Analysis of the Influence of Glycidyl Methacrylate on Molecular Weight and Refractive Index in Styrene-Methylmethacrylate-Glycidyl Methacrylate Copolymers Through Mixture Design of Experiments

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ABSTRACT: To analyze the influence of the percentage of glycidyl methacrylate (GMA) coupled with polymeric chains to determine their effect on molecular weight (M_w) and refractive index (n_D), a Mixture Design of Experiments (MDOE) has been used. A "*d*" optimal mixture design for four components was used for planning the runs and analyzing the information using statistical tools. The prototypes generated were synthesized using styrene (St) 73–89.98%, methylmethacrylate (MMA) 8–22%, and glydicyl methacrylate (GMA) 2–10% at different ratios according to the experiment design. In this sense, the prototypes are terpolymers (St-MMA-GMA). According to the desired properties of the prototypes reviewed in literature and market studies, this is expressed in materials with a preferred n_D (ca. 1.5750–1.5894) and molecular weight (ca. 300,000 g/mol) the ratios were established. In a radical polymerization process using a commercial initiator (Trigonox 22E-50) and a temperature program (120–200°C) simulating an industrial process, the polymerization reactions were conducted. The detailed information derived from DOE here is presented. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 1935–1941, 2009

Key words: design of experiments; molecular weight; refractive index; terpolymers

INTRODUCTION

Copolymers are commonly based on more than two materials, a usually polymeric material for general and special purposes. For example high-impact polystyrene (HIPS) is frequently made from mixtures of polystyrene and polybutadiene to combine properties of base materials. Essentially, through applied research, there are many modifications with which to improve the morphology and to develop an enhanced mechanical performance from virtually the same starting materials.[1] To fulfill the demands on polymer materials with respect to functionality, the incorporation of specific functional groups into the polymer structure is needed.[2]

Miscibility depends on equal polarity or mutual attraction such as hydrogen bonding or cocrystallization. This is not very common, but there are several important examples of such completely miscible blends.[3]

It is well known that polymers have big problems, mainly with interfacial tension, when aiming to physically combine two or more materials and, with the exception of a few cases, nearly all polymers are immiscible. It is thermodynamically explained with eq.[1] based on positively mixing free energy.

$$\Delta Gm = \Delta Hm \geq 0 \quad (1)$$

In this sense, normally immiscible or incompatible blends show serious limitations, such as poor performance, however, there has been an increase in the use of resources based on multiphase polymeric systems (blends or compounds). In multiphase polyblends, a critical factor is the interface between the phases. If the two polymers reject each other and separate into phases, they are likely to reject each other at the interface as well. The availability of methods is undoubtedly related to the fact that they effectively improve the control of the physical and chemical interactions between the interphase.[4] In most cases, it is necessary to add a compatibilizing agent to strengthen the interface. The present study

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TABLE I
Mixture Design of Experiments, Design Factors: A: Styrene (St), B: Methyl Methacrylate (MMA), C: Glycidyl Methacrylate (GMA) and, D: Trigonox 22-E50 (% T-22)

Experiments			Factors			Variable response		
Rdm	Run	A	B	C	D	n_D^{20}[a]	% of GMA[b]	M_w (1×10^{-5} g/mol)[c]
19	1	73.00	22.00	4.98	0.02	1.5649	2.72	3. 55
9	2	73.00	22.00	4.97	0.03	1.5963	2.27	3.55
11	3	77.49	12.49	10.00	0.02	1.5407	2.65	3.52
2	4	89.97	8.00	2.00	0.03	1.5700	0.87	2.79
10	5	82.98	15.00	2.00	0.02	1.5572	1.42	3.73
3	6	81.98	8.00	10.00	0.02	1.5444	2.03	2.28
14	7	75.89	18.70	5.39	0.02	1.5965	2.82	3.22
18	8	89.98	8.00	2.00	0.02	1.5716	0.86	2.37
13	9	82.38	11.70	5.90	0.03	1.5805	1.99	2.73
4	10	73.00	16.98	10.00	0.02	1.5509	2.89	2.64
17	11	81.97	8.00	10.00	0.03	1.5766	2.07	2.98
1	12	89.98	8.00	2.00	0.02	1.5701	0.89	2.44
15	13	75.99	15.66	8.32	0.03	1.5557	2.17	2.58
6	14	85.98	8.00	6.00	0.02	1.5636	1.72	3.11
12	15	78.79	15.40	5.80	0.02	1.5276	1.85	3.44
20	16	73.00	16.98	10.00	0.02	1.5401	2.40	3.13
7	17	73.00	22.00	4.98	0.02	1.6140	2.51	3.41
5	18	81.97	8.00	10.00	0.03	1.5876	2.36	2.92
16	19	89.97	8.00	2.00	0.03	1.6050	0.89	2.68
8	20	75.98	22.00	2.00	0.02	1.5718	1.72	2.54

[a] Uncertainty: 0.00045 ± 0.0001/1°C.
[b] Measured by NMR.
[c] Measured by GPC.

was focused on using mixture design experiments to create prototypes with target values of certain properties, such as refractive index (n_D), molecular weight, and percentage of GMA coupled with the polymer chains. Therefore, the main expectation is to optimize the properties of the synthesized reactive compatibilizer precursors.

EXPERIMENTAL

Monomers GMA (~ 97%) (from Aldrich), St and MMA (donated by Resirene), were distilled under reduced pressure before use. Copolymerization was carried out in a bulk process, dissolving Trigonox 22-E50 (T22) with a mixture of St, MMA, and GMA according to the MDOE layout. The solutions were placed in tubes which were then evacuated, sealed and kept at a temperature program of 120–200°C simulating an industrial process. Under the same experimental conditions, the conversion in the pure thermal polymerization of St was measured. After the predetermined polymerization time, the polymer samples were dissolved in THF and precipitated by adding excess methanol. Under reduced pressure, samples were dried and the monomer conversion was measured gravimetrically. Gel Permeation Chromatography (GPC) (HPLC-1050 from Hewlett-Packard); detectors: n_D and UV, ultrastyragel columns (10^5, 10^4, 10^3 Å); Polystyrene standards (580–3,900,000 g/mole), room temperature, using THF as a solvent[5] determines molecular weight (M_w) and molecular weight distribution of polystyrene. For 1H-NMR, a Nuclear Magnetic Resonance (NMR) spectrophotometer (Jeol Eclipse +300) at room temperature was used. n_D was measured in an ABBE type refractometer (Atago PR-32α) using the Standard Test Method for Index of Refraction of Transparent Organic Plastics (ASTM D542-2006).[6]

RESULTS AND DISCUSSION

Results and interpretation from experiment design

Derived from the experimental results and to establish the influence of the percentage of glycidyl methacrylate (GMA), over interest system responses like the n_D and the molecular weight of terpolymer Styrene-methyl methacrylate-GMA (St-MMA-GMA) an experimental design mixture (MDOE) was used. The design factors were established in accordance with the bulk composition ingredients as follows: A: St, B: methyl methacrylate (MMA), C: GMA y D: Trigonox 22-E50 (%T-22), experimental runs were planned and their randomized layout (Rdm) is shown in Table I. The variable responses were assigned as shown in Table I, known as refractive index, the (n_D), % of GMA coupled with polymer chains and molecular weight of the corresponding polymers (M_w). In accordance with the methods and techniques described and explained in Reference 7 all

prototypes derived from the design were characterized, target values for the responses were established according to state of the art.[8] For n_D, the desired range was established ca. 1.5750–1.5894, this being the reference n_D of polyethyleneterephtalate (PET) and polystyrene (PS), respectively. In the case of M_w, the reference is in the range of ca. 250,000–320,000 g/mol obeying processing feasibility using a GPC for measurement. For instance, a GMA content of ca. 2–5% is desirable; this is a low level obeying mainly to two factors: cost and a low reactivity rate for GMA.[9]

Design expert has been used for statistical analysis, all data responses shown in Table I were evaluated using an Analysis of variance (ANOVA) to examine whether all data belongs to the same population or the variations are due to different sources, clearly here there are subgroups. These are different from each other, made up of completely separate sets of individual numbers,[10] such as our terpolymer that was made of different monomers. Here, it was determined whether the substances have significant effects on n_D, % of GMA, and M_w.

According to the data from all experiments, a correlation matrix, is presented in Table II. This correlation matrix shows the relationship between every mixture factor, it can be observed that the combination of A, B, and C factors has a correlation of 0.302, while the interaction of A, B, and D has a correlation of 0.038. In the meantime, A, C, and B have a correspondence of 0.599. This means components A, B, and C have a medium correlation in a direct sense, and practically zero correlation with component D, because as shown in Table I, it is virtually constant and has no effect over the responses, as demonstrated through the analysis.

ANOVA for responses (n_D, %GMA, M_w)

The value of statistical information is well known, in the case of ANOVA it is used to analyze the total variation in the response in terms of how much of that variation can be attributed to the knowledge of the regressors and how much is unexplainable by the model.[11] In other words, to decide which of the models of increasing complexity provides a sufficiently good fit to the observed data. Through the sum of squares, degrees of freedom (DF), and mean squares from a linear regression fit, three different ANOVA tables were constructed (Tables III–V), one for every system response. These tables show whether the regression model explains enough of the variation in the responses to justify using the model as a predictor of the response. Therefore, two different hypotheses about the regression model were formulated. The first questions whether the regression model explains a significant proportion of the variation in the response. The second considers whether the regression model is worthwhile. This analysis provides evidence of a significant relation between the response and the regressors.

TABLE II
Matrix of Correlation From Factors

	A	B	C	D	AB	AC	AD
A	1						
B	−0.047	1					
C	−0.013	−0.610	1				
D	0.188	−0.382	−0.154	1			
AB	−0.293	−0.543	0.302	0.038	1		
AC	−0.177	0.599	−0.808	−0.108	−0.294	1	
AD	−0.546	0.271	0.146	−0.794	0.095	0.021	1

TABLE III
ANOVA for Refractive Index (n_D)

Source	DF	F	Prob > F	
Model	3	2.891	0.0678	No significative
Adjustment	11	1.07	0.5048	No significative

DF: Degrees of freedom for the model.
F: F value, test for comparing model variance with residual (error) variance.

In the case of n_D ANOVA provides the information shown in Table III. According to the statistical data, it was observed that Prob > F for the model is 0.0678, which is nonsignificant, this means that n_D, has no effects from mixture components. Meanwhile, the Prob > F for the calculated adjustment is 0.5048, the same as the first reported value; here, we have no significance derived from the result. The variation from the prediction and the experimental data has no relevance; this means that the selected model is correct and adequate according to our estimations, as is shown in Figure 1 for the predicted vs. actual, n_D plot.

For % GMA, the ANOVA analysis for this response is presented in Table IV. Here, the value of Prob > F for the model is 0.0001; this result is significant, this means that % GMA (experimental), is affected by the monomer's proportions in the mixture. Meanwhile, the adjustment obtained for the value of Prob > F is 0.2403, and according to this, is nonsignificant, meaning that the variation between the prediction and the actual data has no relevance for % of GMA, as shown in Figure 2.

Finally, the ANOVA for M_w is presented in Table V. A value of Prob > F of 0.0045, as in the case of % GMA, is significant and indicates that molecular weight is affected by the different mixture relationships. The value for the Prob > F for adjustment is 0.4155, meaning that the correlation between the predicted value and the actual data is no significant as shown in Figure 3.

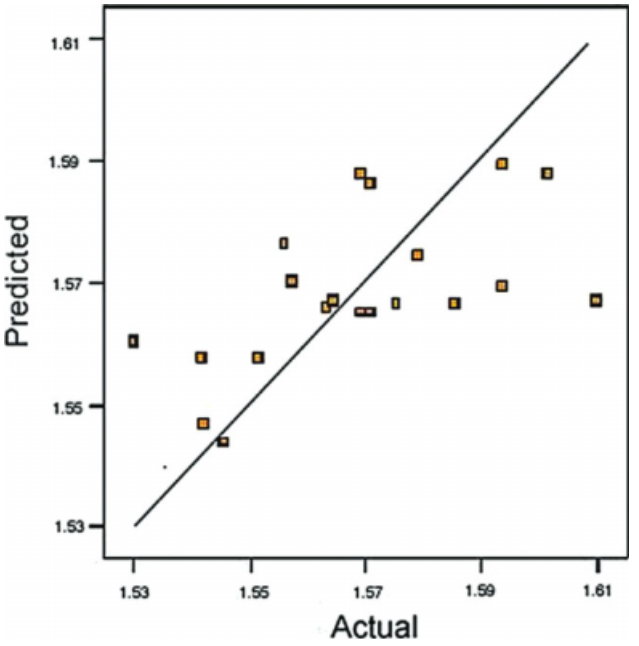

Figure 1 n_D prediction vs. actual. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

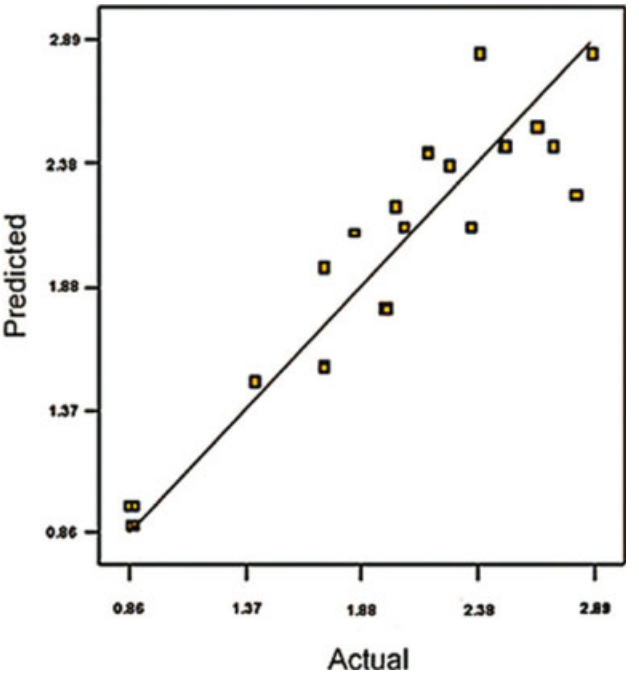

Figure 2 % of GMA prediction vs. actual. [Color figure

Contour graphs for mixture relationships

As was shown by the ANOVA analysis, it has been determined that the influence of the different components over the target properties analyzed n_D, % GMA coupled to polymer chains, and $M_{w.}$ This interaction between components can be seen and analyzed using the contour plots displayed in Figure 4. In Figure 4(a), the influence on n_D was analyzed; the shadowed area limited by continuous lines indicates the area of interest for the target property, n_D, i.e., 1.5750–1.5894. According to this, an increase in % GMA content contributes to diminishing the n_D and with an increase in % MMA, it was observed that n_D increases as well. Regarding the % St content, a low effect was observed on n_D of terpolymer. These different effects were considered normal because in all cases they were directly proportional as was confirmed through the corresponding ANOVA, indicating no wide variations over the response.

On analysis of the contour graph in Figure 4(b), it was observed that the area of interest was on the low region of the plot, from the 1.86 line toward the lower area (shadowed area). It describes the behavior observed for each component. In the case of % MMA, there is a no significant effect over the %GMA coupled to polymer chains. In accordance with the data obtained, it is necessary to consider values of St as component of terpolymer around 73–80% and a greater amount of GMA to assure %GMA coupled to polymer chains, because this last component is necessary to make possible the compatibilizing function of the synthesized terpolymer. Here, the contour graph confirms the well-established criteria from the ANOVA where the % of each of the components of the mixture affect the percentage of GMA coupled to polymer chains of terpolymer.

In the M_w case presented in Figure 4(c), it shows an area limited by lines in 280,120, and 319,265 g/mol. According to this it was shown that M_w

TABLE IV
ANOVA for % of GMA

Source	DF	*F*	Prob > *F*	
Model	3	41.67	0.0001[a]	Significative
Adjustment	11	1.94	0.2403	No significative

DF: Degrees of freedom for the model.
F: *F* value, test for comparing model variance with residual (error) variance.
[a] Prob > *F* value is very small (less than 0.05) then the terms in the model have a significant effect on the response.

TABLE V
ANOVA for M_w

Source	DF	*F*	Prob > *F*	
Model	13	10.39	0.0045[a]	Significative
Adjustment	1	0.79	0.4155	No significative

DF: Degrees of freedom for the model.
F: *F* value, test for comparing model variance with residual (error) variance.
[a] Prob > *F* value is very small (less than 0.05) then the terms in the model have a significant effect on the response.

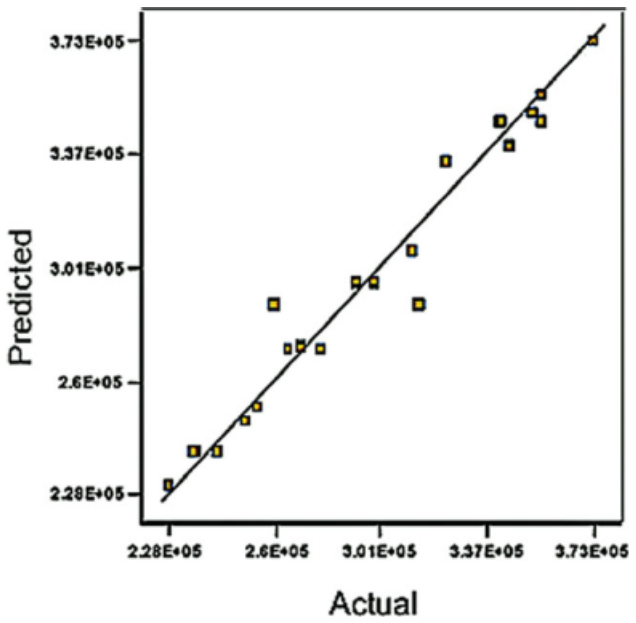

Figure 3 M_w prediction vs. actual values. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

increases along the percentage of GMA, and diminishes when the percentage of St increases, in the case of the percentage of MMA it has no significant effect over M_w of the terpolymer.

Therefore, to achieve the desired conditions, for the molecular weight it would have to make the synthesis of the terpolymer necessary to work in a range of ca. 73–80% of St and a percentage of GMA of ca. 8 to 18.98%. In the same way as in the previous shape graphs, it confirms that as in the ANOVA runs; the percentage of the components considerably affects the molecular weight of the samples. As can be seen here, ANOVA helps to demonstrate that the contour graphs show interactions between the mixture components thus significantly affecting the measured M_w of the terpolymers, and with a slight effect over the n_D and % GMA responses, respectively, coupled to polymer chains as explained above.

Optimization

To optimize the synthesis conditions, desired values for the responses or several sets of values for mixture components were fed into the software tool, which in turn provided five possible solutions; these solutions were taken only as "suggestions" to scale up the synthesis of terpolymers, in accordance with the desired initial criteria. The optimization results obtained are shown in Table VI. In the prediction values, ranges of 74 to 83% were observed for St, 8.5 to 17.5% for MMA and 4.5 to 9.5% for GMA. The expected prediction values for the refraction index, molecular weight, and GMA are within the desired values for terpolymer.

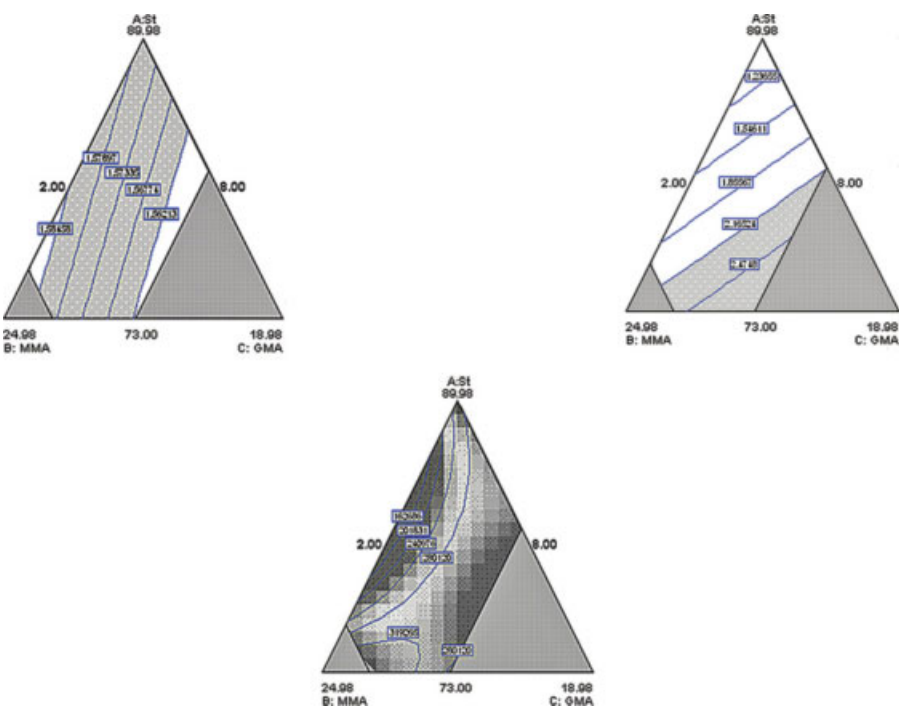

Figure 4 Influence areas for the responses: a) n_D; b) %GMA coupled to polymer chains; c) M_w according with the mixture relationships between St, MMA, and GMA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE VI
Optimization Solutions and Prediction Values

	St	MMA	GMA	T22	n_D[a]	%GMA[a]	M_w (1×10^{-5} g/mol)[a]
1	79.43	13.69	6.86	0.025	1.57	2.09	2.94
2	74.33	17.02	8.63	0.021	1.56	2.63	3.13
3	80.44	10.20	9.33	0.029	1.56	2.19	2.84
4	82.66	8.55	8.76	0.025	1.56	2.00	3.02
5	77.80	17.39	4.79	0.024	1.58	2.04	2.76

[a] Estimated predictions based on a polynomial model.

Optimization criteria graph

The optimization criteria graph (Fig. 5) shows the three response value lines corresponding to the desired criteria. The area marked in yellow reveals the optimum conditions under which to synthesize terpolymer. This area is defined by the refraction index, which is represented by red lines, molecular weight in blue lines, and GMA percentage in green lines. Concluding that optimum initial conditions for terpolymer synthesis should have a 73–80% of St and 5–17% of GMA and by the extension of the area we can conclude that the MMA percentage does not vary the conditions.

Once the composition percentages are obtained, the molecular weight and refraction index can be obtained within established ranges and a grafted GMA percentage of 2.00 to 2.89% can be accomplished. Finally, once all the necessary tests were done, the samples with the desired features were 4–7, 12–17, and 19–20. Concluding that MDOE helps to establish the influence of refraction index (n_D), M_w, and %GMA coupled to polymer chains as well as the mixture optimization. These relations allow us to improve results for future projects.

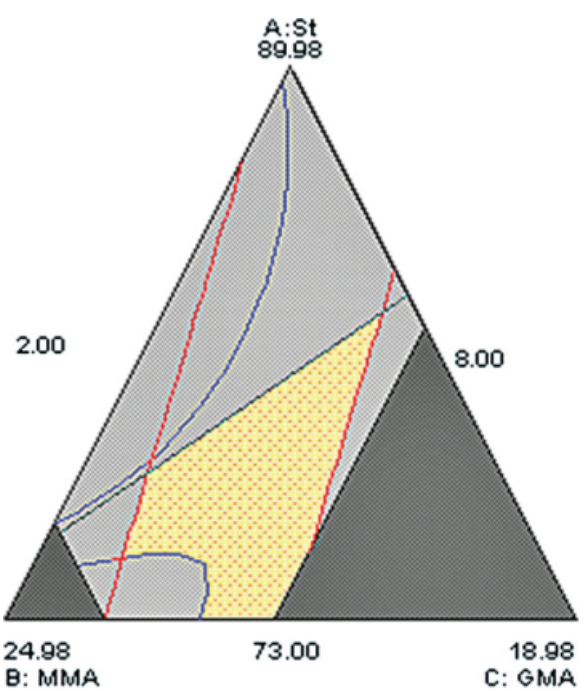

Figure 5 Optimization plot derived from experimental data. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

CONCLUSIONS

The article presented helped to conclude that GMA, is able to influence the refraction index in the terpolymer studied, and when the percentage of GMA increases proportionally it produces a slightly decrease in the refraction index, due to the characteristics themselves of the occupied volume by the monomer units and the influence of the intermolecular forces of the GMA units that modify the manner of light refraction. The molecular weight is affected in greater measure when increasing % of GMA in direct proportion. The effort made in modeling the characteristics of the material using the MDOE tool for mixtures allows for the possibility that all prototypes be synthesized with the desired characteristics developed through this research. The main interest is to first develop a material that acts as compatibilizer for blends of PET and PS immiscible in nature.

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