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RADIATION-INDUCED PREPARATION OF POLYESTER/ GYPSUM/ COMPOSITE

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Composites based on commercial available gypsum and polyester-styrene resins have been prepared using gamma rays. Some properties of the prepared composites and the influence of the irradiation dose on them have been studied as: compression strength, hardness, glass transition temperature (Tg), thermal decomposition temperature, and the change in weight in aqueous solutions with different pH values. Increasing the irradiation dose leads to an enhancement of the compression strength of the pure polymer at low doses, and it decreases with increasing irradiation dose. The compression strengths of the prepared composites are lower than that of the pure polymer and decreases with increasing the filler ratio. The irradiation dose does not affect the compression strength considerably. Tg of the composites increases slightly with increasing irradiation dose, and becomes higher than that of the pure polymer. The irradiation dose does not seem to affect the thermal decomposition temperature of the pure polymer or the composites significantly. Soaking experiments show that the weight of composites does not change in distilled and alkaline medium, but there is a limited increase in acidic medium of about 1% after 1228 hours.

INTRODUCTION

Polymeric materials have been used increasingly in building construction, in the automotive industry and in aerospace technology. Polymeric materials are virtually able to compete with conventional materials in most industrial fields. In the factory, the appliances, and in the recreation and leisure industries, polymers have contributed substantially to the development of better, cheaper and more functional products.

Desired properties of composites could be achieved by incorporating special fillers into a polymer matrix to suit various applications.[1] Addition of finely divided particulate fillers to polymeric materials has already been utilized in the rubber industry for modifying polymer properties. Carbon black has been used for a long time; some work has already been puplished regarding this theme recently as.[2-3] Silicas are also used to modify polymeric materials.[4-6] Gypsum and alumina were also used as filler for preparing polymer composites with some monomers.[7-8] Unsaturated polyester resin has already been used as a cheap polymer for preparing polymer/ composites with inorganic fillers.[9-10]

The present work reports the preparation of composites consisting of unsaturated polyester-styrene resin and commercially available gypsum using gamma radiation, and the investigation of the influence of gamma radiation on some of their properties.

RESULTS AND DISCUSSION

1. Compression strength

Fig. 1 represents the stresses at break of the polyester-styrene resin and polyester-styrene resin/ gypsum/ composites with respect to the irradiation dose for various gypsum ratios. The stress of the pure polyester-styrene resin increases for doses below 50 kGy, and then it decreases with increasing irradiation dose up to 300 kGy. The last value at 300 kGy is still comparable with the starting value at 20 kGy; it is only 1.6% lower than the starting value. It can also be seen that the stresses of the composites are lower than that of the pure polyester-styrene resin because the tensile strength of gypsum (filler) is lower than that of the polymer, which worsen the total mechanical

properties of the mixture.[13] Moreover, it can be observed that the stress of the composites becomes lower with increasing the filler ratios in the composite system due to the same reason mentioned above. The irradiation dose does not seem to affect the stress of the composites considerably.

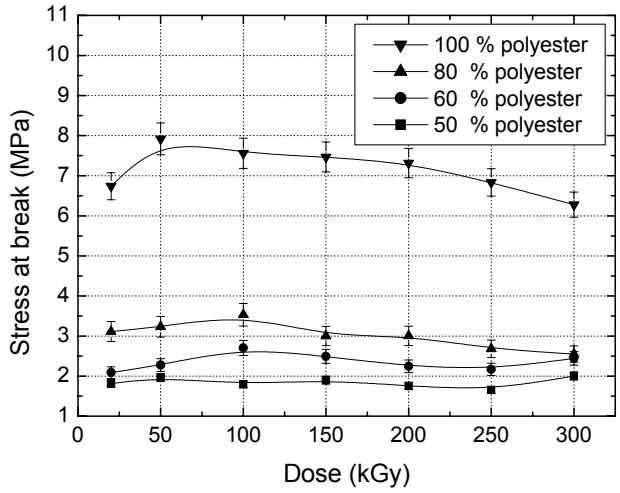

Fig. 1 – Stress at break (compression strength) of pure polyester-styrene resin and the prepared composites versus the irradiation dose (commercial gypsum).

2. Hardness

The hardness of polyester-styrene resin and the prepared polymer composites is represented in Fig. 2 versus the irradiation dose. The hardness is not affected significantly by the irradiation, but the hardness of the polymer composite seems to be a little higher than that of the pure polymer, what may be due to the used filler particles.

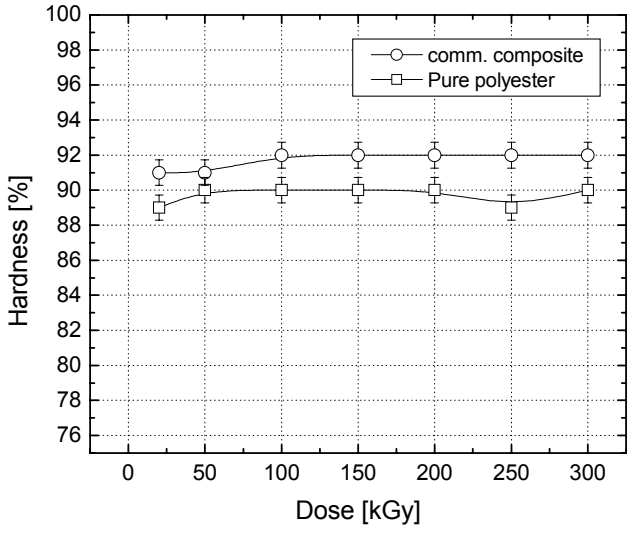

Fig. 2 – The hardness of pure polyester-styrene resin and the prepared composites versus the irradiation dose.

3. Thermogravimetry

The prepared composites have been investigated using thermogravimetry (TGA) in order to follow the thermal degradation reactions. Typical dynamic TGA thermograms of pure gypsum, pure polyester-styrene resin and polyester-styrene resin/ gypsum/ composite are shown in Fig. 3.

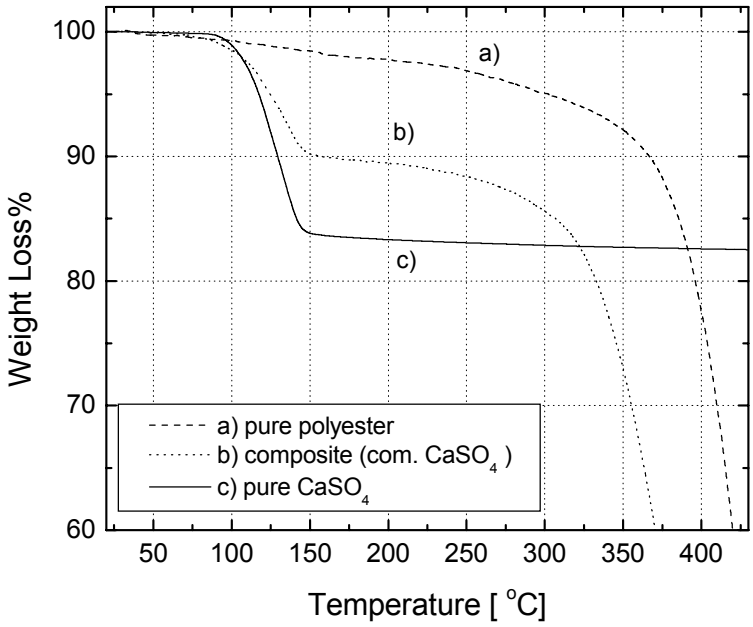

Fig. 3 – TGA thermograms of polyester-styrene resin and polyester-styrene resin/ gypsum/ composite in presence of nitrogen for samples irradiated at 20 kGy.

The TGA thermogram of the gypsum powder shows only one step (on-set = 107.55 °C) related to hydration water, and there is no interference with the other steps related to the polyester or the composite decomposition. The polyester and composite samples were prepared at a dose of 20 kGy, which is a little higher than the dose required for the solidification of polyester-styrene resin. By comparison of the decomposition temperatures of the pure polymer and the composite, the temperature is significantly decreased in presence of the inorganic filler; the filler seems to affect the mechanism of thermal degradation of the polymer. This is a generally observed behavior that inorganic particles, irrespective of the amount and type of filler, decrease the thermal stability of the polymer composites. The main reason for inducing of thermal instability is believed to be an indirect one, namely improved and effective transfer of heat to the polymer phase through the dispersed inorganic phase.[12]

The influence of irradiation dose on the thermal degradation reaction of polyester-styrene resin and polyester-styrene resin/ gypsum/ composites in presence of nitrogen has also been investigated. The decomposition temperatures for both systems are determined for irradiation doses ranged between 20 and 300 kGy. No significant change in the decomposition temperature could be observed.

4. Glass Transition Temperature

Fig. 4 represents (as a demonstration example) a TMA thermogram with alternated force for a polyester-styrene resin sample irradiated at 20 kGy; this dose is more than enough to harden the composites. The elongation increases significantly at the glass transition interval. In order to locate the T*g,* TMA thermograms were also recorded using a constant force.

Fig. 5 shows the Tg's of polyester-styrene resins and polyester-styrene resin/ gypsum/ composites versus the irradiation dose. The Tg of the pure polyester increases slightly for low irradiation doses (< 50 kGy), and then the Tg decreases. The increase in the Tg can be explained that the segmental mobility of the polymer chains is reduced due to the crosslinks built between the polymer chains via irradiation. The decrease of the Tg can be attributed to the degradation of the polymer induced by radiation. The Tg of another polymer used previously from the company Abrasivi Civitanovese, Italy (trade name: Super Mastics) increased with increasing irradiation dose up to 320 kGy.[9] This different influence of the radiation on the polymers can be due to different chemical components in the resin.

It can also be seen that the glass transition temperature of the polyester-styrene resin/

gypsum/ composites increases with increasing irradiation dose, than it becomes higher than that of the pure polyester-styrene resin for doses higher than 100 kGy. This increase in the Tg of the composite system could be attributed to reduced segmental mobility in the vicinity of the filler particulates, which is also observed in other composite systems.[7,12]

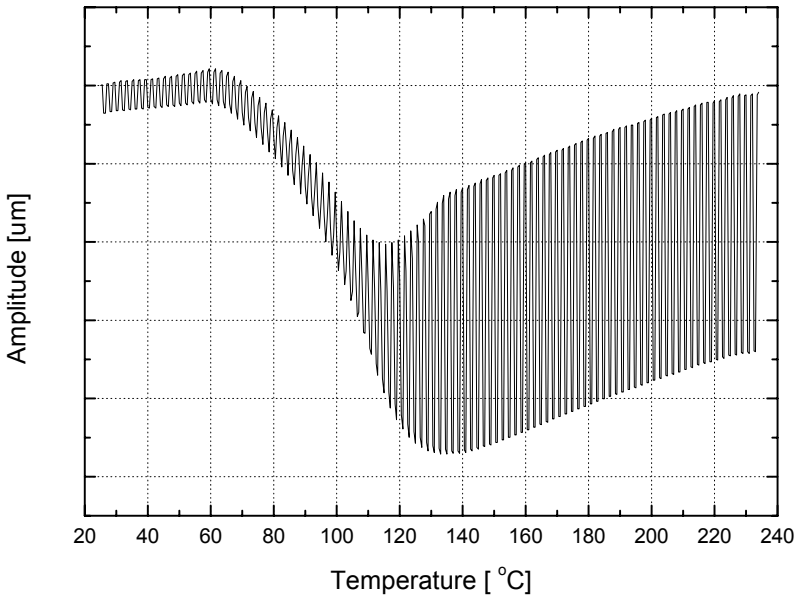

Fig. 4 – TMA thermogram with alternated force for polyester-styrene resin sample irradiated at 20 kGy.

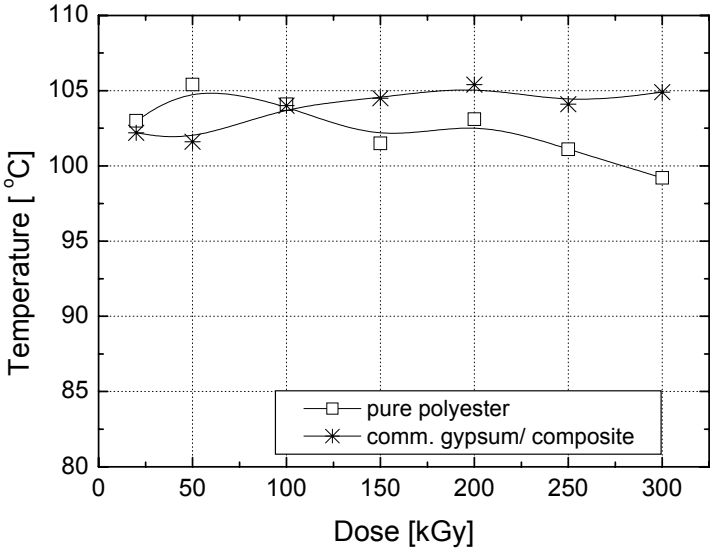

Fig. 5 – Glass transition temperatures of polyester-styrene resins and polyester-styrene resin/ gypsum/ composites versus the irradiation dose (TMA measurements with constant force).

5. Water uptake

Samples irradiated at 20 kGy were soaked in distilled water, acidic and alkaline mediums and the weights were measured at different time intervals.

Fig. 6 shows the water uptake% versus the soaking time. A very small change in weight was observed in distilled water and alkaline medium; a small increase in the weight around 1% weight was observed in acidic medium after 1228 hours of soaking. This fact suggests the use of such composites in contact with aqueous solutions.

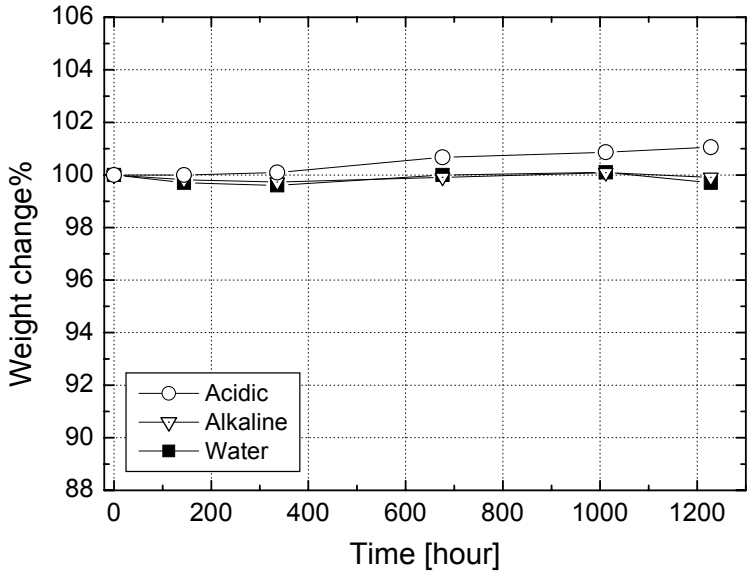

Fig. 6 – Water uptake of composites in solutions of different pH values, which are prepared at an irradiation dose of 20 kGy.

EXPERIMENTAL

Natural gypsum powder was used, which is produced domestically from natural rocks in a mine near the city of Latakia in Syria. Unsaturated polyester-styrene resin was supllied by General, Modena, Italy (trade name: General): degree of unsaturation = 53%; viscosity (60 ^{o}C) = 315-328 mPa.sec; acid number = 17-18 [mg KOH/g]; refractive index (25 ^{o}C) = 1.5365.

The gypsum powder was added to the liquid polymer step by step during stirring at room temperature; the highest achieved ratio was 1:1 in weight. The polymer/ gypsum/ mixtures were filled up in polyethylene (PE) containers with the dimensions 1.2×1.8×13 cm^3. The samples were then exposed to gamma rays using a Russian ^{60}Co γ-irradiator type ROBO (at ambient temperature), and the dose rate was around 6.0 kGy/h.

1. The compression strength

The samples were grinded using a sampler machine (IPT, Germany) to obtain flat surfaces from all sides. Then the compression strength was determined using an Instron instrument Model 1011; for each point, the average of five specimens was calculated.

2. The hardness test

For the hardness tests, the samples were treated as mentioned above; then the hardness was measured with a hardness tester (Kobunshi Keiki Co., LTD., Japan), which is specified according to ASTM D 2240-68 (type D). It was determined by forcing a hard indenter into the surface of the material, and the average of five specimens was calculated for each point.

3. Thermogravimetric Measurements (TGA)

The dynamic weight loss tests were conducted using a Mettler instrument (TG50). The tests were carried out in a nitrogen or oxygen atmosphere, purged (30 ml/ min) using sample weights of 10-15 mg at a heating rate of 10 ^{o}C / min. The resolution of the balance is given, as 1 microgram for weights less than 100 milligram, and the temperature precision of the instrument is ± 2 ^{o}C. The total experimental errors in the determination of the decomposition temperatures were estimated to be not more than ± 3 ^{o}C. The decomposition temperatures of the prepared samples were determined from the dynamic TGA curves using the on-set method, and the intervals are chosen with the help of the first derivative of the curves.

4. Thermomechanical Analysis (TMA)

TMA was used to locate the glass transition temperatures of the prepared samples. A Mettler equipment (TMA 40) was utilized in order to record the TMA spectra. The used instrument has a precision of ± 2 ^{o}C, and the total experimental errors in the measurements were estimated to be about ± 3 ^{o}C.

The PE container, used for the preparation of the samples, was removed and then sheets of ≈ 1mm were cut, polished, and cleaned. TMA spectra were recorded in two modes. The first mode was using an alternated force in order to ensure that there is a real glass transition; alternated force between 0.1 and 0.3 N was applied in the most cases. The second mode was using a constant force of 0.1 N, and the Tg was determined from these TMA thermograms using the on-set method.

CONCLUSION

Polyester/styrene resin/ gypsum/ composites have been prepared using gamma radiation, and some physico-chemical properties of the composites were investigated with respect to irradiation dose. Low irradiation doses < 50 kGy enhance the compression strength of the pure polymer, and the stress decreases then with

increasing the irradiation dose. The compression strengths of the prepared composites are lower than that of the pure polymer and decreases with increasing the filler concentration. The irradiation dose does not affect the compression strength considerably; the hardness of the pure polymer and the composites is not affected significantly by gamma irradiation.

The Tg of the pure polymer seems to be affected by increasing the irradiation dose, and the Tg of the composites increases with increasing the irradiation dose and becomes higher than that of the pure polymer. The irradiation dose does not seem to affect the decomposition temperature of the pure polymer or the composites significantly. The thermal degradation temperature is also shifted to lower temperatures compared with the pure polymer, and the irradiation dose does not seem to influence this property. The swelling experiments showed that the weight has not been changed significantly in solutions with different pH values; lowering in the weight of around 1% was found after 1228 hours of soaking in acidic medium.

Thus this composite system may be considered at places, where materials should resist gamma irradiation up to the studied dose, and it is in contact with aqueous solutions.

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