



Preparation of random and graft copolymers of GMA and MMA using reactive melt mixing and solution polymerization

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Abstract- In this study Poly(MMA-g-GMA) copolymers was prepared via reactive melt mixing of Poly (methyl methacrylate) PMMA and glycidyl methacrylate (GMA) using benzoyl peroxide (BPO) and dicumyl peroxide (DCP) as initiators. Poly(MMA-ran-GMA) was synthesized by solution copolymerization of methyl methacrylate (MMA) and GMA in the presence of BPO as initiator. It was found that the feed ingredient, initiator type and content influenced the chemical compositions of obtained copolymers. Chemical composition was studied qualitatively using FT-IR spectroscopy and quantified using titration method through estimation of the epoxy content in GMA units. It could be concluded that the MMA-GMA copolymers have been successfully synthesized using both melt mixing process and solution copolymerization with different efficiencies, however the solution method results into higher grafting efficiency. Accordingly, the epoxy content of product could be increased by increasing GMA fraction in the feed ingredient.

Keywords - Copolymerization, graft copolymer, random copolymer

I. INTRODUCTION

Poly methyl methacrylate (PMMA) has been used in many applications but, in general, its use is limited by its lack of functional groups. Thus, functionalization reactions have been used to increase its interfacial interactions. The grafting process is one of the methods most frequently used to modify polymers [1]. Graft polymerization by hydrogen abstraction from tertiary carbon or make free radicals with chain scission of backbone offers an effective approach to introducing some desirable properties into the polymers, but for expanding its applications we need the first method without affecting the backbone architecture [2].

The aim of this work was the functionalization of poly methyl methacrylate by a process of free radical grafting with glycidyl methacrylate using benzoyl peroxide and dicumyl peroxide as initiator in an internal mixer and it occur in other method i.e. solution polymerization. We studied some factors

involved in the grafting process such as initiator and copolymerization method, then evaluated the reactivity of the GMA epoxy group after its grafting onto PMMA.

II. EXPERIMENTAL

Materials

Pellets of PMMA (Acrylic EG920, supplied by LG Co., Korea) dried at 700C for 12 hours and kept in vacuum. Glycidyl methacrylate (GMA, Sigma-Aldrich), methyl methacrylate (MMA, Merck) and the initiator benzoyl peroxide (BPO, Merck) and dicumyl peroxide (DCP, Merck) and solvents i.e. methanol, 1,4 dioxane (Merck) were used as received.

Grafting Process

First of all copolymerization process was occurred in solution copolymerization it would be resulted a random

copolymer i.e. Poly (MMA-ran-GMA) using 0.5ml GMA, 4.5 ml MMA and 0.5 g BPO dissolved in 50 ml 1,4 dioxane then mixed heated at 90°C by a heater-stirrer for 2 hour.

The copolymer was precipitated by addition of methanol as a non-solvent. After that the products were tested by FT-IR and titration and normalized the height of peak to measuring the grafting percentage for the other samples by the PGMA that was synthesized by this method and pure GMA and BPO as an initiator that was dissolved in 1,4 dioxane. Grafting GMA onto PMMA in melt mixing and characterization is the next step. Grafting was occurred in internal mixer for 10min at 185°C and 60 rpm.

TABLE I: MECHANICAL PROPERTIES

Sample	GMA wt. %	PMMA (MMA) wt. %	Initiator
PGMA	100	0	BPO
PGMS10	10	90	BPO
PGMM10	10	90	BPO
PGMMD10	10	90	DCP
PGMM6	6	94	BPO

III. RESULTS AND DISCUSSION

1. FT-IR

The precipitation of solution polymerization of GMA was dried in 70°C under vacuum and its weight was measured about 4g it means the conversion was 80%. In the FT-IR test the peak of wavenumber 910 cm⁻¹ belongs to the epoxy group and the peak of 1724 cm⁻¹ shows the methacrylate group in this case we should normalize other samples by 910 cm⁻¹ because 1724 cm⁻¹ is visible for both PMMA and GMA.

We titrated 0.5 g of PGMA and used the information for normalize other samples as 100%. Other samples tested by FT-IR Spectroscopy too.

Figure 1(a-d) shows the FT-IR results of the samples which were prepared based on Table 1 information and the peak in the mentioned wavenumbers can illustrate that epoxide functional groups are grafted on the main chain of PMMA.

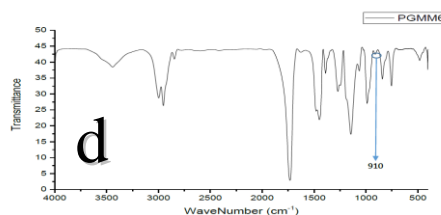
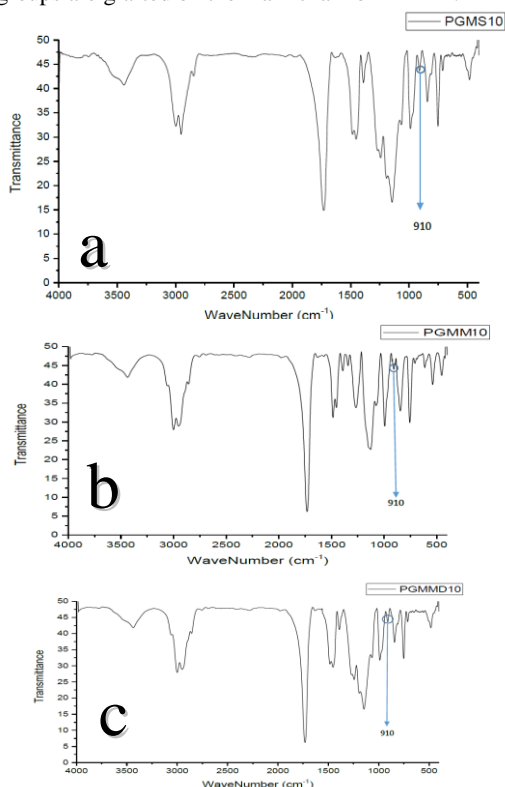


Fig. 1: Copolymers FT-IR Spectroscopy, 10wt.% Solution(a), 10wt.% Melt grafting with BPO(b), 10wt.% Melt grafting with DCP(c), 6wt.% Melt grafting with BPO(d)

2. Titration of epoxy value

According to these figures and titration's results we can measure grafting percentage of GMA or presence of GMA in the backbone of Poly (MMA-co-GMA), results is shown in Table2.

TABLE 2: EFFICIENCY OF GRAFTING

Sample	Grafting (presence)percentage	Efficiency %
PGMS10	~10	100%
PGMM10	~7.5	75%
PGMMD10	~7.8	78%
PGMM6	~4.1	69%

The efficiency increased by increasing the GMA fraction in the feed, we think the reason is the possibility of collision of GMA radicals and MMA macro-radicals together increased by increasing of GMA fraction. In melt grafting, grafting efficiency increased with changing the initiator from BPO to DCP maybe it's caused by longer half-life of DCP at 185°C under shear fields.

IV. CONCLUSION

Poly (MMA-co-GMA) was synthesized via solution radical polymerization and Poly (MMA-g-GMA) was grafted via melt mixing technique and use BPO and DCP to initiate the free radical grafting reaction. The results showed that increasing the GMA fraction increase the efficiency of grafting because of more possibility of collision of GMA radicals and MMA macro-radicals and more efficiency with increasing the half-life of initiator.

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