HOLLOW GLASS MICROSPHERES TREATED WITH SILANE COUPLING AGENT

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The paper presents the results of research on the modification of the surface of empty glass microspheres (quality iM16K) with silanes, to improve the adhesiveness of polyamide 6 (PA6). As a coupling agent, 3-aminopropyl triethoxysilane (APTES) was used; and for its attaching to the surface of the glass microspheres containing borosilicate glass it is necessary to create as many OH radicals as possible on their surface.

Preliminary attempts to generate these reactive groups from water and ethanol by changing the APTES: H2O dilution ratio, contact time, and temperature did not lead to obtaining a continuous and adherent layer of silanes on the surface of the glass microspheres. Under these conditions, it was decided to apply a preliminary chemical treatment to the glass microspheres with about 6% NaOH solution. The best results highlight both by FTIR and SEM analysis were obtained in the condition of NaOH pretreatment followed by 0.5 g from the treated hollow glass microspheres (HGMd) stirred at 60˚C for 1 hour with a laboratory magnetic stirrer in 40 millilitres of APTES.

Keywords: hollow glass microspheres, 3-aminopropyl triethoxysilane, polyamide

1. Introduction

In the current context of the global energy crisis, materials engineering research is focused on obtaining materials that contribute to reducing energy consumption, especially in economic sectors known to be high consumers, such as transportation. Among the ways to reduce energy consumption, especially fuel, specialists' attention is directed towards the use of lighter materials that preserve their basic mechanical and electrical properties depending on the specific application. Hybrid materials like fibre or fibreless-reinforced polymer, come with excellent specific strength and stiffness [1] [2].

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An extremely important aspect in the realization of hybrid materials is the adhesion between the polymeric matrix, for example, polyamide, and the reinforcing materials because the interface properties can cause breakage and delamination [3] [4]. To prevent that, preliminary treatment of reinforcement materials has to be used, and it is noticeable that some studies were made to solve this issue [5-6] [7,8], especially in the case of epoxy /glass balls hybrid materials.

The present work is part of research whose main objective is to obtain a lightweight polymeric material for transportation, based on polyamide 6 (PA6) and 3M Hollow Glass Microspheres (HGM), and it is focused on the attachment of amine terminal groups to the surface of hollow glass microspheres [1] to improve adhesion with the polyamide matrix. There is not much information about PA6/HGM hybrid materials, so the possibility of adapting the surface treatments of glass microspheres, performed by other researchers for hybrid materials with different thermoplastic or thermoset matrices, was studied.

The most used treatment for the functionalization of glass-based materials to achieve their adhesion to the polymer matrix are silanes. The authors [9] studied different types of silanes, with the same organo-functional group, but a different number of alkoxy groups, according to adhesion strength measurements. Their results indicate that di- and tri-alkoxy silanes can increase the bond strength due to their increased stability binding to the glass surface and their ability to form more extensive interphases with the polymer and for that, we decided to use 3-aminopropyl triethoxysilane KH550 (APTES) to treat the bubbles' surface.

Another author F. N. Mutua [1], recommends the application of preliminary treatments of reinforcing materials from glass (hydrochloric acid HCI, piranha solution, NaOH) before APTES binding.

This research was directed to finding the optimal surface treatment conditions for 3M glass Hollow (H2O: APTES ratio, contact time, temperature, drying regime) to ensure uniform coverage of the bubbles with APTES. After preliminary experiments only with APTES in different proportions with water or ethanol as OH sources-in order to introduce the OH groups, was concluded the necessity for special treatment of the surface of the bubble glass using NaOH.

The effectiveness of the treatment was analyzed by the FTIR method which revealed the presence of organic groups and by SEM for the uniformity of the coating.

2. Experimental Details

2.1. Materials

HGM compound of soda-lime borosilicate grade iM16K, density 0.46 g/cm^3 was obtained from 3M, Zwijndrecht, Belgium, 3-aminopropyl triethoxysilane, 98% (APTES, Silane Coupling Agent KH550) was supplied from

Thermo Fisher Scientific, Sodium hydroxide (NaOH), Ethanol - Ethyl alcohol was purchased from Aldrich.

2.2. Characterization methods, techniques and used apparatus

The molecular structure of hollow glass microspheres and attached amino silane was confirmed by Fourier Transform Infrared (FTIR - Thermo Scientific Nicolet iS10) analyses from the Institute of Physical Chemistry Ilie Murguleascu from Bucharest. The Nicolet iS10 FTIR was equipped with a smart diamond ATR accessory and an infrared range of 4,000 to 500 inverse cm, which can run solid or liquid samples. The optical bench is sealed and desiccated with a protective coating on KBr windows [10].

In the end, the apparatus was restarted and calibrated to the normal values, which in end started to display normal results in the test reports and allowed the team to continue with the research.

The morphology of the treated and untreated hollow glass microspheres was investigated using a High-Resolution Scanning Electron Microscopy (HR-SEM, resolution of 1.2 nm) from the department of Science and Engineering of Oxide Materials and Nanomaterials, University of Politechnica of Bucharest. The scanning electron microscope could perform a resolution of up to 1.2 nm and had three vacuum modes (high vacuum, variable vacuum and ESEM mode). The system could also provide energy-dispersive x-ray analysis (EDAX) to identify the elemental composition of the materials. All the images of the analyzed surfaces were recorded in a digital format which helped to have a rapid data transfer of the information [11].

2.3. Amine terminated hollow glass microspheres preparation and procedures

To have a better adhesion of amino, NaOH is a convenient agent in attaching hydroxyl groups on the surface of hollow glass microspheres for the subsequent reaction with APTES silane coupling agent in the fabrication of amino terminated HGMs. After several trials under different conditions, was achieved the optimal chemical ratio and percentage, eventually used in the experiments [1].

Amine-terminated hollow glass microspheres were fabricated using ten different ways, as it is shown in (Table 1).

The first three mixtures (Table 1) were made under the same conditions of preparation, only the amount (ml) of APTES was different; 0.5 grams of hollow glass microspheres (HGM) were used every time and stirred at 90˚C for 1 hour with a laboratory magnetic stirrer in 1/ 5/ 10 millilitres of APTES, diluted in 75/ 71/ 66 millilitres of distilled water ($H2O_d$), filtered through a laboratory paper filter and let dry naturally.

Table 1.

Mixture techniques used in the research study

Condition of prepartion	HGM (iM16K) (g)	Treated with NaOH	APTES KH550 (ml)	Distilled Water H2Od (ml)	Ethanol (ml)	Laboratory magnetic stirrer (h)	Temperature (˚C)	Laboratory thermostat incubator dryer (˚C, min)	Natural dried
1	**0.5**	N/a	1	75	N/a	1	90 ˚C	N/a	Yes
2	**0.5**	N/a	5	71	N/a	1	90 ˚C	N/a	Yes
3	**0.5**	N/a	10	66	N/a	1	90 ˚C	N/a	Yes
4	**5**	N/a	10	66	N/a	1	90 ˚C	65 ˚C, 30 min	N/a
5	**5**	N/a	15	61	N/a	1	90 ˚C	65 ˚C, 30 min	N/a
6	**5**	N/a	20	56	N/a	1	90 ˚C	65 ˚C, 30 min	N/a
7	**5**	N/a	25	51	N/a	1	90 ˚C	65 ˚C, 30 min	N/a
8	**0.5**	Yes	40	N/a	N/a	1	60 ˚C	65 ˚C, 30 min	Yes
9	**0.5**	Yes	60	N/a	60	1	80 ˚C	65 ˚C, 30 min	Yes
10	**0.5**	Yes	60	60	N/a	1	70 ˚C	65 ˚C, 30 min	N/a

The following four mixtures (Table 1) had different conditions of preparation, and the number of APTES was different. 5 grams of hollow glass microspheres (HGM) were used every time and stirred at 90˚C for 1 hour with a laboratory magnetic stirrer in 10/ 15/ 20/ 25 millilitres of APTES diluted in 66/ 61/ 56/ 51 millilitres of distilled water ($H2O_d$). After that was filtered through a laboratory paper filter, from Filtrak, with medium-wide pores/ medium-fast filtering for crystalline deposits, using a laboratory separating glass funnel and then dried at 65˚C for 30 minutes in a laboratory vacuum oven. When the samples were removed from the oven, it was noticed a hard crust on top of the mixture.

Because no results were obtained within the first 7^{th} condition of preparation, preliminary treatment with sodium hydroxide was considered necessary. Initially, we considered using hydrochloric acid, but in the end, sodium oxide was chosen. Therefore, for the last three mixtures, 2g of hollow glass microspheres (HGM) were pretreated in an aqueous solution of 20g sodium hydroxide (NaOH) and 300 ml of distilled water ($H2O_d$), resulting in a concentration of about 6%. This solution was stirred at 90˚C for 1 hour with a laboratory magnetic stirrer, then dried at 60˚C for 10 minutes in a laboratory vacuum oven [1]. Preliminary research was done to introduce oxydryl groups that would be able to bind the HGM from water or ethanol.

0.5 g from the treated hollow glass microspheres (HGM_d) were stirred at 60˚C for 1 hour with a laboratory magnetic stirrer in 40 millilitres of APTES, representing the 8^{th} condition of preparation (Table 1) from this study. The resulting sample was filtered off and washed two times with ethanol followed by distilled water and dried at 65˚C for 30 minutes in a laboratory incubator, then for the next 24 hours were let dry naturally.

For the 9^{th} condition of preparation (Table 1), another 0.5 grams taken from the treated HGM_d were stirred at 80˚C for 1 hour with a laboratory magnetic stirrer in 60 ml of APTES and 60 ml of Ethanol (50-50). The resulting sample was filtered off and washed two times with ethanol then distilled water and dried at 65˚C for 30 minutes in a laboratory vacuum oven, then for the next 24 hours were let dry naturally.

Finally, for the last condition of preparation (Table 1), another 0.5 grams taken from the treated HGM_d were stirred at 70˚C for 1 hour with a laboratory magnetic stirrer in 120 ml of aqueous solution (60 ml of diluted APTES in 60 ml of distilled water). After that, the mixture was filtered off and washed two times with ethanol and distilled water and dried at 65˚C for 30 minutes.

The amine-terminated hollow glass microspheres have been characterized from a composition and morphology point of view, using two methods, FTIR and SEM.

3. Results and Discussions

3.1. FTIR spectroscopy

(Fig. 1) shows FTIR spectra of modified hollow glass microspheres modified using the first four mixture techniques. The FTIR spectrum of HGMs of all first four mixtures does not show any characteristic peak corresponding to the primary amine between 2500 - 3500 cm^{-1}, which is corresponding to the primary amine in HGMs-KH550 [12]. FTIR spectrum of untreated hollow glass microspheres shows a characteristic stretching peak between 1000 - 1100 cm^{-1} corresponding to the Si-O-Si bond [1]. The presence of the S=O group band has been noticed between 1415-1380 cm^{-1}[12], while the spectra show a peak between 2000 - 2300 cm^{-1}, usually corresponding to CO_2. Noticeable presence of C-H stretching, shows a characteristic peak between 3000 – 2840 cm^{-1} and O-H stretching shows a characteristic peak between 3700 – 3584 cm^{-1} with a medium/ low appearance [12].

FTIR spectra (Fig. 1) showed the main characteristic peaks in all four graphics as follows:

(a): Original HGM and Modified HGM with 10% of KH550 (silane coupling)
(b): Original HGM and Modified HGM with 15% of KH550 (silane coupling)
(c): Original HGM and Modified HGM with 20% of KH550 (silane coupling)
(d): Original HGM and Modified HGM with 25% of KH550 (silane coupling)

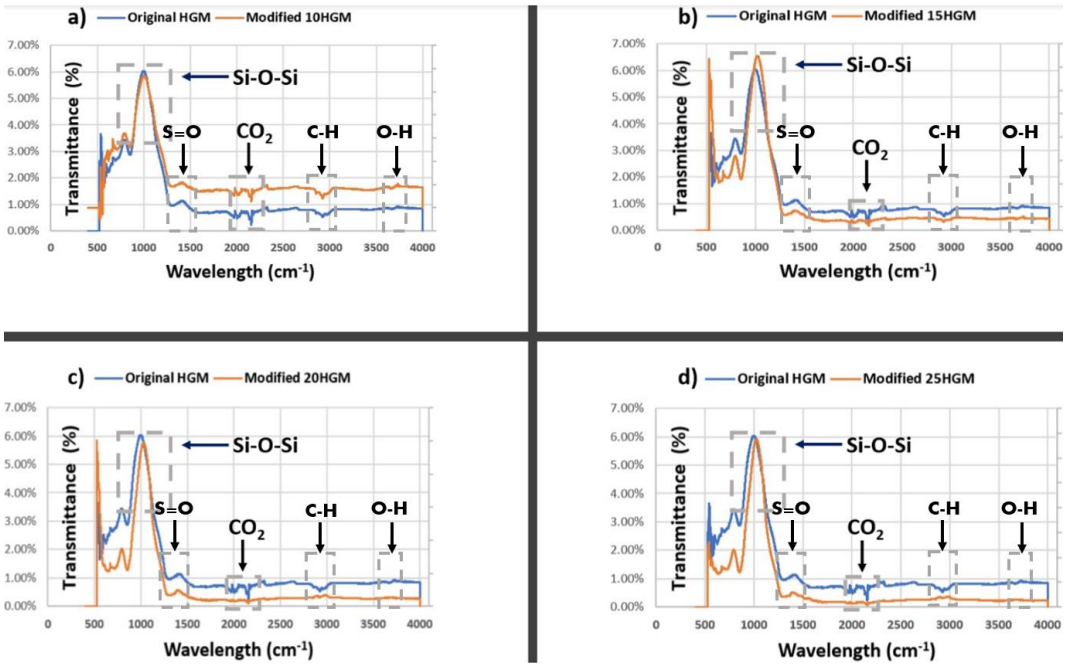

Fig. 1. FTIR spectra of hollow glass microspheres treated with silane coupling agent at different ratio

For example, (Fig. 2) presents FTIR spectra of modified hollow glass microspheres modified with NaOH (hydroxyl groups) used in a different study. FTIR spectrum of hollow glass microspheres shows a characteristic stretching peak between 1000 - 1100 cm^{-1} corresponding to the Si-O-Si bond [12] (7.5% transmittance for the original HGM and over 10% transmittance for the modified HGM). The noticeable presence of hydroxyl groups shows a characteristic peak between 1300 - 1500 cm^{-1} for the modified HGMs [12].

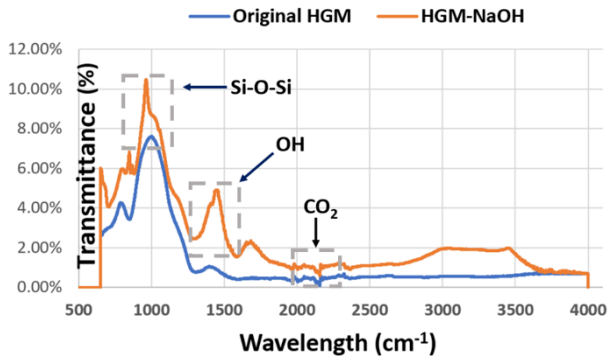

Fig. 2. FTIR spectra: Original HGM and Modified HGM with NaOH

(Fig. 3) shows FTIR spectra of hollow glass microspheres modified with NaOH (hydroxyl groups), KH550 3-aminopropyl-triethoxysilane, 98% diluted with ethanol, respectively distilled water, described above (*Section 2.3*) - routines 8,9,10.

FTIR spectrum of hollow glass microspheres shows a characteristic stretching peak between 1000 - 1100 cm^{-1} corresponding to Si-O-Si [12] bond 56% transmittance for graph (a), 54% transmittance for graph (b), 64% transmittance for graph (c) and 13% transmittance for graph (d). The noticeable presence of hydroxyl groups is shown by a characteristic peak between 1300 - 1600 cm^{-1} [12] in all 4 FTIR spectra (Fig. 3).

FTIR spectrum of HGMs of all four mixtures corresponding to the routines 7-10 (Table1) (Fig. 3(a), (b), (c) & (d)) shows a characteristic peak between 2500 - 3500 cm^{-1} corresponding to the primary amine in HGMs-KH550. The difference in transmittance (%) intensity between all four mixtures is in good agreement with the amount of amino used in each routine of the mixture techniques: 11% transmittance for graph (a), 12% transmittance for graph (b), 14% transmittance for graph (c) and 3% transmittance for graph (d).

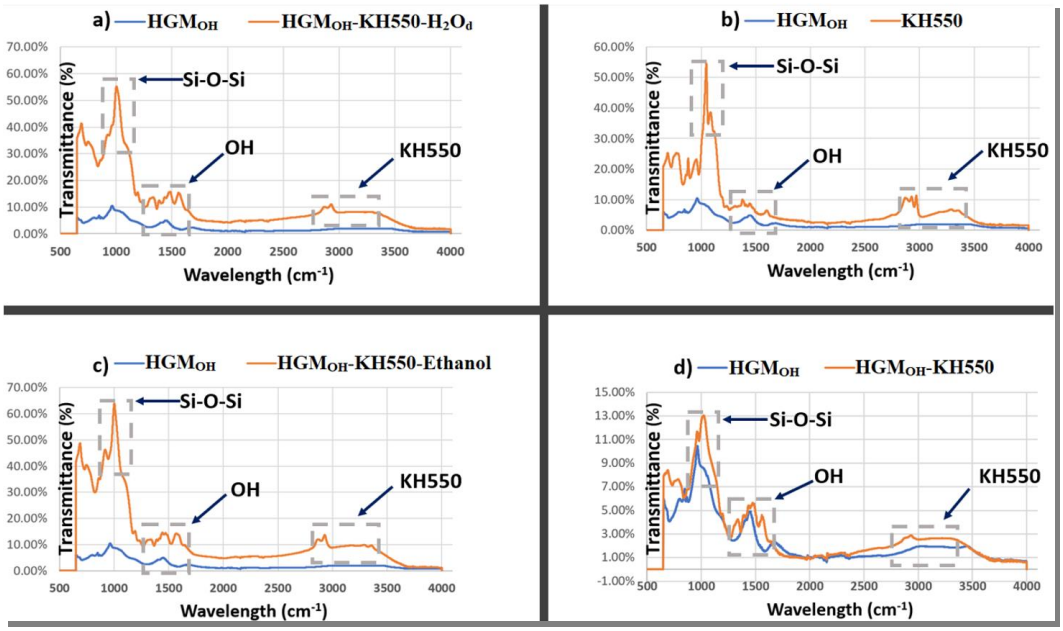

Fig. 3. FTIR spectra of hollow glass microspheres modified with NaOH(hydroxyl groups) treated with silane coupling agent at different ratio

It can be concluded that NaOH is a good agent in attaching groups of hydroxyls on hollow glass microspheres (HGM) for the subsequent reaction with a silane coupling agent in the fabrication of amine-terminated hollow

glass beads. FTIR spectra represent a result of a combination of 10 trials under different conditions, for the optimal chemical ratio and percentages used. The peak between 2500 - 3500 cm^{-1} corresponding to the primary amine in HGMs-KH550 (Fig.3) shows a high intensity of 14% transmittance for spectra represented in graph (c), which represents the highest coupling intensity of the silane agent on the hollow glass microspheres surface.

3.2. Scanning Electron Microscopy (SEM)

(Fig. 4) shows the scanning electron microscopy microphotographs at different magnifications for original hollow glass microspheres. The results point to a smooth clean surface.

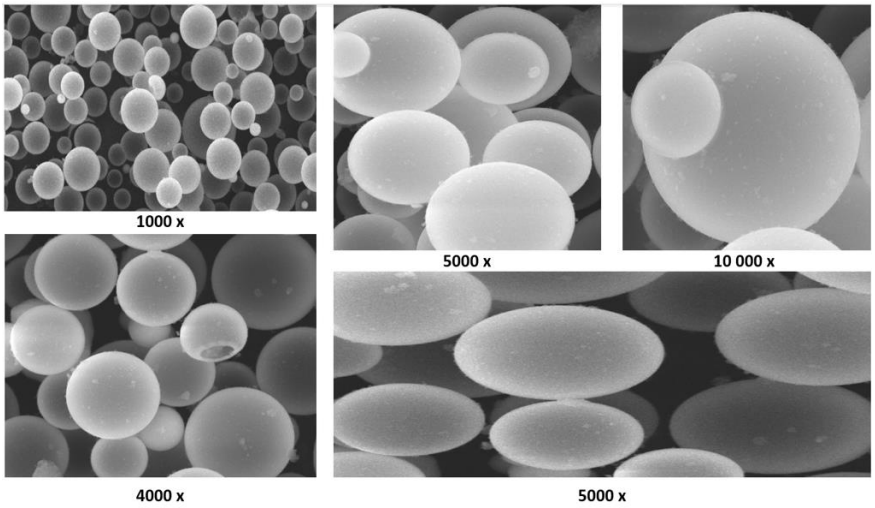

Fig 4: SEM image of HGM before surface modification

(Fig. 5) shows the scanning electron microscopy microphotographs at 10 000x of microspheres modified with KH550, 3-aminopropyl-triethoxysilane, 98%, explained above. The results for the (a), (b) & (c) show no difference based on neat HGM reference. At 25% amino, the bond between hollow glass microspheres created a strong crust (d) which broke 60% of the bubbles and surprisingly, no silane adhered on the surface. This aspect ratio is in correlation with (Fig. 1) from FTIR which concluded that no amino presence on hollow glass microspheres was found.

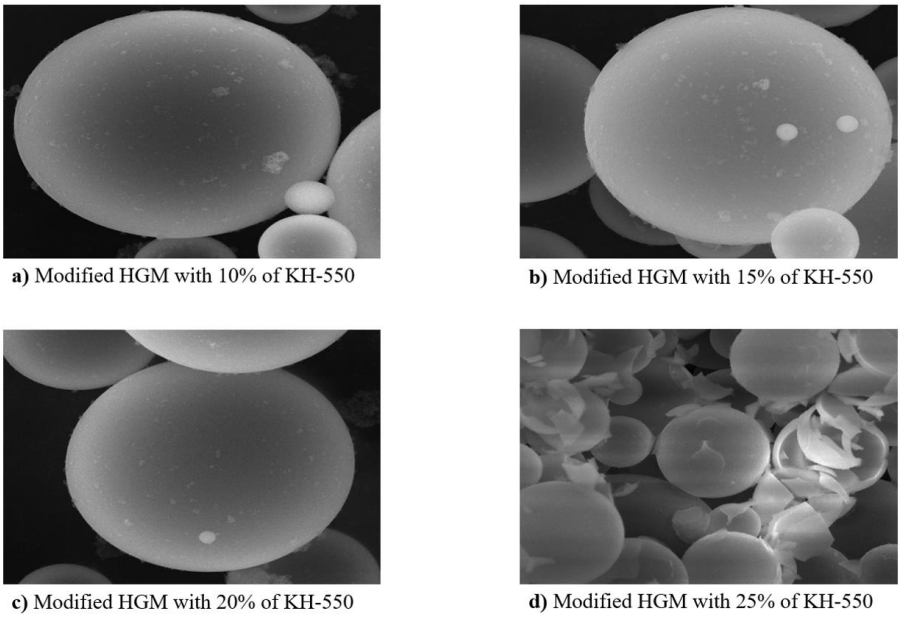

Fig 5: SEM images with modified HGM with silane coupling agent at different ratio

The results of hollow glass microspheres (Fig. 6) after treatment with sodium hydroxide (NaOH) granules, were diluted in distilled water, which is correlated with FTIR (Fig. 2).

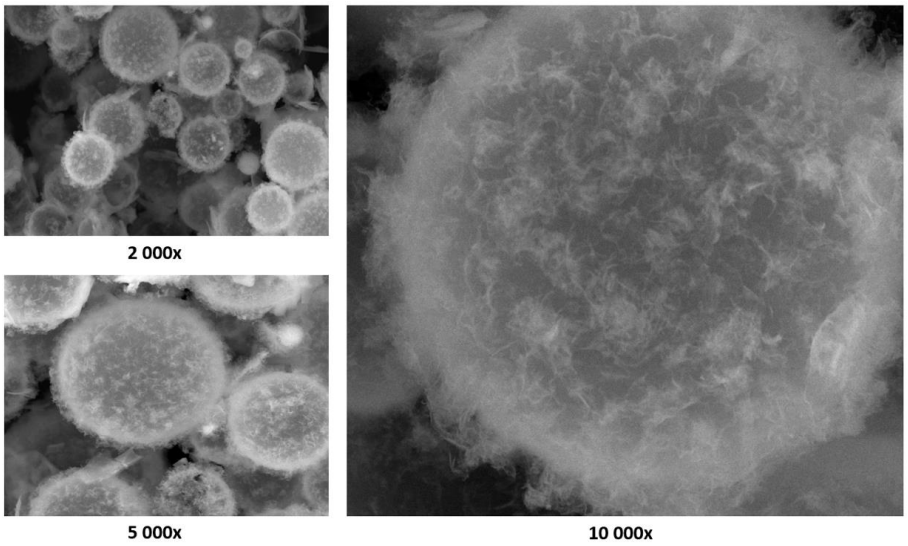

Fig. 6: SEM images of HGMs modified with NaOH (sodium hydroxide)

(Fig**. 7**) displays the SEM images of the sodium hydroxide (NaOH) pretreated hollow glass microspheres; SEM images from all three mixtures (a), (b) & (c) show the presence of silane coupling agent, differently.

SEM images (Fig. 7a) in agreement with preparation (8) conditions (Table 1), as well as with the FTIR spectroscopy showed good surface adhesion (Fig. 3d), show good surface adhesion between HGMs and APTES, without any crust cracking or excess of the primary amine. NaOH is a good agent in attaching hydroxyl groups to the surface of hollow glass microspheres and can be concluded that homogeneous adhesion was created in the mixture.

Considering the condition of preparation (Table 1, line 9) and the FTIR scanning graphic (Fig. 3c) the SEM results from (Fig. 7b) images show a cracked crust of the silane coupling agent, due to the high amount of alkali groups on top of the hollow glass microspheres.

The modified HGM-KH550 (silane coupling) and distilled water linked with the SEM (Fig. 7c) images and FTIR scanning graphic (Fig. 3a), corresponding to (Table 1) the condition of preparation (10) shows a high amount of coupling agent which eventually the exterior adhesion from filler started to crack as well due to the increased amount of alkali.

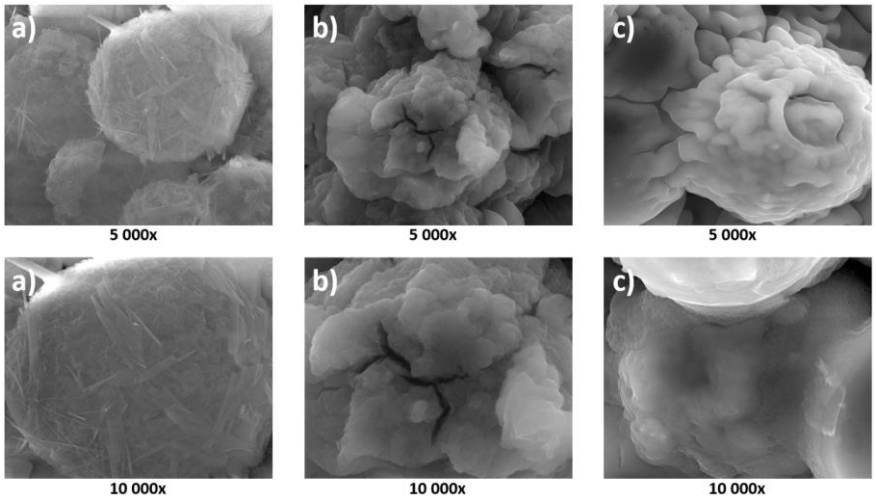

Fig. 7: SEM images of HGMs modified with NaOH (sodium hydroxide) and coupling agents

SEM images (Fig. 7) showed the exterior surface of the hollow glass microspheres after treatment with coupling agents in all three graphics as follows:

(a): Modified HGM_{OH} with KH550 (APTES)
(b): Modified HGM_{OH} with KH550 (APTES) and ethanol

(c): Modified HGM_{OH} KH550 (APTES) distilled water

4. Conclusions

Surface modification is important in ensuring good interfacial adhesion between hollow glass microspheres (HGM) and the polymeric matrix. Using a silane coupling agent creates a strong interfacial bonding between the reinforcement and the matrixes that increased the properties of the resultant composites by stimulating a good load transfer, good mechanical properties, and better surface adhesion.

Based on the obtained results from this study, in both conditions with and without sodium hydroxide, it can be considered that NaOH is a good agent in attaching hydroxyl groups on the surface of hollow glass microspheres and can be concluded that homogeneous adhesion was created in the mixture. SEM results from (Fig. 7a) images in correspondence with the (Table 1) condition of preparation (8) and FTIR scanning graphic (Fig. 3d), show a good surface adhesion between HGMs and APTES, without any crust cracking or excess of the primary amine and was selected as the best condition from this study.

Therefore, can be concluded that homogeneous adhesion was created in the mixture, which eventually will be selected to be used in a future hybrid mixture between polyamide 6 (PA6), a filler and hollow glass microspheres at different ratios. The optimal percentages and chemical ratios used in this study differ from the referenced articles, hence the originality/ novelty of the work.

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