

X- Ray Diffraction And Scanning Electron Microscopy Of Fullerene Based Poly (Glycidylemethacrylate) Polymers

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Abstract

This paper provides a brief, easy to understand description of X-ray diffraction techniques and scanning electron microscopic studies on fullerene based poly (Glycidylemethacrylate) which are proving useful and remarkable in the analysis of the structural and surface properties of these polymers. The polymeric materials have been prepared by using polymerization process at different concentration of fullerene and glycidylemethacrylate (GMA). X-ray scattering patterns have been highlighted to analyse the FWHM, crystallite size and interchain separation of prepared polymeric materials, besides this surface properties reported very exciting results in the success of polymer morphology.

Keywords: Fullerene, Glycidylemethacrylate, XRD, SEM, Crystallite size, Interchain - separation, surface characterization.

1. Introduction:

The versatility of polymeric materials, which are widely used in the form of plastics, films, coatings and fibers, arises from the complex structural organization in these materials. X-ray diffraction (XRD) has long been successfully used to study various aspects of these structures in semi crystalline polymers, which includes thermoplastics, thermoplastic elastomers and liquid crystalline polymers. While many of the well established methods for the determination of molecular structure, evaluation of crystallinity and analysis of texture, continue to be improved to enhance the speed and precision of these measurements, new techniques

are also being continuously introduced. With the availability of intense X-ray sources, high-speed detectors and faster methods of analyzing the data, it is now possible to examine the structure at higher spatial resolution [1–4], or examine the structural in homogeneities that induced over distance of a few micrometers by the temperature and stress gradients that exist during processing [5–7]. These developments also permit combining XRD analysis with other characterization techniques such as scanning electron microscopy and spectroscopy [8,9]. Here we introduce fullerene based polymers in which fullerenes have three-dimensional arrays of reactive double bonds that present an unusually difficult problem for controlling the topology of multiple addition reactivity. Intercalation of poly (GMA) in solid C₆₀ leads to form a conducting polymer. Since the first synthesis of macroscopic amounts of fullerene, there have been a number of studies of the behavior of fullerene based polymers. A remarkable feature of C₆₀ molecules is that they may form bonds with each other leading to a variety of crystal structures and physical properties. On the other hand, it is known that C₆₀ can develop cycloaddition reactions of different types. It has been even reported that exposure to light can cause the polymerization of the molecules into clusters of different numbers of molecules. Here we prepared fullerene based poly (glycidylemethacrylate) and examined with x-ray diffraction and scanning electron microscopy. X-Ray Diffraction (XRD) provides important solid-state structural information for polymers and composites. Useful XRD analysis data is obtained from crystalline, semi-crystalline, amorphous polymeric and composite materials. The scanning electron microscope (SEM) is a very useful imaging technique that utilized a beam of electrons to acquire high magnification images of specimens. The electron beam requires extremely high vacuum to protect the filament and electrons must be able to adequately interact with the sample. Polymers are typically long chains of repeating units composed primarily of “lighter” (low atomic number) elements such as carbon, hydrogen, nitrogen, and oxygen. These lighter elements have fewer interactions with the electron beam which yields poor contrast, so often a stain or coating is required to view polymer samples. In this paper, poly (glycidyl methacrylate) (PGMA) was chosen as a monomer with fullerene due to high reactivity caused by superficial epoxy groups and good resistance to acid, heat, weather and solvent .Samples description is given below:

Table I. Variation of fullerene with Poly (glycidylemethacrylate)

Sample name	Fullerene (mol/L)	Poly(GMA) (mol/L)	BPO (mol/L)
FG1	1.984×10^{-4}	1.0733	1.1806×10^{-2}
FG2	3.968×10^{-4}	1.0733	1.1806×10^{-2}
FG3	5.952×10^{-4}	1.0733	1.1806×10^{-2}
FG4	7.936×10^{-4}	1.0733	1.1806×10^{-2}
FG5	1.984×10^{-4}	1.5026	1.1806×10^{-2}
FG6	1.984×10^{-4}	1.9319	1.1806×10^{-2}

2. Experimental Details:

Glycidylemethacrylate was purified by standard methods and purified solvents were used as received. Benzoylperoxide (BPO) was recrystallized in chloroform. Fullerene (Alfa Aesar, 99.9% C₆₀) was used as received and was dissolved in toluene as required. The polymerization reactions were carried out under an inert atmosphere of nitrogen for 1½ hr at 70°C in toluene using BPO as an initiator. A series of samples of fullerene-grafted poly (glycidylemethacrylate) were synthesized by systematic variation of fullerene and GMA as given in Table I. The polymer was precipitated in acidified methanol and vacuum dried until a constant weight was obtained.

3. Result and Discussion:

3.1 X-Ray Diffraction Analysis

The x-ray diffraction results are shown in fig.1, 2, 3, 4,5 and 6. These figures show that all the samples are homogeneous and semi crystalline. The crystallite size shows at least two phases. Figures 1,2,3,4,5 and 6 show the x-ray diffraction pattern for samples FG1,FG2,FG3,FG4,FG5 and FG6 respectively.

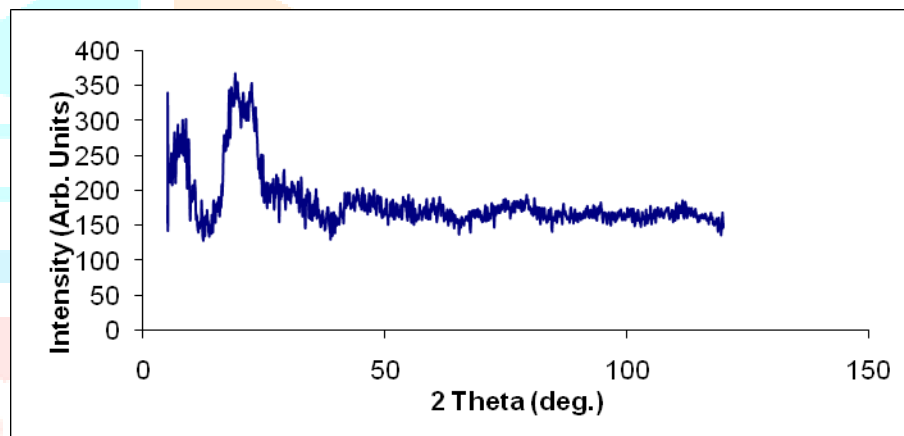


Fig.1 (X-Ray diffraction of sample FG1)

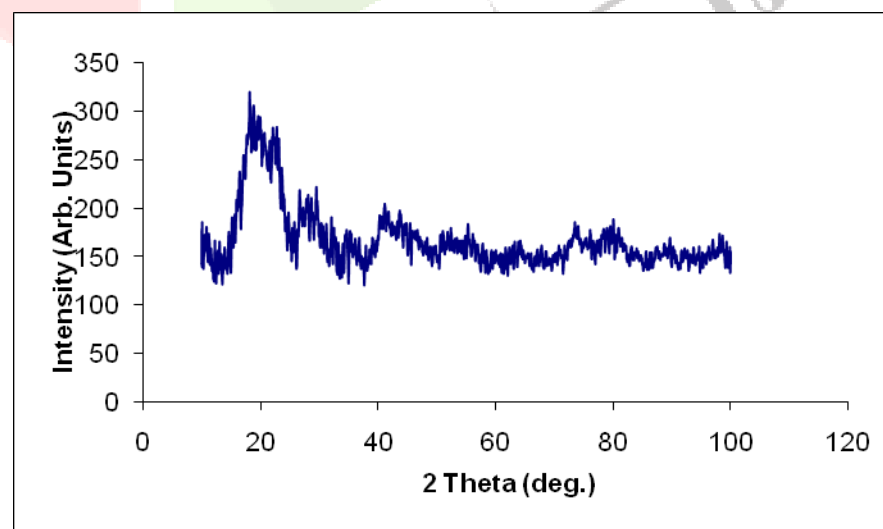


Fig.2 (X-Ray diffraction of sample FG2)

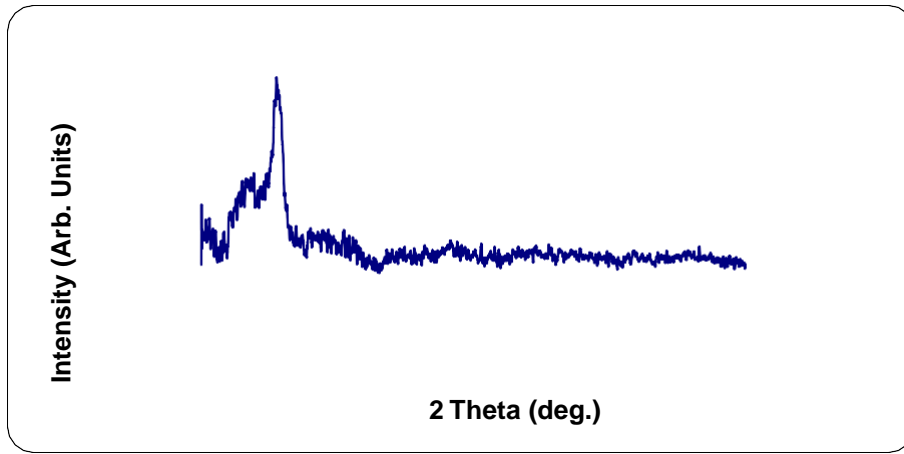


Fig.3 (X-Ray diffraction of sample FG3)

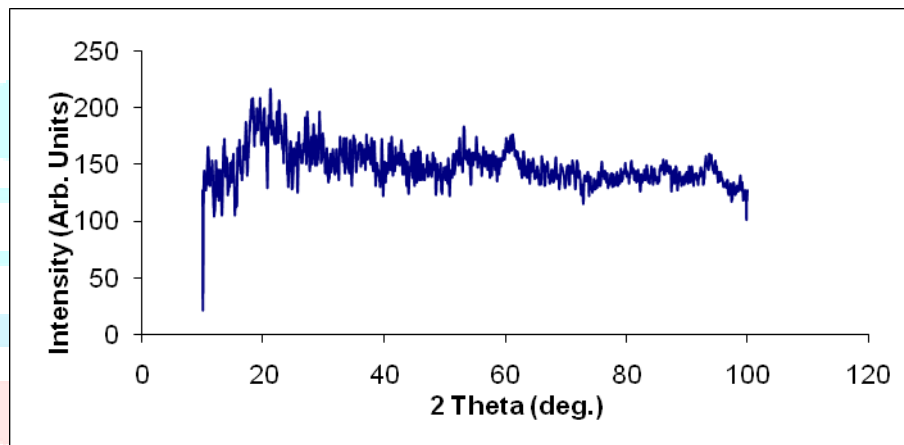


Fig.4 (X-Ray diffraction of sample FG4)

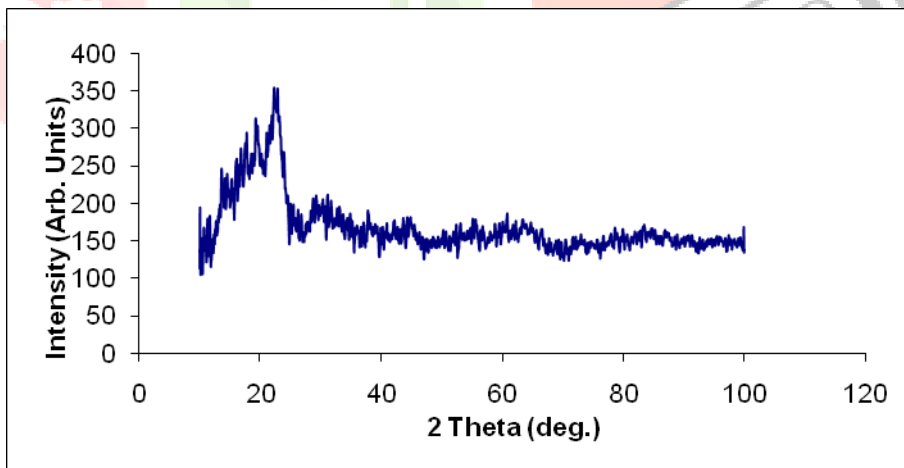


Fig.5 (X-Ray diffraction of sample FG5)

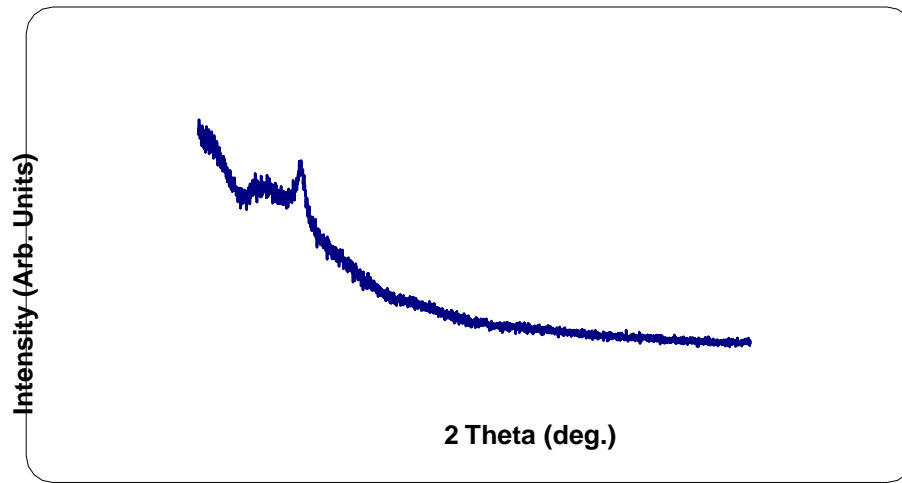


Fig.6 (X-Ray diffraction of sample FG6)

In experimental result of x-ray diffraction we observe the following data for the polymeric samples;

(i) Sample FG1:

At $\lambda = 1.54 \text{ \AA}$, the values of full width of half maxima vary as: $\beta = 0.1221, 0.1395, 0.1744$ and 0.3140 . The values of full width of angle of diffraction vary as: $\theta_{\beta} = 4.25, 12, 22.5$ and 36.5 (deg.)

At the above values crystallite size varies as: $t = 11.3 \text{ \AA}, 10.16 \text{ \AA}, 8.60 \text{ \AA}$ and 5.49 \AA Interchain separation varies as: $13, 4.63, 2.51$ and 1.61

(ii) Sample FG2:

At $\lambda = 1.54 \text{ \AA}$, the values of full width of half maxima vary as: $\beta = 0.0872, 0.1744, 0.1918$ and 0.1046 . The values of full width of angle of diffraction vary as: $\theta_{\beta} = 10.25, 14.5, 23.75$ and 40.5 (deg.)

At the above values crystallite size varies as: $t = 16.15 \text{ \AA}, 8.21 \text{ \AA}, 7.89 \text{ \AA}, 8.87 \text{ \AA}$, and 17.43 \AA Interchain separation varies as: $5.41, 3.84, 2.39$ and 1.48

(iii) Sample FG3:

At $\lambda = 1.54 \text{ \AA}$, the values of full width of half maxima vary as: $\beta = 0.0697, 0.1221, 0.1395$, and 0.1744 .

The values of full width of angle of diffraction vary as:

$$\theta_{\beta} = 8.5, 12.75, 22 \text{ and } 27.5 \text{ (deg.)}$$

At the above values crystallite size varies as: $t = 20.11 \text{ \AA}, 11.64 \text{ \AA}, 10.71 \text{ \AA}$ and 8.96 \AA .

Interchain separation varies as: $6.51, 4.36, 2.57$ and 2.08

(iii) Sample FG4:

At $\lambda = 1.54 \text{ \AA}$, the values of full width of half maxima vary as: $\beta = 0.1395, 0.0872, 0.1221$, and 0.1046 .

The values of full width of angle of diffraction vary as:

$$\theta_{\beta} = 7, 12.75, 22 \text{ and } 30.5 \text{ (deg.)}$$

At the above values crystallite size varies as: $t = 10.01 \text{ \AA}, 16.30 \text{ \AA}, 12.24 \text{ \AA}$ and 15.38 \AA .

Interchain separation varies as: $7.90, 4.36, 2.57$ and 1.89

(iii) Sample FG5:

At $\lambda = 1.54 \text{ \AA}$, the values of full width of half maxima vary as: $\beta = 0.1744, 0.0697, 0.1046, \text{ and } 0.0872$.

The values of full width of angle of diffraction vary as:

$$\theta_{\beta} = 7.5, 10, 13.5 \text{ and } 31.25 \text{ (deg.)}$$

At the above values crystallite size varies as: $t = 8.01 \text{ \AA}, 20.20 \text{ \AA}, 13.62 \text{ \AA} \text{ and } 18.60 \text{ \AA}$.

Interchain separation varies as: 7.37, 5.54, 4.12 and 1.85

(iii) Sample FG6:

At $\lambda = 1.54 \text{ \AA}$, the values of full width of half maxima vary as: $\beta = 0.1395, 0.0872, 0.1221 \text{ and } 0.1395$.

The values of full width of angle of diffraction vary as:

$$\theta_{\beta} = 4, 9.75, 13.25 \text{ and } 18 \text{ (deg.)}$$

At the above values crystallite size varies as: $t = 9.96 \text{ \AA}, 16.13 \text{ \AA}, 11.66 \text{ \AA} \text{ and } 10.45 \text{ \AA}$.

Interchain separation varies as: 13.79, 5.68, 4.20 and 3.11

A comparative tabular representation of crystallite size and interchain separation of all the samples has been depicted in Table (II) and Table (III) which shows the non-uniform variation in the value of crystallite size.

Table-II: Comparative data of crystallite size

Samples	t ₁ (in Å)	t ₂ (in Å)	t ₃ (in Å)	t ₄ (in Å)
FG1	11.3	10.16	8.60	5.49
FG2	16.15	8.21	7.89	8.87
FG3	20.11	11.64	10.71	8.96
FG4	10.01	16.30	12.24	15.38
FG5	8.01	20.20	13.62	18.60
FG6	9.96	16.13	11.66	10.45

Table-III: Comparative data of interchain separation

Samples	d ₁ (in Å)	d ₂ (in Å)	d ₃ (in Å)	d ₄ (in Å)
FG1	13	4.63	2.51	1.61
FG2	5.41	3.84	2.39	1.48
FG3	6.51	4.36	2.57	2.08
FG4	7.90	4.36	2.57	1.89
FG5	7.37	5.54	4.12	1.85
FG6	13.79	5.68	4.20	3.11

A graphical presentation of average crystallite size and interchain separation with variation of fullerene concentration can be shown in fig.8 & fig.9 as:

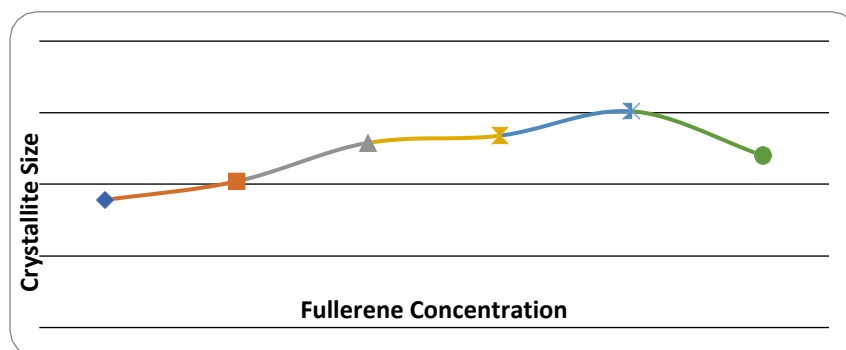


Fig.7(Variation of crystallite size with fullerene)

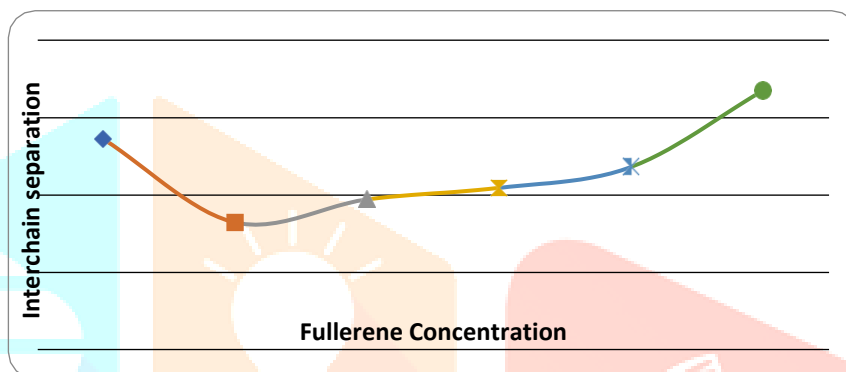


Fig.8 (Variation of interchain separation with fullerene)

X-ray results show fullerene based poly (GMA) polymers have crystal like structure but they are not having perfect crystalline structure. Their interchain separation [10] and crystallite size vary as we increase the concentration of fullerene among these samples. In the graphical representation of x-ray diffraction, the existence of peaks shows a semi-crystalline nature of prepared samples. A continuum of structures between the extremes of what are generally regarded as amorphous and crystalline phases are present in a real polymer, and these entities have complex organization. But, a model that describes the semicrystalline polymers in terms of two phases, an average amorphous and an average crystalline phase, has been found to be adequate for many practical purposes. Crystallinity can be determined from a X-ray diffraction scan by comparing the area under the crystalline peaks to the total scattered intensity [11-12]. The accuracy and the precision of these measurements can be improved by drawing a proper base-line, using an appropriate amorphous template, and by carefully choosing the crystalline peaks [13,14]. The disorder in the crystalline domains can be evaluated by measuring the crystallite sizes, which can be calculated by the Scherer equation. In reality, there are two contributions to the width: one is the size and the other is the paracrystallinity or micro strain [15, 16]. The disorder in the crystalline domains is also reflected in the unit cell dimensions. But, calculation of the unit cell parameters requires an accurate measurement of the positions of many crystalline peaks, which can be difficult. Therefore, in practice, relative positions of selected crystalline peaks are used as accurate measures of the changes in unit cell parameters [17- 19].

Structures at length scales larger than a unit cell (10 nm instead of 1nm) can be investigated using X-ray scattering. The methodology for this analysis is now highly developed and can be found in any standard literature [9, 20–24]. While XRD is used to study the orientation of the crystals, and the packing of the chains within these crystals and also used to study the electron density fluctuations that occur over larger distances as a result of structural inhomogeneities. XRD is widely used to study the structure by measuring parameters such as inter-planer spacing and thickness of the transition layer between the crystalline and amorphous domains. This information is somewhat similar to that obtained from a scanning electron microscopy.

3.2 Scanning Electron Microscopic Analysis

SEM analyses of prepared samples are given in fig. 7,8,9,10,11 and 12.

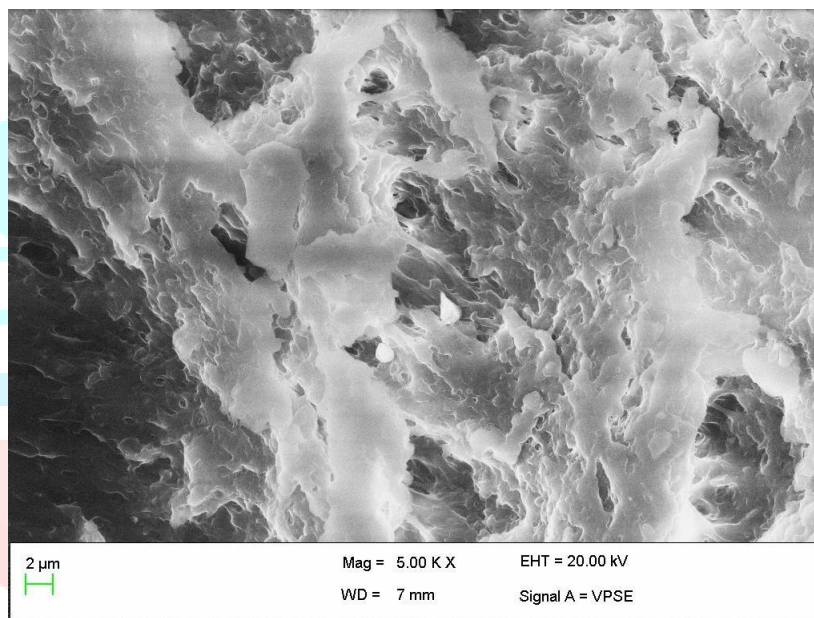


Fig. 7 (SEM image of FG1)

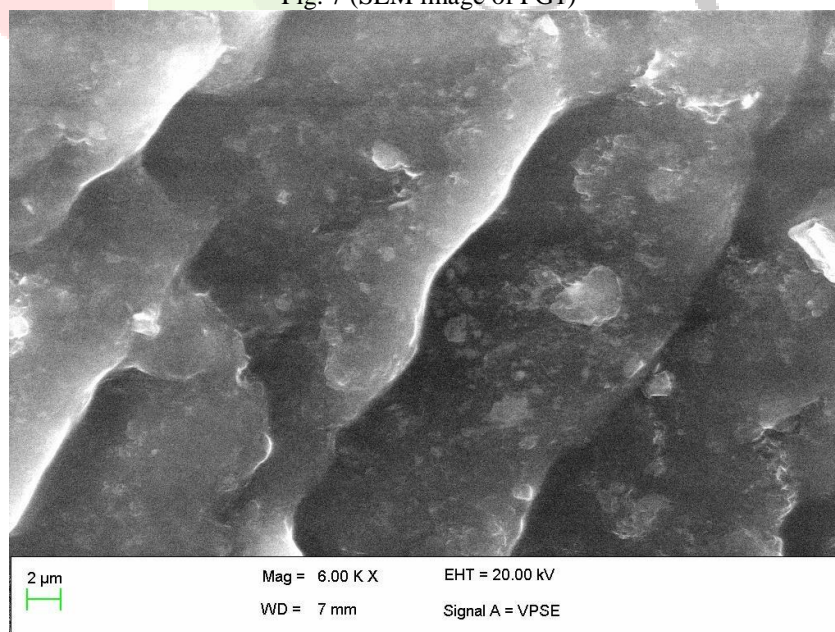


Fig.8 (SEM image of FG2)

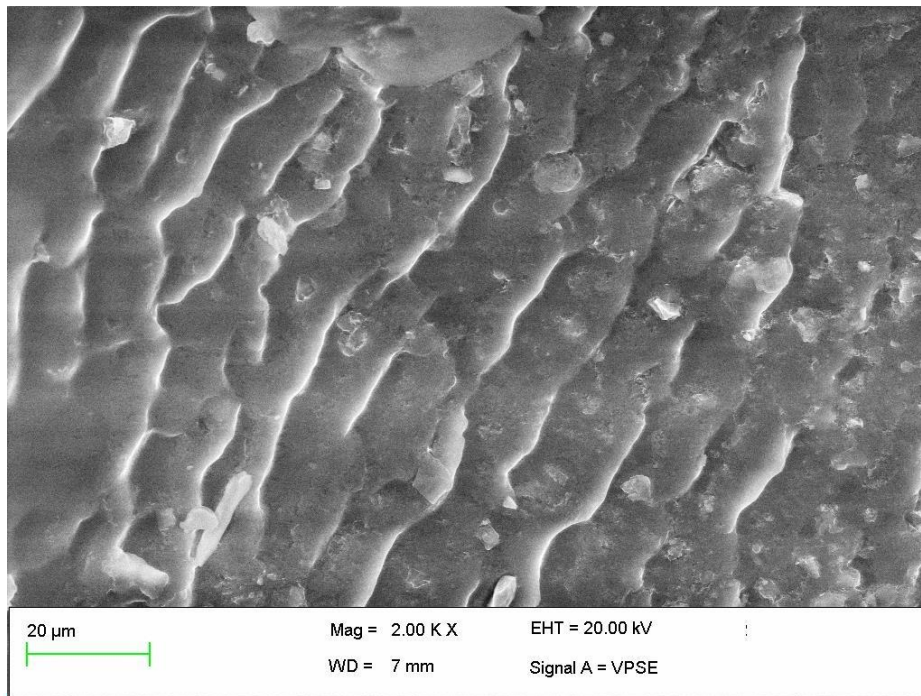


Fig.9 (SEM image of FG3)

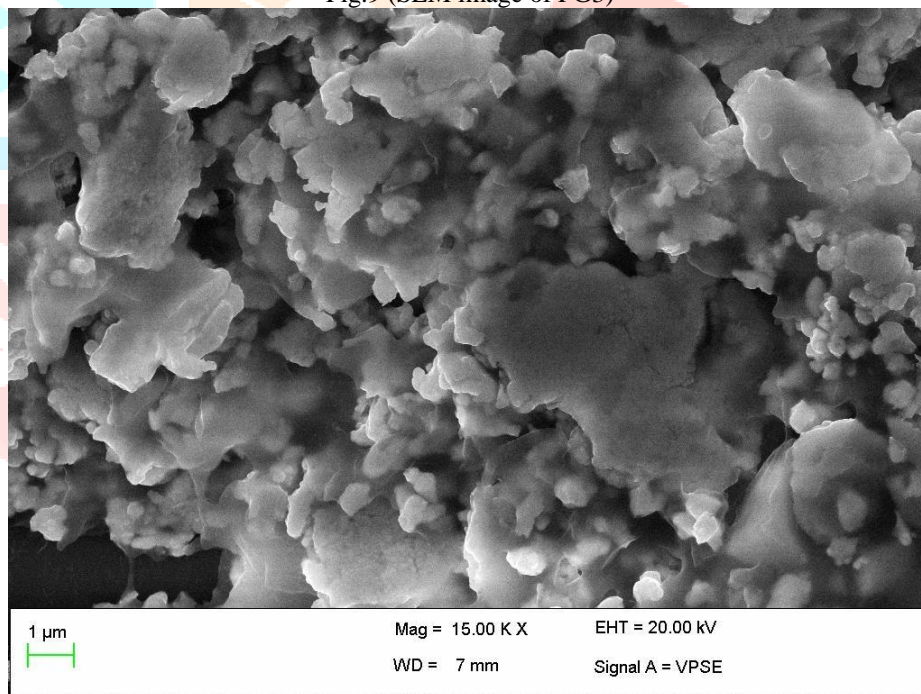


Fig.10 (SEM image of FG4)

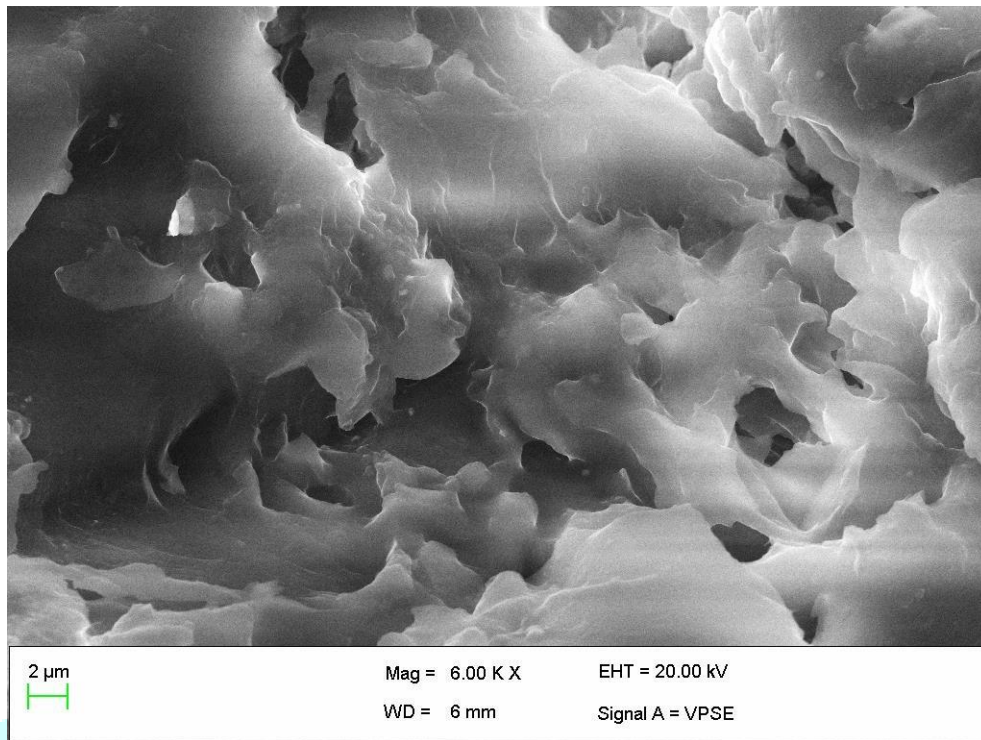


Fig.11 (SEM image of FG5)

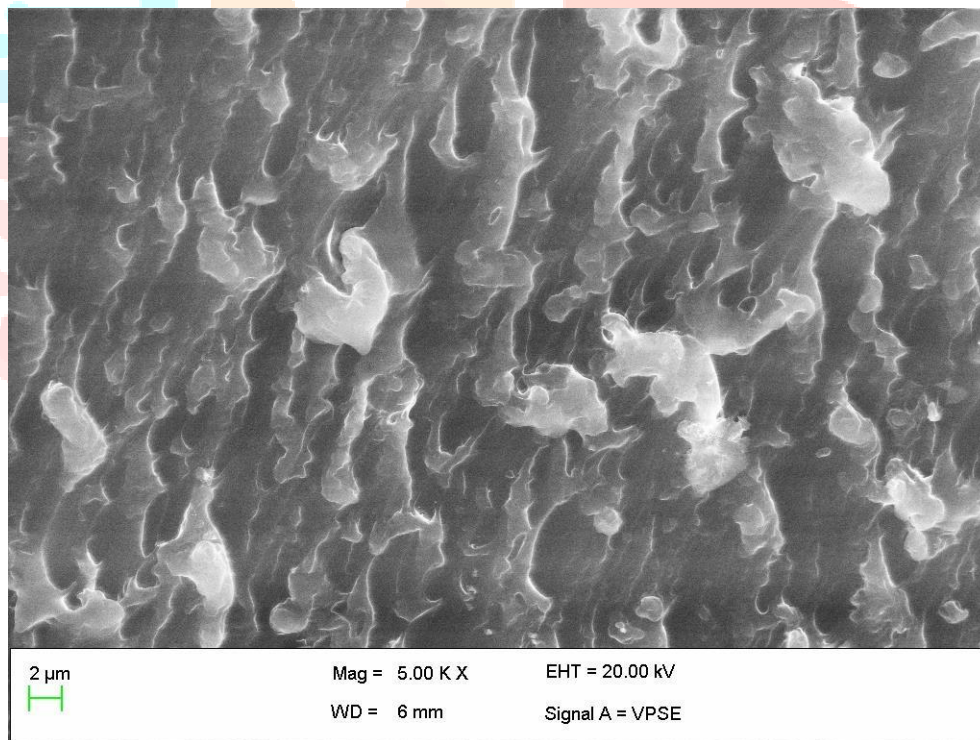


Fig.12 (SEM image of FG6)

Scanning electron microscopy (SEM) is commonly used for studying the surface morphology of polymers [25,26]. These techniques make use of a primary beam of electrons that interact with the specimen of interest, in a vacuum environment, resulting in different types of electrons and electromagnetic waves being emitted. The secondary electrons ejected from the specimen surface are collected and displayed to provide a high-resolution micrograph. SEM sample preparation involves fixation followed by drying, attachment to a

metallic stub, and then coating with a metal prior to data collection. It should be noted that the drying and metal coating processes used in the preparation of some polymeric materials might alter surface morphology, particularly those surfaces that may undergo changes in a hydrated environment. Upon insertion of the sample into the SEM, acquisition of the micrographs can usually be done fairly quickly allowing for a large number of images to be obtained with varying magnifications. Surface morphology of polymers, the SEM can be combined with other analysis methods such as energy dispersive X-ray analysis (EDX) to determine elemental distribution [27] and IR and Raman spectroscopy to monitor surface modification procedures [28].

However, it should be noted that the use of even different microscopic techniques might give rise to a different view of the surfaces obtained. Figures 7,8,9,10,11 and 12 show SEM images respectively of the same fullerene based poly(glycidymethacrylate) polymers. The results obtained by SEM analysis show a layered like surface, indicating the incorporation of GMA on the fullerene surface. Thus, the combination of microscopic techniques used may play a valuable role in the characterization of surface features and morphology of polymeric materials.

4. Conclusion:

In this paper we have provided an overview of techniques commonly used in polymers characterization, as well as some discussion of emerging methods that have recently come to the forefront of polymer research. The studied X-Ray diffraction indicates a perfect crystalline structure only with a certain composition of C₆₀ and GMA (FG3) while with others shows semicrystalline structure (FG1, FG2, FG5 & FG6) up to amorphous (FG4) that indicates a perfect polymeric property and higher C₆₀ content is not successful to form a crystalline structure. SEM analysis reported layered surface morphology which clearly indicates that C₆₀ existed in the poly (GMA) domain. The electronic spectral data therefore also supports the homogeneous incorporation of C₆₀ in the PGMA. The prepared polymers containing C₆₀ may find many application areas such as organic photovoltaic and biomedical imaging probes.

5. Acknowledgments:

The author is grateful to Dr Supriya Singh for giving her assistance in the experimental work. The author is also thankful to, IIT Kanpur, India for providing Xray and SEM facilities.

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