ISSN : 0974 - 7486 Volume 11 Issue 8

Materials Science

An Indian Journal

Full Paper

MSAIJ, 11(8), 2014 [282-290]

Thermal mechanical and morphology characterization for epoxy/ grafted marble and granite powder composites

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ABSTRACT

Direct radiation method has been used to graft styrene and acrylic acid monomer on to marble and granite powders. The grafted marble and granite powders were used as a filler of epoxy composites, they added to epoxy resin at weight percentage 20, 60 and 100 then cured at room temperature. The experimental results showed that the dispersion of marble powder in polymer matrix is remarkably improved, when the marble powder is grafted with monomers, the micro-hardness and impact strength of epoxy filled the modified marble were higher than those of unmodified. When the epoxy was filled by unmodified and modified marble powder, its thermal stability was remarkably improved.

KEYWORDS

Epoxy;
Filler;
Surface modification;
Gamma radiation.

INTRODUCTION

Epoxy resins are one of the most important classes of thermosetting polymers, epoxy resins are widely used for many applications from microelectronics to space vessels in modern technology. Research efforts on epoxy resins have been focused on improving their thermal and mechanical stability, raising glass transition temperatures, increasing dimensional stability, lowering the dielectric constant, and enhancing flame retardance. An approach aiming to simultaneously achieve these objectives is reasonably attractive for epoxy resins used in modern electronic and electrical products, sealants, paints, coatings, and adhesives[1]. Epoxy resins are relatively expensive; however, the long service time and good physical properties often help by providing a favorable cost–performance ratio when compared to other thermosets. The main fields where fire-retardancy of epoxy resins is required are electronics (printed wiring boards and semiconductor encapsulation) and transportation (automotive, high speed trains, military and commercial aircraft) in composite structural and furnishing elements[2].

In the plastics industry, the addition of filler materials to a polymer is a common practice. This improves not only stiffness, toughness, hardness, heat distortion temperature, and mold shrinkage but also reduces the processing cost significantly. In fact, more than 50% of all polymers produced are in one way or another filled with inorganic fillers to achieve the desired properties[3].

Formation of organic–inorganic nanocomposites has shown the ability to provide such a simultaneous improvement in several properties. To improve toughness and thermal resistance, the addition of filler particles of micro- or nano-size is becoming a common practice, because it not only improves the mechanical properties of the resulting polymer but also significantly reduces the processing cost[4]. This improvement depends strongly on the particle content, particle shape and size, surface characteristics, and degree of dispersion[5].

Surface treatment of fillers is one of the techniques often used to modify interactions in particulate-filled polymers. Among all the rigid fillers used in polymer matrix, calcium carbonate is one of the most preferred. However, there are two obvious disadvantages for calcium carbonate. Firstly, the higher surface energy and unstable thermodynamic state of calcium carbonate induce the poor dispersion of fillers. Secondly, the poor compatibility between calcium carbonate and polymer as the result of hydrophilic characteristics of CaCO3 will influence the mechanical properties of final composites[6].

In the present paper, direct radiation method has been used to graft acrylic acid and styrene monomers onto marble and granite powder fillers. The properties of grafted marble and granite powders were studied. Furthermore, the effects of grafted marble and granite powders on the properties of epoxy composite were discussed.

MATERIALS AND EXPERIMENTAL

Materials

Marble

Marble and granite (G) wastes were collected from Suez and Aswan respectively, Egypt. It was grinding by using Boll mill and sieved at ≤ 63 μm powder. The chemical composition of the marble and granite is summarized in TABLE 1.

Epoxy

The studied system is based on a commercial diglycidyl ether of bisphenol A, (DGEBA) (kimapoxy 150), from chemicals for modern building international (CMB) Co., with epoxide equivalence weight in the range of 182–196 g/equiv and density at 25 °C (1.11 g/cm^3). The curing agent used was cycloaliphatic polyamine supplied by (CMB).

Monomers

Styrene monomer with density 0.905gm/Cm^3 and stabilized by 0.001 to 0.002 tert- butylcatechal. It has been supplied by the Aldrich chemical Co. The acrylic acid monomer has been supplied by the spectrum, Min 98%, color (APHA) 15 and water 0.07%.

Solvent

Methyl Alcohol**,** Pure reagent for analysis and molecular weight 32.04, Min. assay 96%, wt. per mL at 20°C about 0.79-0.7939. Methyl Alcohol has been supplied by the (Elnasr Pharmaceutical chemical. Co) Adwic, and ionizing water

Surface modification of marble and granite

Marble and granite powders grinding by using Boll mill and sieved at different grain size (360, 250, 200, 100, and 63) μm, the ≤ 63μm powders were used. Solvent (*Methyl Alcohol: Ionizing Water*) (70:30) % percent. Monomers (*Styrene*, *Acrylic Acid*) soluble in solvent and then added to powder at different ratio. The mixer magnet stands for 30 min by using magnetic starrier. Put the mixture in dry oven at 50°C for time 24h. The dried powder irradiated at (30, 10) KGy for respectively.

Preparation of epoxy / marble (granite) composites

Hardener should be poured into epoxy resin at different ratio and mixed together using a suitable mechanical mixer for a period of 3 minutes. The velocity of the mixer must not exceed 300 r.p.m. In the case epoxy / marble (granite) composites, fillers is added to the mixture and mixed again for a period of 3 minutes. The mixture is then transferred to molded (12 ×1.5 mm) for 24 h. The samples de-molded and then analysis.

TABLE 1 : Chemical composition (wt %) of marble [M] and granite [G]

Commercial Name	Na	K	Mg	Ca	Cl	S	Al	Si	Mn	Fe	Cu	Zn
Glalla- ElSuez [M]	**	**	0.2	97.8	0.3	0.1	0.13	**	**	**	0.9	0.9
Fray - Aswan [G]	9	7	**	2.73	0.2	0.2	12.6	57	0.5	10	0.8	0.9

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X-ray diffraction (XRD)

A sample of the prepared powder materials are put in an appropriate aluminum holder. XRD patterns of the slab samples of the prepared were then measured. Here, XRD scanning was carried out by a fully computerized X-ray diffractometer, (Shimadzu type XD-6000).

Scanning electron microscope (SEM)

SEM was used to characterize the powder particles, and also to identify the interfacial adhesion between polymer resin particles and powders particles. Fracture surfaces were obtained by compression of the specimens. Surface of fracture was sputtered with thin layer of gold. SEM micrographs were obtained with a JSM-5400 (Jeol / Japan).

Thermal analysis

Differential thermal analysis (DTA)

Differential thermal analysis (DTA) is the technique of measuring the heat effects associated with the physical or chemical transformations that take place as the substance is heated at a controlled rate. Measurements of the temperature T and the difference ΔT over suitable range will give a program characteristic of the occurred reaction. A Shimadzu micro-DTA model DT-30 was used.

Thermal gravimetric analysis (TGA)

The thermal decomposition behavior of the different composites were investigated by thermo-gravimetric analysis (TGA) using a TG-50 instrument from Shimadzu (Japan) at a heating rate of 10 ° C/min.

Vickers hardness test

Microhardness (HV0 tested (Shmadzu Micro-Hardness HMV-2) are performed on epoxy and its composites at load 25 kgf and speed 10 mm/min.

Impact toughness measurements

The impact toughness (IT) measurements have been carried out on the unnotched composite test samples. A pendulum impact apparatus PSW-4J (Gerhard Zorn

TABLE 2 : Glass transition temperature T_g of epoxy / marble (M) and granite (G) powders composites before and after treated with acrylic acid (AA) and styrene (S) monomers

Composition	T_g [untreated Filler]		T_g [Treated with AA]		T_g [Treated with S]	
Ratio of filler	M	G	M	G	M	G
Epoxy	63.11	****	****	****	****	****
20 %	64.93	63.33	57.35	56.77	61.07	59.3
60 %	63.82	61.75	57.41	56.47	56.13	58.73
100 %	62.55	65.2	58.7	57.61	58.67	58.29

TABLE 3 : Weight remaining (%) of epoxy / marble (M) and granite (G) powders composites before and after treated with acrylic acid (AA) and styrene (S) monomers

Temperature [°C]	Epoxy	Epoxy/ untreated M			Epoxy/ grafted M with AA			Epoxy/ grafted M with S		
		Filler content [%]			Filler content [%]			Filler content [%]		
	****	20	60	100	20	60	100	20	60	100
350 °C	77	74.1	83.3	83.6	61.7	84	82.9	73.8	81.9	83.9
440 °C	32.4	39.3	38.5	62.5	38.5	56.1	56.5	37.5	47.3	59.1
560 °C	20.2	16.9	21.2	45.3	20	38.5	37.1	25.8	32.9	44.4
680 °C	1.59	9.95	7.54	37.1	10.2	31.1	34.9	10.6	20	32.7
		Epoxy/ untreated G			Epoxy/ grafted G with AA			Epoxy/ grafted G with S		
		Filler content [%]			Filler content [%]			Filler content [%]		
	20	40	100		20	40	100	20	40	100
350	78.37	81.77	80.85		71.66	81.54	81.85	72.21	80.9	83.19
440	45.55	59.91	59.19		27.21	54.94	57.59	45.5	53.27	58.49
560	25.9	40.16	37.09		25.09	36.61	41.54	25.09	32.92	41.21
680	20.52	40.86	36.39		12.27	35.44	40.38	19.81	31.79	40.86

Mechanische Werkestatten, Stendal, Germany), have been used in this test according to ASTM standards (D-256, 1987).

RESULT AND DISCUSSIONS

Surface modification of marble (M) and granite (G) powders

Marble (M) and granite (G) modified by used monomers (styrene and acrylic) at different ratio (2.5, 5, 7.5 and 10) and choose the percent 7.5% to study before and after irradiation.

X- Ray Diffraction

Figure 1 & 2 shows the X-ray diffraction patterns of the marble (M) and granite (G) with (7.5%) acrylic and styrene, respectively. It can be noted that the marble and granite materials are constituted by calcium carbonate silica and minor amounts of elements. Figure 1 show that the additive of present (7.5) of acrylic and styrene monomer before and after irradiating by using dose (10, 30) KGy, respectively. Few change in grafted marble with AA and appear clear in grafted marble with styrene. Meanwhile in Figure 2 the acrylic increases the amorphous phase and with styrene the crystallinty increase after irradiated. The styrene monomer affected on granite powder before and after irradiated by dis-

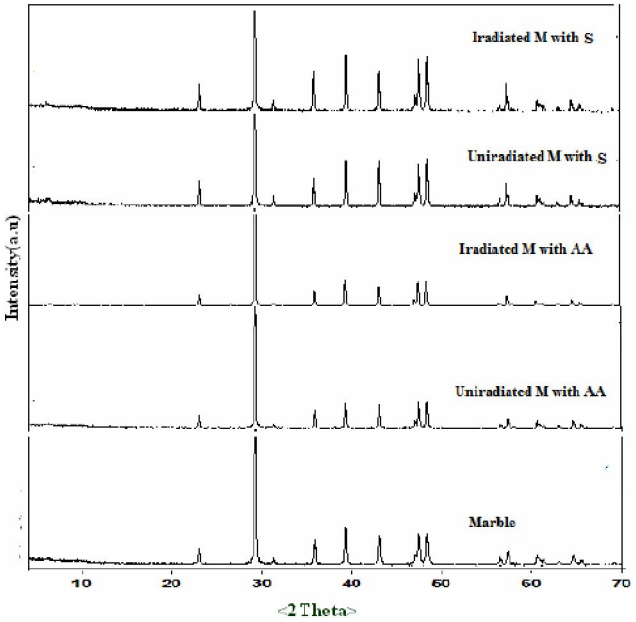

Figure 1: XRD of untreated and grafted marble with 7.5% of acrylic acid and styrene monomers

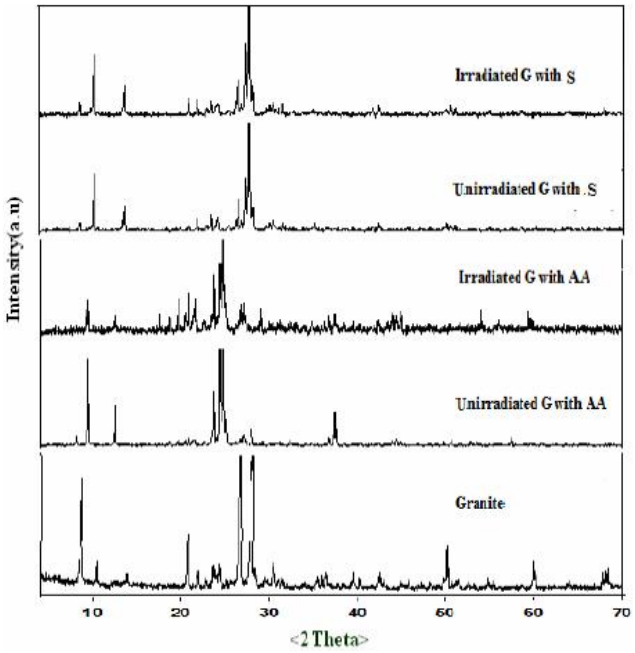

Figure 2: XRD of untreated and grafted granitewith 7.5% of acrylic acid and styrene monomers

appear some phases, meanwhile in marble no affected. This is related to crosslink inter the network of composition. Styrene monomer linked with atoms in marble and granite higher to acrylic.

Scanning electron microscope

The morphology of the sample is shown in Figure 3. a, b, c, d with acrylic and styrene monomer. Exhibit a continuous grain growth, this is related to coated with irradiation. Shows individual grains, which are irregular in size & shape, and separated by well defined inter – grain boundaries. The droplets are substantially spherical and have convex surfaces, this increase after irradiation with acrylic and decrease with irradiation. Figure (3, a) show coat clear after irradiation with increase meanwhile decrease the size of grain with still the island.Figure (3, b) show coated with a few change in structure. The shape and size of grain in Figure (3, c) increase with irradiation and arrangement of island structures, this is related to silica. Meanwhile, in Figure (3, d) show big grain with styrene after irradiation but redo nearly the same structure.

Characterization of epoxy / marble composite

Mechanical properties of epoxy /marble composites

Micro –hardness

Micro –hardness expresses the stress required to

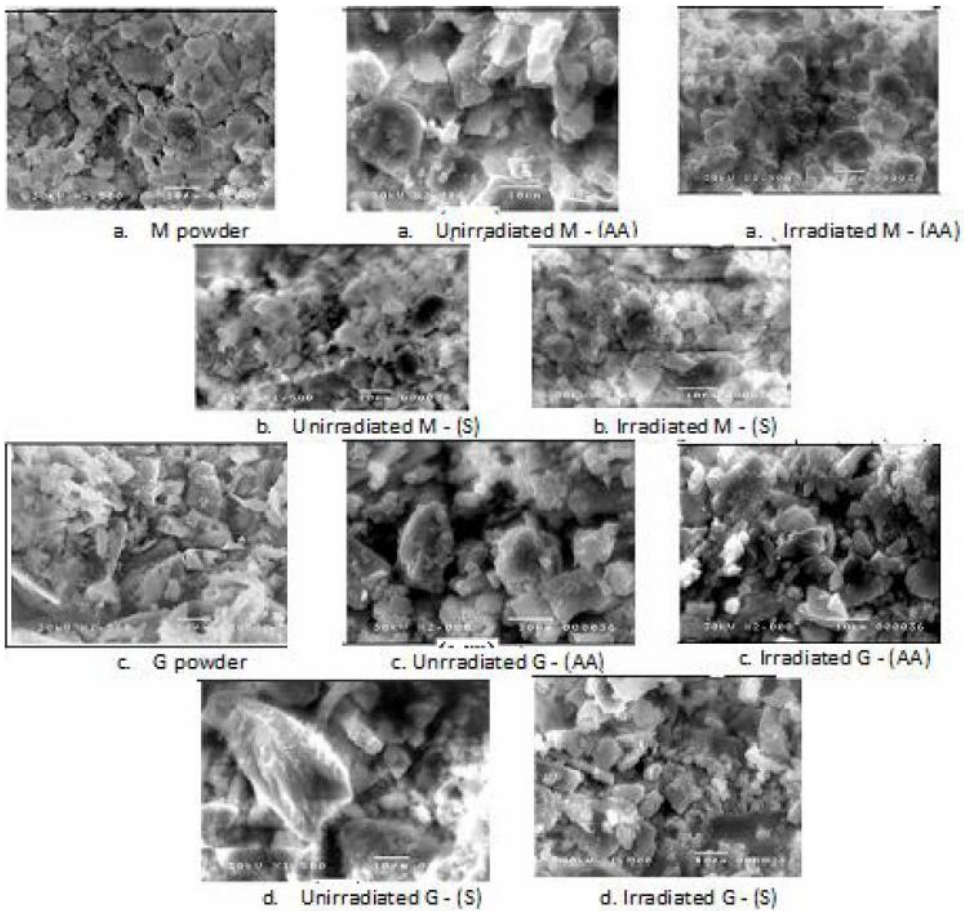

Figure 3 : SEM of untreated and grafted marble (granite) with 7.5% of acrylic acid and styrene monomers

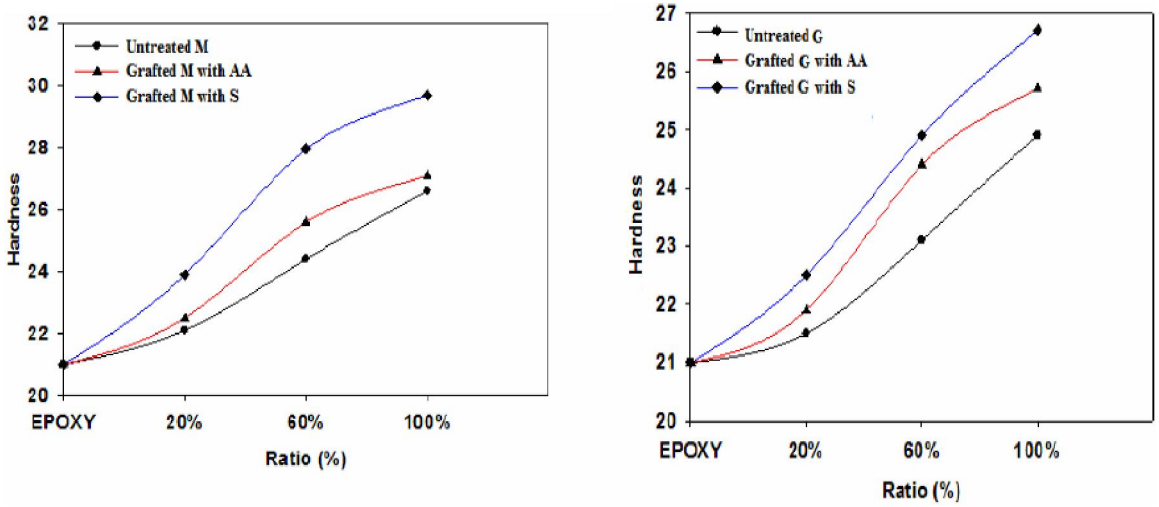

Figure 4 : Effect of untreated and grafted marble (granite) ratio on micro-hardness of epoxy /marble (granite) composites

eliminate the free volume (deformation of the network) of the sample. As seen from Figure 4, the micro-hardness increases as (M, G) content increases indicating the increase in the rigidity[7]. These indicated that with increase (M, G) the hardness increase and the hardness of (M)> (G) with epoxy. Meanwhile, after treatment marble and granite fillers, the hardness of (M, G) with styrene and epoxy higher than to acrylic. This is related to the close of network of atom increase with styrene.

Impact strength

Figure 5 illustrates the effect of irradiation on the

impact resistance of the (M, G) with epoxy at different ratio. These results show that increase of impact resistance values for composition with increase the percentage of (M,G). In Figure 5 the impact strength with acrylic had greater than styrene after irradiation, meanwhile, in Figure 5 granite irradiation before greater than after irradiation. The irradiation effect on marble higher than granite. These results indicate that irradiation treatment of (M, G) with epoxy. In composition there improvements in the interfacial bond as results the presence of delocalization, which is higher sensitive towards the irradiation.

Thermal properties

Differential thermal analysis (DTA)

Thermal behaviors of the marble and granite wastes in terms of DTA, are displayed in Figure 6, respectively. The transition glass temperature Tg (M & G)before and after irradiation listed in TABLE 2. A loss in weight equivalent to 45 % indicates the relatively high content of $CaCO_3$, SiO_2 in the composition about 100%. DTA curve in Figures. a shows a sharp endothermic peak attributed to the dissociation reaction of $CaCO_3$, SiO_2. DTA curve of the stoichiometric from the wastes CaO: SiO_2, 1:1, Figure 6 at (100 % M), show a sharp endothermic peak attributed to the dissociation reaction of CaCO3 and an exothermic attributed to the formation of metasilicate (calcium and magnesium silicate[8].

In all curves except the latter one, the shift of the endothermic peaks towards higher temperature is very slight with increase (M, G) and epoxy; it indicates that the activation energies associated with these processes are very high. As (M, G) rises, an endothermic reaction process appears, which can be dependent on the T_g of epoxy inside the composition. This result is in good agreement with the equilibrium phase diagram which is dominated by their temperature dependent thermodynamic equilibrium. With increasing (M, G) the samples yields asymmetric exothermic peaks. At the higher temperature side, the fusion follows the crystallization process. This figure shows that the present results are in agreement with previous DTA analysis at a heating rate of the 10 deg/min.

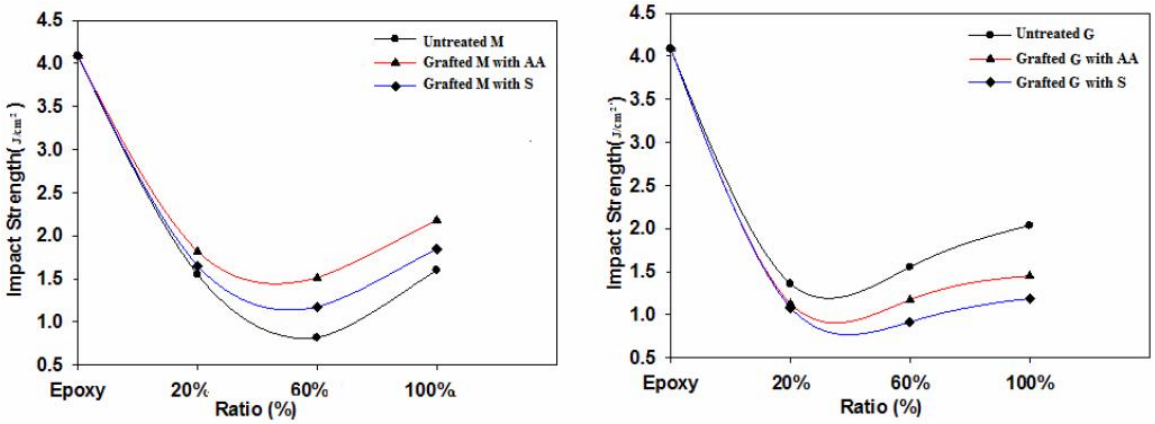

Figure 5 : Effect of untreated and grafted marble (granite) ratio on impact strength of epoxy/ marble (granite) composite

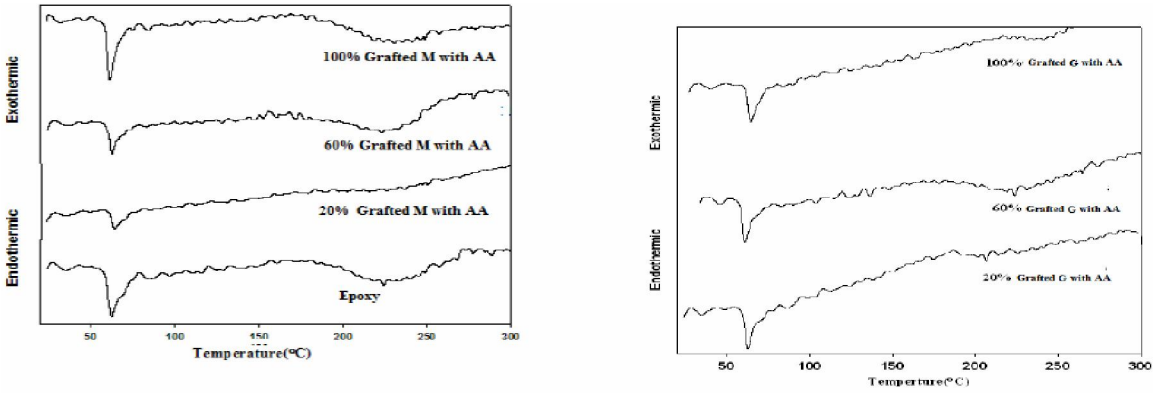

Figure 6 : DTA thermogram for epoxy/ grafted marble with acrylic acid composites

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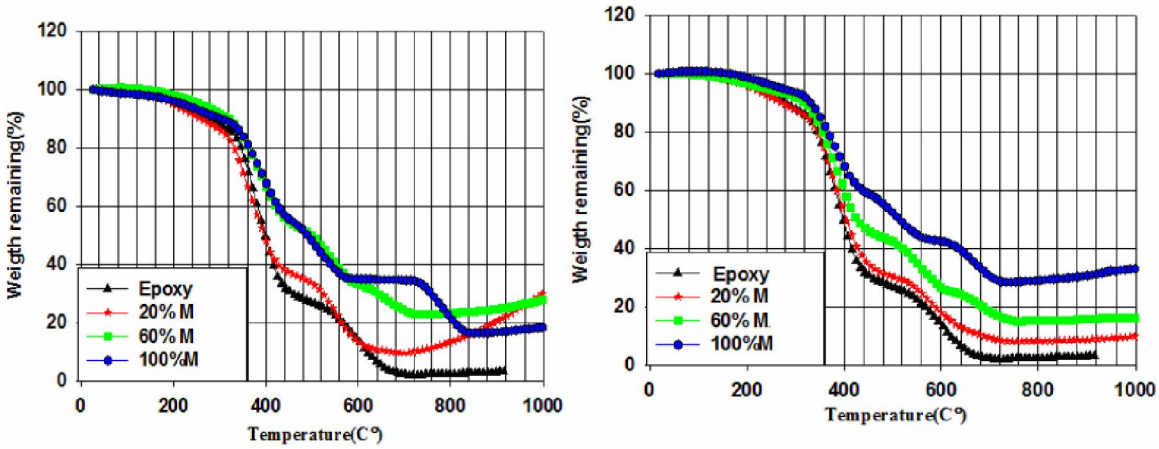

Figure 7 : TGA thermogram of epoxy/ grafted marble with acrylic acid composites

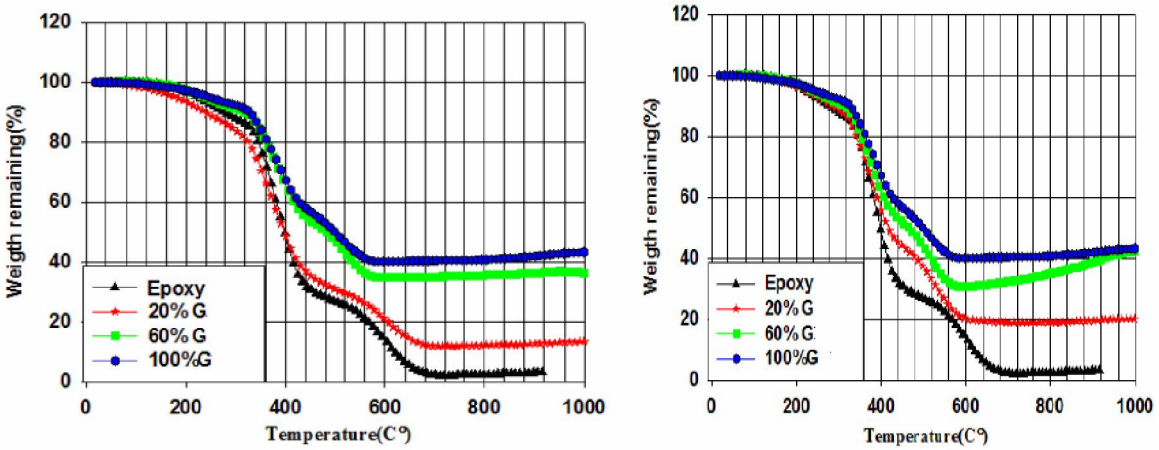

Figure 8 : TGA thermogram of epoxy/ grafted granite with acrylic acid composites

Thermal gravimetric analysis (TGA)

TGA is the most favored technique for rapid evaluation in comparing and ranking the thermal stability of various polymer[9,10] Thermo-gravimetric (TG) and differential thermal analysis's (DTA) are considered important tools to qualifying the different phases.

Figure (7 : 10) shows the TGA, curves of (M, G) with epoxy before and after irradiation, respectively.it exhibited weight remaining at temperatures (350, 440, 560 and 680) °C, shown data in TABLE 3. The results indicated that (M, G) cured with various weight ratios have higher char yield than before irradiation and thermal stability than after irradiation. It can be seen that TG curve for (M, G) paste consists of three to four zones in most samples but in some ratio after irradiation the zones increase to five and six step as (100% M with styrene and acrylic), respectively. While decrease this zone tow zones with (G) after irradiation as shown in TABLE 3. This phenomenon played an important role in improving the composition. The incorporation of (M1, G11) into epoxy resin improves thermal stability and enhances the degradation.

Temperature according to its percentage concentration Figure (7: 10). The presence of $CaCO_3$, SiO_3 networks in the epoxy system delays the degradation process, since high thermal energy is required to attain the same percentage weight loss than that required for unmodified epoxy system. The thermal degradation temperature of the $CaCO_3$, SiO_3 modified epoxy systems are increased with increasing M, G concentration. This may be due to the formation of inter crosslinking network between epoxy and $CaCO_3$, SiO_3 and the presence of rigid heterocyclic ring structure[11]. The thermal stability of unmodified epoxy and siliconized epoxy coating systems cured by M1 and G11 was studied using thermogravimetric[12].

Scanning electron microscope

The morphology of the samples is shown in Figure

9& 10 with epoxy. Shows small grains, which are irregular in size & shape, and separated by well defined inter – grain boundaries. Exhibit a continuous cavities growth, this is related to increase (M) Figure 9. These cavities could have that have fallen away from the resin after failure under tensile loading. Premature failure of the material may result from cracks initiating at the voids or at the interfaces where possible poor adhesion exists between the agglomerates and the resin. Another possibility is that because the (M, G) has a much greater modulus than the polymer, stresses concentration may have existed at the interfaces of the (M, G) and epoxy matrix. Therefore, under tensile loading, cracks can initiate at those weak points and cause the specimen to fail at relatively low strains[13]. And Figure 10 this convex to stick to each other, and to present in the same co-matrix phase[14]. These two last regions are characterized by a steady increase of the surface roughness and by the presence of conic marks. The micrographs of the materials modified with (M, G) presented aspects of the fracture mechanism Figure 9, 10 in which the (CaO,SiO) particles were partly pulled out from the epoxy matrix and partly fractured. In this case, it shows that the crack developed through the (CaO, SiO) particles and indicates that the interaction between the particle and the matrix has occurred. The presence of the elastomeric particles also led the materials to fracture in a way more akin to ductile materials than in the case of the neat epoxy[15].

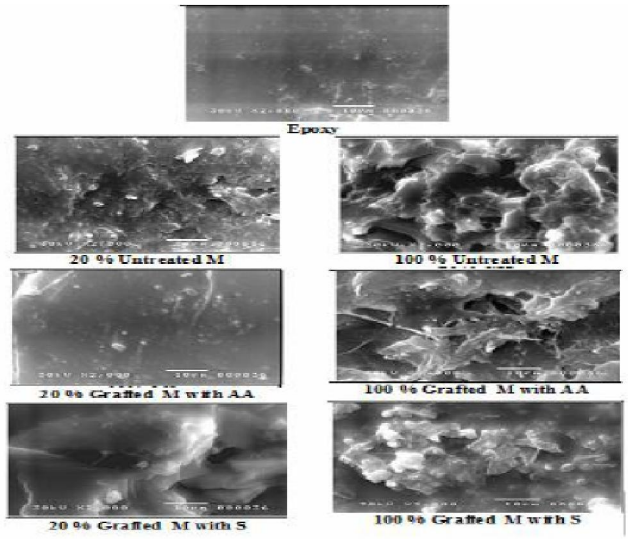

Figure 9 : SEM of epoxy/ grafted marble composites

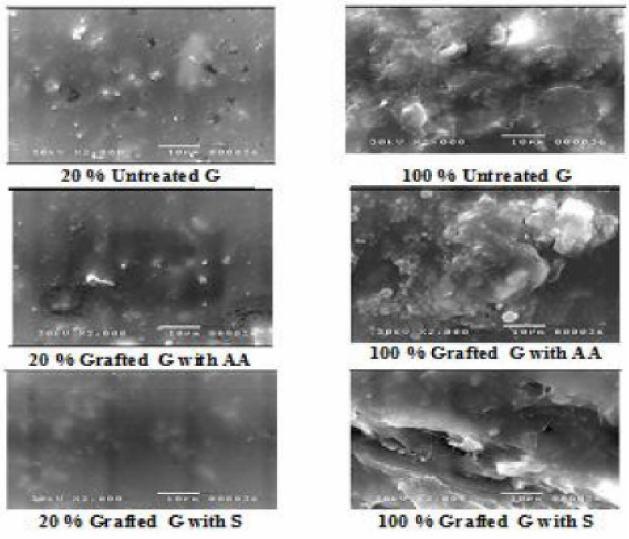

Figure 10 : SEM of epoxy/ grafted granite composites

CONCLUSION

The micro-hardness increased as (M, G) content increased indicating the increase in the rigidity. Meanwhile, before irradiation the hardness of (M, G) with styrene and epoxy were higher than to acrylic. Impact resistance values for composition increased with increase the percentage in mix composition. It was also observed that the impact strength of M with irradiation greater than G.

Differential thermal temperature (DTA). In all curves except the latter one, the shift of the endothermic peaks towards higher temperature is very slight. This result is in good agreement with the equilibrium phase diagram dominated by their temperature dependent thermodynamic equilibrium. Thermal gravimetric analysis (TGA). The incorporation of marble (granite) into epoxy resin improves thermal stability and enhances the degradation.

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