

Chapter 2

MWI Synthesis and Characterization of RGO-AgNPs/Polymethyl Methacrylate Nanocomposites

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Abstract Polymethyl methacrylate and reduced graphene oxide/silver (PMMA/RGO/(RGO))AgNPs) nanocomposites were prepared via in situ bulk polymerization method using two different preparation techniques. In the first approach, mixture of silver nitrate, Hydrazine hydrate and polymethyl methacrylate containing graphene oxide (PMMA/GO) were reduced by microwave irradiation (MWI) to obtain R-(GO-PMMA)/AgNPs nanocomposites. In the second approach, a mixture of (RGO/AgNPs) nanocomposite, which was produced by microwave, and MMA monomers were polymerized using in situ bulk polymerization method to obtain PMMA-RGO/AgNPs nanocomposites. The two nanocomposites were compared and characterized by FTIR, XRD, XPS, HRTEM, and TGA. The results indicate that the nanocomposites obtained using the first approach, which involved MWI, had a better morphology and dispersion with enhanced thermal stability compared with the nanocomposites pre-pared without MWI.

2.1 Introduction

Graphene (GR) is an excellent two-dimensional filler material for polymer composites for application in many technological fields [1–5]. Good dispersion is crucial for achieving the desired enhancement in the final physical and chemical properties of the composites [6]. However, one of the challenges is achieving good dispersion of the nanoscale filler in the composites, especially for GR, which has a strong tendency to agglomerate through the intrinsic van der Waals forces and $\pi-\pi$ stacking due to its hydrophobic nature [7]. Various techniques have been developed for the synthesis of these polymer-graphene composites, including solution mixing; melt blending and in-situ polymerization [8–10]. Recently, a novel approach for the production of metal

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nanoparticles (MNPs) supported on reduced graphene oxide nanosheets (RGO) via MWI method is reported, the resulting product is composed of metal nanoparticle supported on graphene sheets with polar functional groups even after the reduction [11]. Polymethylmethacrylate (PMMA) is an important polymeric material that has been used in medicine (bone cement), dentistry, radiation shield, the paper, paint and automobile industries and in many other applications [11–16]. Several studies have reported the successful incorporation of GR nanosheets into the PMMA matrix with different preparation techniques using various methods of GR preparation, such as from reduced GO, functionalized RGO sheets or chemical vapor deposition [17–20], however, there is no published reports on such nanocomposites that is functionalized by the in situ bulk polymerization with (RGO/AgNPs) as a filler. In this letter, we report two different synthesis techniques of (PMMA/RGO/AgNPs) nanocomposites by employing in situ bulk polymerization via MWI.

2.2 Experimental Methods

2.2.1 Preparation of RGO/AgNPs

A mixture of 25 ml of 0.02 M of AgNO_3 and 0.40 g GO [21], were stirred and sonicated for 1 h. Then the solution was reduced via conventional microwave oven after adding 400 μl of the hydrazine hydrate (HH) for 1.2 min. For comparison, AgNPs were pre-pared using the same method but without the addition of GO.

2.2.2 In Situ Preparation of PMMA-RGO/AgNPs Nanocomposites

A mixture of 2.0 g MMA, 0.04 g of (RGO/AgNPs), and 0.1 g of benzoyl peroxide (BP) initiator was sonicated for 1 h, and then the mixture were maintained at 60 °C for 20 h to promote *in situ* free radical bulk polymerization. The neat PMMA was prepared for comparison using the same procedure, but no RGO/AgNPs were added.

2.2.3 Preparation of R-(PMMA-GO)/AgNPs Nanocomposite via MWI

A mixture of 2.0 g of MMA, 0.04 g of GO, and 0.1 g of (BP) was sonicated for 1 h, then it was polymerized by the in situ bulk polymerization method as in the previous section, to produce GO-PMMA composites. Then a mixture of 0.40 g (GO-PMMA), 400 μl HH, and 0.08 g of AgNO_3 were then sonicated for 1 h and then reduced using MWI.

Fig. 2.1 FTIR spectra of **a** RGO/AgNPs, **b** PMMA-RGO/AgNPs, and **c** R-(PMMA-GO)/AgNPs nanocomposites

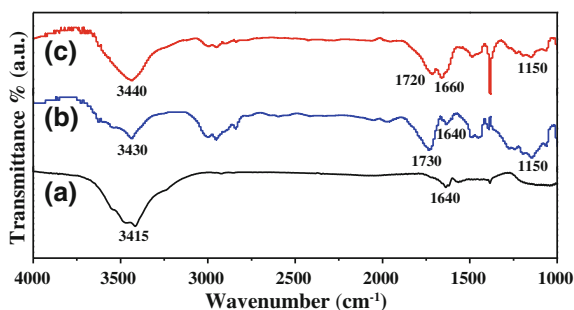
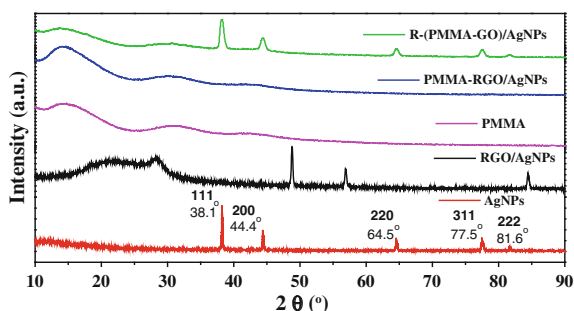


Fig. 2.2 XRD patterns of PMMA/RGO/AgNPs nanocomposites



2.3 Results and Discussion

Figure 2.1 shows the FTIR spectra of the all PMMA/RGO/AgNPs nanocomposites. For the PMMA-RGO/AgNPs (Fig. 2.1b), the spectrum shows the presence of the characteristic bands of PMMA/RGO. The bands at 3430, 1730, 1640, 1150 cm^{-1} that correspond with the O–H, C=O, C=C, C–O–C groups, respectively. This confirms the presence of PMMA/RGO composite. Interestingly, for R-(PMMA-GO)/AgNPs, (Fig. 2.1c) the spectra show that some of these characteristics peaks are much shifted to 3440 and 1660 cm^{-1} in comparison with (Fig. 2.1b) when the microwave was not used, this may suggest that the acrylate group of PMMA and RGO sheets opened by the MWI, which will induce more electron chain transfer sites, and therefore will promote more interfacial interactions between RGO and AgNPs within PMMA matrix [20]. Moreover, (Fig. 2.1c) shows that in the C=O stretching (at 1720 cm^{-1}), the aliphatic C–H, and $-\text{CH}_2$ (at 2950, 2840 cm^{-1}), and the C–O–C stretching (at 1150 cm^{-1}) regions, the bands were reduced in intensity compared to (Fig. 2.1b).

XRD analyses of PMMA/RGO/AgNPs composites were conducted. The XRD pattern of the AgNPs (Fig. 2.2) reflects a peaks at 2θ values of about 38.1°, 44.4°, 64.5°, 77.5°, and 81.6° representing the (111), (200), (220), (311), and (222) indicating the formation of metallic silver (Ag) with face-centered cubic (fcc) symmetry [22]. For PMMA-RGO/AgNPs, it is difficult to find the AgNPs in the XRD pattern,

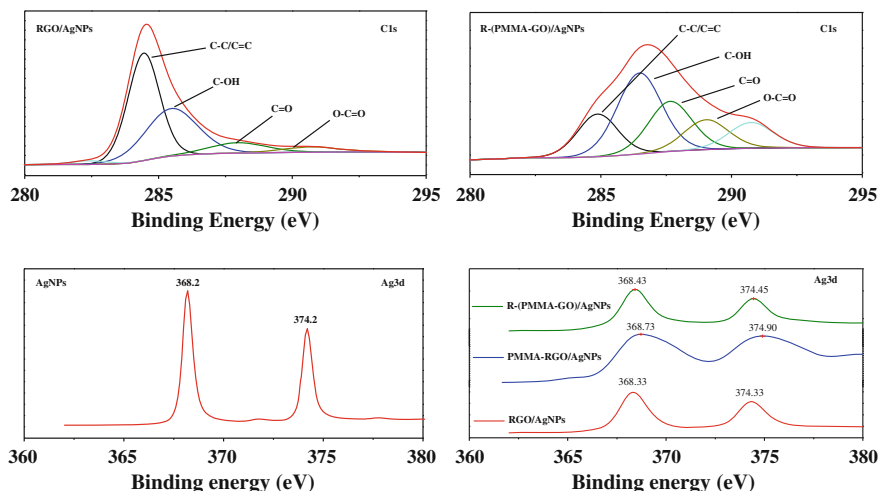


Fig. 2.3 C1s and Ag3d XPS spectra of PMMA/RGO/AgNPs nanocomposites

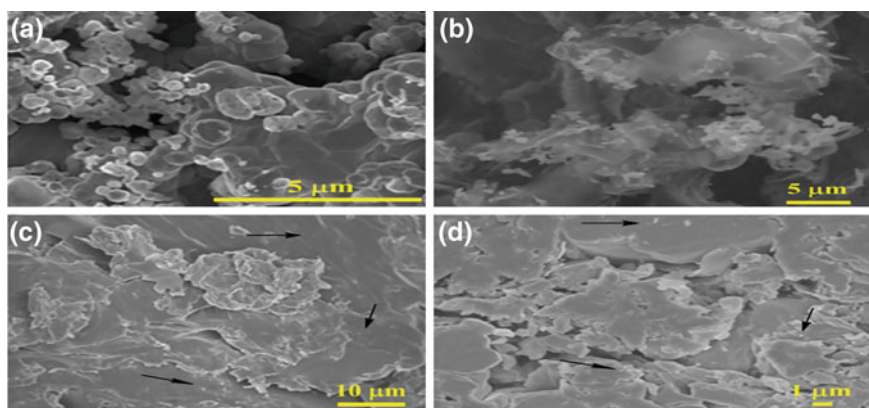


Fig. 2.4 The SEM images of **a** AgNPs, **b** RGO/AgNPs, **c** PMMA-RGO/AgNPs, **d** R-(PMMA-GO)/AgNPs nanocomposites

which might suggest that the AgNPs are intercalated within the PMMA/RGO composites.

The formation of AgNPs-RGO/PMMA nanocomposites were further confirmed by XPS and is summarized in Fig. 2.3. Note that the oxygenated functionalities were fully reduced when the MWI is used indicating the formation of RGO-AgNPs within the PMMA composites.

The morphology of the nanocomposites was studied by SEM as displayed in Fig. 2.4. The SEM image of the RGO/AgNPs-PMMA nanocomposites prepared via in situ method (Fig. 2.4c) shows that the RGO/AgNPs wrinkled and crumpled profile was observed and well dispersed within the PMMA matrix. When the MWI were used

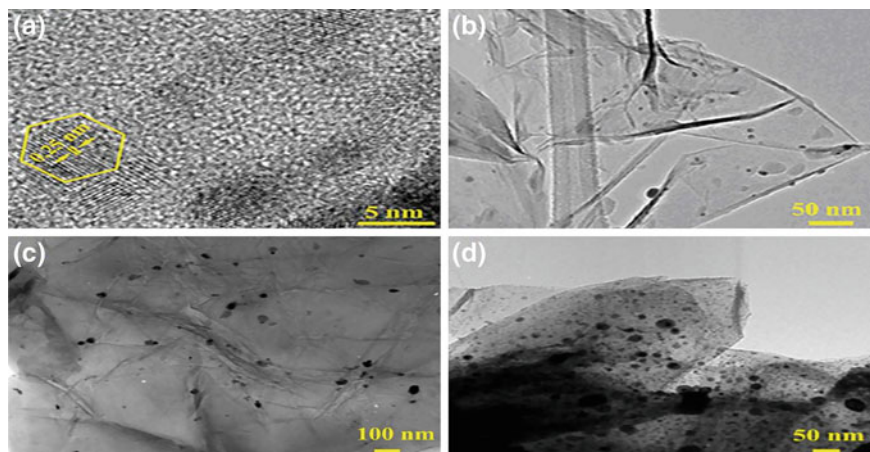
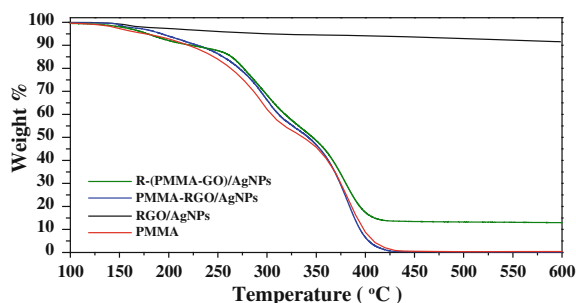


Fig. 2.5 The HRTEM images of **a** AgNPs, **b** RGO/AgNPs, **c** PMMA-RGO/AgNPs, **d** R-(PMMA-GO)/AgNPs nanocomposites

Fig. 2.6 TGA thermograms of PMMA/RGO/AgNPs nanocomposites



R-(PMMA-GO)/AgNPs (Fig. 2.4d), the AgNPs (white spots) were well dispersed within PMMA matrix, and embedded within the matrix.

The morphology of the nanocomposites was also studied by using HRTEM as displayed in Fig. 2.5. Note that RGO-AgNPs sheets are weakly dispersed within PMMA matrix (Fig. 2.5c). However, when the MWI were used R-(PMMA-GO)/AgNPs (Fig. 2.5d), the image clearly shows the RGO/AgNPs is well dispersed within PMMA matrix, and embedded within the matrix.

Thermal gravimetric analyses (TGA) were used to investigate the thermal stability and the interfacial interaction between RGO/AgNPs and the PMMA matrix. Interestingly, in the case of the R-(PMMA-GO)/AgNPs, the curve clearly shows strong enhancement in the thermal stability in comparison with the neat PMMA and PMMA-RGO/AgNPs. We attributed this result to the homogenous dispersion and random alignment of the RGO-AgNPs filler within the PMMA matrix. Therefore, incorporation of RGO/AgNPs by MWI can improve the thermal stability of the composites (Fig. 2.6).

2.4 Conclusion

In conclusion, we report a new *in situ* method to incorporate RGO/MNPs within polymers matrix by the in situ bulk polymerization via MWI. The results indicate that the nanocomposite obtained using our experimental approach, which involved MWI, had a better morphology and dispersion with enhanced thermal stability compared with the nanocomposites prepared without MWI.

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