GRAFTING OF GLYCIDYL METHACRYLATE ONTO MDPE IN SCCO2 AND NEW METHOD IN PURIFICATION USING SCCO2

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Abstract:

In this study the solid state grafting of Glycidyl Methacrylate (GMA) onto Medium Density Polyethylene (MDPE) has been studied in supercritical carbon dioxide ($SCCO_2$) media. Two sets of experiments has been designed, first one was soaking and grafting following by soxhelt extraction of unreacted components and the other one was soaking, grafting and purification by $SCCO_2$ flow.

In the first sets of experiments Central Composite Design was applied to design of experiments and evaluate optimized conditions, parameters such as pressure (90-290 bar), grafting time (20-180 min) and concentration of GMA (4-12 phr), Styrene (0-10 phr), and Benzoyl Peroxide (BPO) (0.025-0.525 phr) was investigated in five levels (-2, -1, 0, 1 and 2). In the second sets of experiments a new method for purification of grafted polymer was applied, Box-Behnkon Design have been employed to design of experiments and evaluate optimized conditions, parameters such as pressure (80-280 bar), dynamic time (20-120 min) and temperature (35-65^{o}C), were investigated in three levels (-1, 0, and 1). The dependent variable Y_1 and Y_2 were taken as the overall grafting yield and purification yield, respectively.

Comparison between melt grafting and supercritical grafting showed that depolymerization of GMA hasn't occurred in supercritical grafting with reaction time and Longer residence time results higher grafting yields in this condition, furthermore styrene co monomer wasn't effective in supercritical condition unlike melt grafting also purification tests showed that $SCCO_2$ purification method is much more efficient and faster than purification by soxhelt extraction technique.

Keywords: Supercritical carbon dioxide, Grafting, Glycidyl methacrylate, Purification

Introduction:

Grafting of GMA onto polyethylene have been studied by different techniques such as UV, gamma radiation[1-3], and grafting by peroxide initiation in Molten state[4-10] But a few studies about solid state supercritical grafting of GMA onto polyolefins have been done [11, 12]. Grafting process using $SCCO_2$ is a solid state grafting process and has several advantages: First, Materials keeps the original shape and melting is not necessary. Second, solid state process temperature is lower than ceiling temperature and depolymerization doesn't take place.

Third, $SCCO_2$ is capable of dissolving nonpolar and not exceedingly polar compounds, on the one hand, and plasticizing and/or swelling polymer matrix on the other hand, therefore, penetration of monomers into polymer matrix is very fast. Forth, it is easy to tune the density of $SCCO_2$ from gas like to liquid like by changing temperature or pressure and thus its solvability, this should provide the ability of control the degree of plasticization/swelling of polymers and partitioning of monomers between the plasticized/swollen polymer phase and the SCCO2 fluid phase. Fifth, CO_2 can be further used to advantage to help extract undesired molecules from the final product. Sixth it's gaseous at ambient conditions and its removal from the final product is easy. Seventh, it is non-flammable, relatively non-toxic, relatively inexpensive and relatively easy to reach a supercritical state (critical temperature: 31.1 ◦C and critical pressure: 7.38MPa[13]) .Disadvantage of this method is low processing temperature which leads to longer grafting time.

Solid State grafting of GMA and MMA onto PP using $SCCO_2$ as solvent and swelling agent have studied by Liu et al.[14], Kunita et al.[11, 12] and Tong et al.[13]. It's found that pressure is a key component in controlling of graft copolymerisation in supercritical condition and soaking step is very effective to elevate grafting yield, in above studies soxhelt extraction have been applied to removing unreacted components (monomers and initiator) but no one haven't been studied on SCCO2 extraction.

Cartier et al.[6] have showed that the use of styrene (St) as a comonomer greatly promotes both GMA's grafting yield and grafting rate onto polyethylene (PE) in molten state but no one haven't been studied its efficiency in $SCCO_2$ grafting condition.

In this study effect of styrene on grafting yield and $SCCO_2$ efficiency in extraction of none reacted components was studied for the first time.

MATERIALS AND METHODS

Powder of Free additive MDPE from Tabriz petrochemical company (density of 0.913 g/mL and MFI (190˚c,2.16kg) =4g/10min) was used, GMA (96%) and Styrene (99.5%) were purchased from Merck and used as received; BPO produced by Atofina was used after drying and carbon dioxide with purity of 99.95% was supplied from Zam Zam Co. Ltd (Isfahan, Iran). A supercritical fluid extraction apparatus consist of CO_2 pressurized vessel, high performance liquid chromatography pump (P_{max}=50MPa), stainless still cell and backpressure regulator was used for grafting and purification experiments.

Two sets of experiments has been designed, first one was included soaking and grafting following by soxhelt extraction of unreacted components and the other one was contained of soaking, grafting and purification by $SCCO_2$ flow. In soaking step the reaction vessel was heated to 50 ˚C with oven and then was kept at that temperature for one hour, during which the monomer and free radical initiator soaked the MDPE powder homogeneously, After that, it was further heated up to the reaction temperature of 120 ◦C (below the melting temperature of MDPE over the whole $SCCO_2$ pressure range in this work) and then pressure was increased to desired value (according to experimental design), Grafted products were purified by Soxhelt extraction with acetone (24 hr) and then was analysed by Fourier Transform Infrared Spectroscopy (FTIR) to determination of grafting yield.

Both sets of experiments have been designed according to response surface methodology using MINITAB software package, Central Composite Design was applied for the first one and

Box-Behnkon Design was applied for the second one, Effect of independent variables on the responses (for both sets) was evaluated according to the following equation (1).

$$\mathbf{Y = \beta_0 + \sum \beta_j X_i + \sum \beta_{jj} X_j^2 + \sum \beta_{jk} X_j X_k} \quad (1)$$

Where Y = Response variable, β_0 = intercept, β_j = linear coefficients, β_{jj}= squared coefficients, β_{jk}= interaction coefficients, X_i, X_j^2, X_j X_k = level of independent variables [15], Table 1 shows the five levels for the variables of the first set of experiment and Table 2 shows the three levels of variables for the second set .

Table 1: Range of values for the first set of experiments

Variables \ Levels	-2	-1	0	1	+2
GMA (phr)	4	6	8	10	12
STY (phr)	0	2.5	5	7.5	10
BPO (phr)	0.025	0.15	0.275	0.4	0.525
Pressure (bar)	90	140	190	240	290
Grafting time (min)	20	60	100	140	180

In the second sets of experiments $SCCO_2$ has employed for extraction of residual species, flow rate of $SCCO_2$ was fixed at 1mL/min and all these experiments have been done on the same grafted samples, the grafted samples have been prepared with the same composition (GMA=8phr, styrene=5 phr, BPO=0.275 phr) and same reaction conditions ($t_{Soaking}$=1 hour, $T_{Soaking}$=50 ˚c, $P_{soaking}$=70 bar, $T_{grafting}$=120 ˚c, $P_{grafting}$=190 bar, $t_{grafting}$=100 min)

Table 2: Range of values for the second set f experiments

Variables \ Levels	-1	0	1
Temperature (^oC)	35	50	65
Pressure (bar)	80	180	280
Time (min)	20	70	120

RESULTS

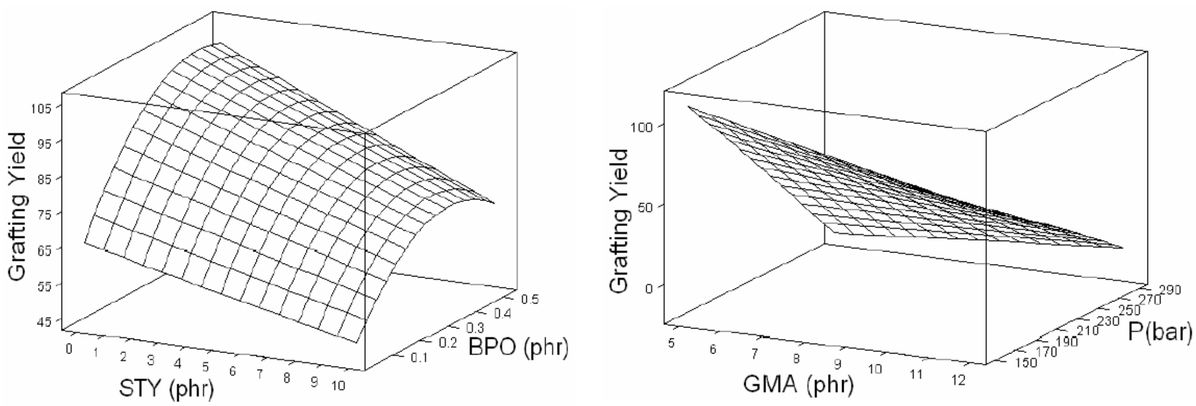
For the first set of experiments after elimination of ineffective parameters according to calculated p-values the equation of grafting yield have been presented as:

$$\mathbf{Y_1 = 216.364 - 10.462\,G - 4.819\,S + 126.38\,B - 0.777\,P + 0.217\,t - 217.67\,B^2 - 0.0003\,P^2 - 0.0004\,t^2 + 0.1813\,G\times S - 7.425\,G\times B + 0.0547\,G\times P - 3.42\,S\times B + 0.0176\,S\times P + 0.759\,B\times t - 0.0015\,P\times t} \quad (2)$$

Where Y_1, G, S, B, P, t are the yield of grafting, GMA, STY, BPO, pressure, and time of grafting, respectively. The R^2 adjusted of the yield of grafting was 86.8 %; it means that the disability of the developed models to predict the yield of grafting was only 13.2 % of the total variations. The linear regression coefficient, R^2 for the yield of grafting was 95.3 % that indicates good performance of the model, p-value of styrene is bigger than other linear parameters and it shows that styrene in supercritical grafting unlike melt grafting is not an effective comonomer to improve grafting yield, It should take into account that presence of styrene in molten state elevates ceiling temperature of graft copolymerization and prevents depolymerization but in supercritical condition reaction temperature is below the ceiling temperature and presence of styrene is not important from this point of view.

Fig1-A shows that increase of BPO concentration has increased grafting yield to some extent (producing more radicals) but when it becomes higher than some extent grafting yield decreases because of deolymerization of grafted chains, increment of styrene concentration in pressure of 152 bar has enhanced side reactions such as copolymerization of styrene with GMA and crosslinking of macro radicals and therefore grafting yield has decreased.

Increase in pressure leads to increase in swelling of polyethylene and salvation strength of carbon dioxide[13], first effect has ascendant effect on grafting yield and second one is reducer but later is stronger and thereupon grafting yield has been decreased, furthermore Increasing in GMA concentration with constant value of BPO has decreased BPO/GMA ratio and therefore Grafting yield has been decreased (Fig1-B).



A B

Fig 1-Grafting yield; A) GMA=6.36 phr, $P_{grafting}$=152 bar, $t_{garfting}$=150 min; B) styrene=0, BPO=0.32 phr, $t_{garfting}$=150 min

Fig 2 shows that longer residence time causes to more decomposition of initiator and results higher grafting yield, furthermore study on grafting yield changes versus BPO concentration is similar to Fig 1-A.

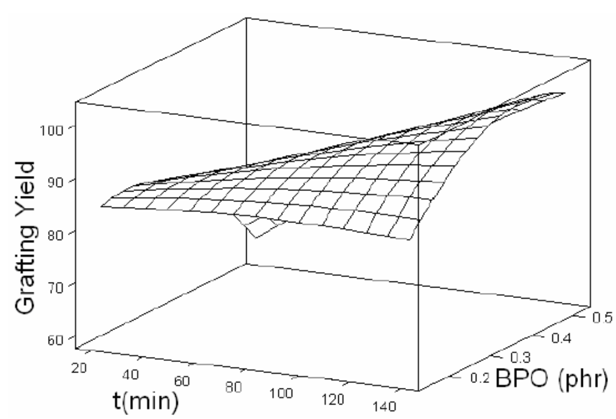


Fig 2-Grafting yield; GMA=6.36 phr, $P_{grafting}$=152 bar, Styrene=0

For the second set of experiments after elimination of ineffective parameters according to calculated p-values and coefficients, the equation of purification yield presented as:

$$Y_2 = -132.7450 + 3.2184\ T + 0.5416\ P + 0.8088\ t - 0.0251\ T^2 - 0.0013\ P^2 - 0.0038\ t^2 + 0.0020\ P \times t \qquad (3)$$

Where Y, T, P and t, are the yield of purification, temperature, pressure, and time of purification, respectively. The R^2 adjusted of the yield of purification was 93.6 %; it means that the disability the developed models to predict the yield of grafting only 6.4 % of the total variations. The linear regression coefficient, R^2 for the yield of grafting was 97.7 % that indicates good performance of the model.

Fig 3-A and 3-B have shown the area of the carbonyl group peak of one of the samples after two different purification methods, Fig 3-A is related to $SCCO_2$ extraction and its carbonyl peak area is 11.46, Fig 3-B is related to soxhelt extraction and its carbonyl peak area is 14.33, it shows that 24 hour soxhelt extraction has not been as effective as 106 min extraction using $SCCO_2$ (pressure of 245 bar and temperature of 50 ˚c) ,later method has extracted more residual GMA monomers and it shows that $SCCO_2$ extraction is much more faster than the conventional method.

In higher pressures density of $SCCO_2$, it's salvation strength and therefore purification yield increases also it's evident that longer purification time leads to higher purification (Fig 4-A). The effect of pressure on purification was the same as Fig 1 and the best purification has been occured in 50 ˚c (Fig 4-B)

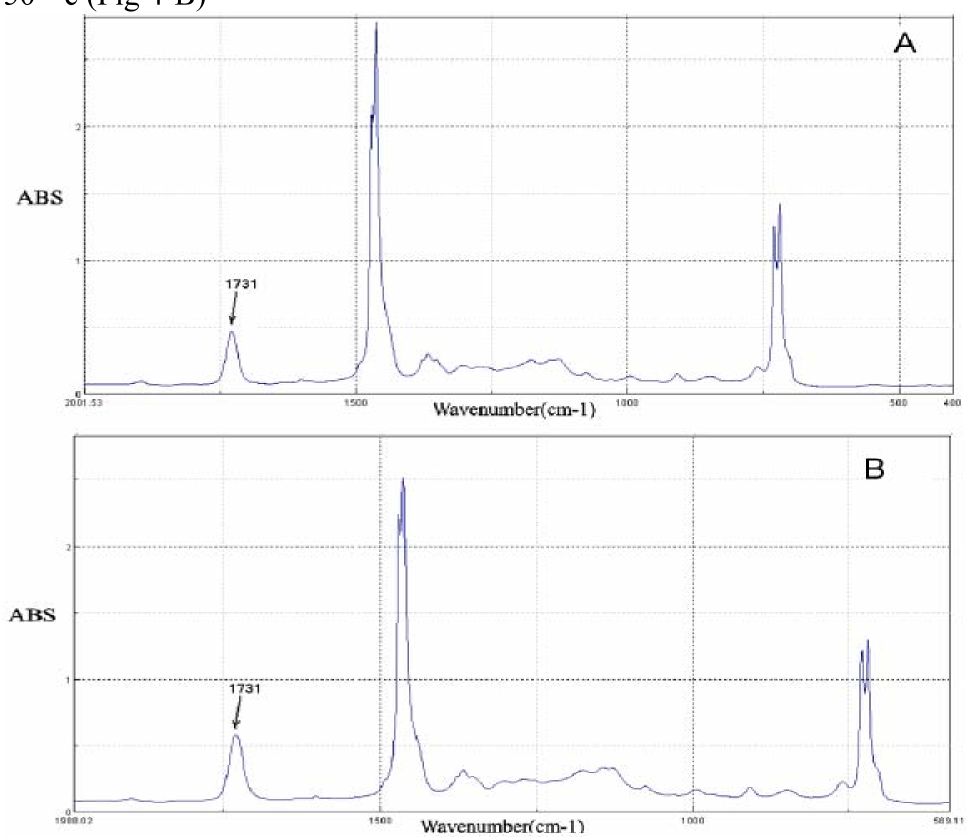
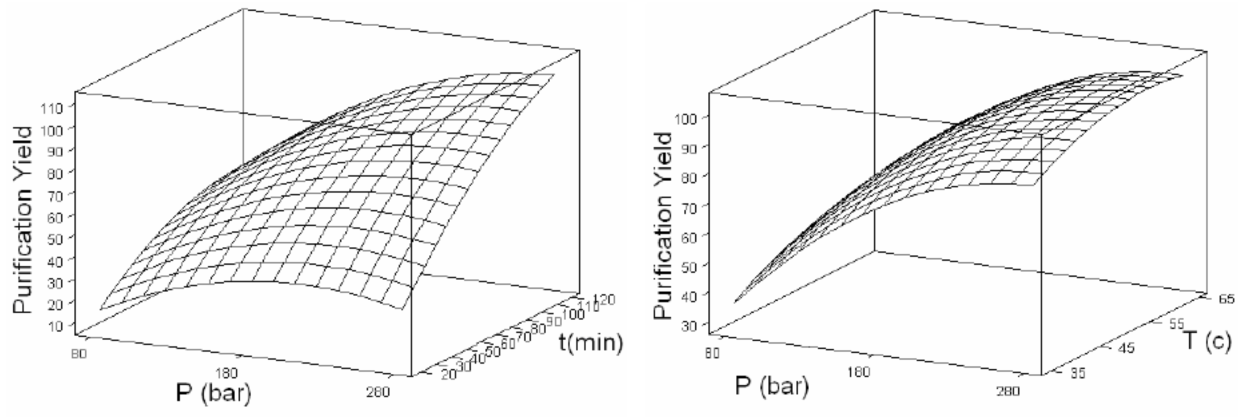


Figure 3 - FTIR spectrum of purificated samples; A) SCCO2 purification; B) soxhelt extraction



A B

Figure 4-Purification yield; A) T=50 ˚c; B) $t_{purification}$=106 minute

CONCLUSION

This paper is shown several scientifically interesting results. It‘s found that styrene comonomer isn’t so effective in supercritical condition unlike melt grafting, furthermore longer reaction time up to 150 minutes leads to higher grafting yield. For approaching to yield of grafting equal 1.0, the conditions of GMA, STY, BPO, pressure, and grafting time were 6.36 phr, 0, 0.32 phr, 152 bar, and 150 min, respectively.

SCCO2 purification tests showed that SCCO2 purification technique is much more efficient and faster than purification by soxhelt extraction technique, furthermore For approaching to yield of purification equal 1.0, the conditions of temperature, pressure, and time were 50 ˚c, 245 bar, and 106 min, respectively.

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