials is the diametrical compressive of a solid disk. This test was performed on disk using a compression test Instron device. Sample was fixed between the upper and lower platens of the device to start compressing at a rate (cross-head speed =0.5 mm/min) until fracture occurs. By applying equation (2.1) the flexural strength (σ_f) was determined [18]

$$\sigma_f = \frac{2F}{\pi d\, h} \quad \text{……(7)}$$

.6- RESULTS AND DISCUSSION:-

1- Transmittance of epoxy / silica hybrids :-

The UV-vis absorption spectra in the range 400-800 nm for the TEOS/epoxy and pure epoxy, the transparence of sample A (R=1) (88-94%) is much higher than pure epoxy but the transparence of sample B (R=2)(77-80) and sample C (R= 3) (75-80) is a little lower than of pure epoxy showed figure (2) due to the sample A small silica particles compared with samples B and C large silica particles with large scattering area are likely to cause opaqueness sample which agree with [19] due to the increased scattering loss and low transparence.

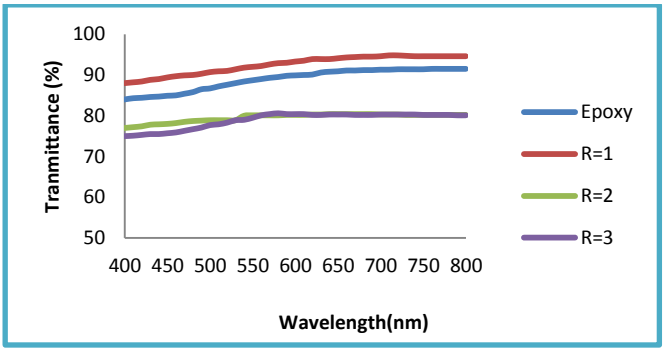

Figure (2) transmittance spectra of silica / epoxy hybrids

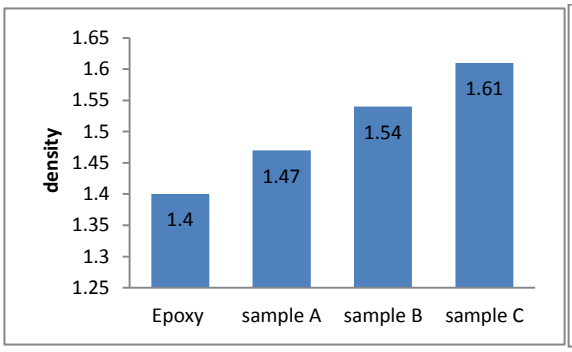

Figure (3) the density as a function of epoxy and hybrids.

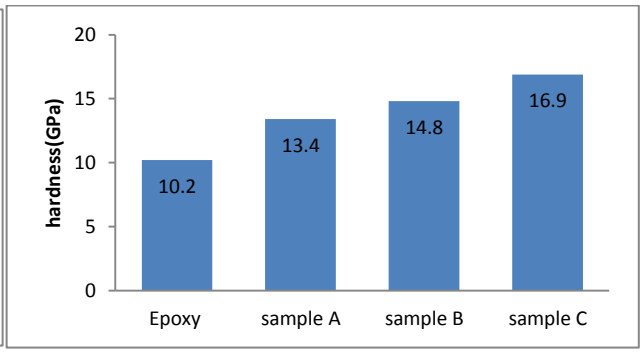

Figure (4) values of hardness as a function of epoxy and hybrids.

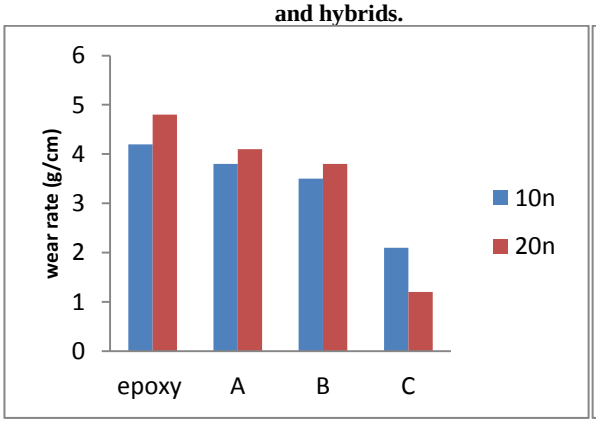

Figure (5) wear rate as a function of epoxy and hybrids .

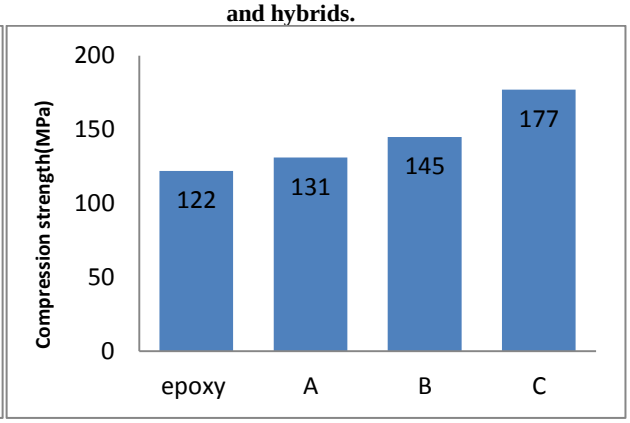

Figure (6) compression strength as a function of epoxy and hybrids.

2- Physical properties :-

2.1 Density :-

The density of hybrids increases as compared to epoxy pure, due to chemical and ceramics composition of the materials, has a significant effect on the density as shown in figure (3).

2.2 Micro hardness

Figure (4) represents Micro-hardness. The hardness test indicates the deformation which happens on the surface of a material. The hardness could be attributed to the increase in the intensity of the cross links between the bonds of the materials. The results show agreement with others [20].

2.3 Wear rate test :-

Figure (5) shows the wear rate of the epoxy pure and hybrids materials, tested at a sliding speed of 10 mm/s as a function of molar ratio (R), decrease in the friction coefficient of the hybrids with an increase in the molar ratio of R. The silica became harder than the epoxy which can easily be removed at sliding surfaces; the results agree with others[21].

2.4 Brazilian disk fracture test :-

Figure (6) compression strength values increasing with increase in the molar ratio (R), the epoxy pure 122 MPa and the samples (R=3) up to 177 MPa. The silica dispersed in epoxy matrix may create creased structures that have a tendency to unfold rather than stretch under applied load, showing agreement with others [22]

7-CONCLUSIONS :-

Sol-gel method when applied, resulted in a new class of epoxy/silica nano-hybrids. An improvement in the compatibility between the polymer and silica phases and other mechanical properties, like hardness, wear resistance and compression strength was observed.

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