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Evaluation of Effective Parameters for the Synthesis of Poly(propylene fumarate) by Response Surface Methodology

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ABSTRACT: Poly(propylene fumarate) (PPF) is an unsaturated linear polyester, which was synthesized for potential applications in filling skeletal defects. The synthesis was carried out according to a two-step polymerization reaction. In this research, a functional relationship among three reaction factors [temperature, reaction time, and stoichiometry of the monomers] in the PPF synthesis was established by responses of the surface methodology/central composite design (CCD). After that, on the basis of the responses of CCD [increasing intensity ratio of the C—H/O—H peaks in Fourier transform infrared (FTIR) spectra], designed substances were synthesized and analyzed by FTIR spectroscopy. The synthesized PPF, based on the optimized synthesis conditions from CCD, had a high molecular weight, low hydroxyl group content, and optimum viscosity. According to the CCD response, the best product was obtained through with a molar ratio of diethyl fumarate/propylene glycol/$ZnCl_2$/hydroquinone of 1:3.5:0.01:0.002 and a 17-h reaction time at 140°C. Eventually, the synthesized PPF was characterized by FTIR spectroscopy, NMR, and gel permeation chromatography analyses. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40932.

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INTRODUCTION

These days, biodegradable materials are becoming popular in packaging, agriculture, medicine, and other areas. Biodegradable unsaturated polyesters, because of their ability to crosslink *in situ* and degrade gradually, are the most promising materials for tissue engineering.[1]

Because of slow hydrolysis, polyesters are the most common degradation synthetic polymers in tissue engineering. For example, polyesters, such as poly(L-lactic acid) and poly(d,l-lactic-*co*-glycolic acid), are biocompatible and biodegradable materials that can form *in situ* tissue engineering scaffolds.[2,3]

One of the most important biodegradable polymers is poly(propylene fumarate) (PPF), a linear, unsaturated polyester that consists of alternating propylene glycol (PG) and fumaric acid units.[4] The main advantage of the unsaturated polymers is their ability to cure the material *in vivo;* thereby, the skeletal defects in any shapes or sizes will be filled with minimal surgical intervention. PPF has the inherent advantage of fumarate units; these allow the polymer chains to be covalently crosslinked through its carbon–carbon double bonds with relatively low levels of heat release.[5,6] Thus, PPF can be fabricated *in situ* to obtain a three-dimensional scaffold.

The molecular weight of linear PPF affects the mechanical and degradation properties of a crosslinked composite used in the orthopedic applications.[2,5–10] To synthesize reproducible polymers, an understanding of the reaction kinetics is required. Although many different methods have been reported for synthesizing PPF,[7–13] few publications have dealt with the reaction kinetics.[7]

PPF is synthesized in a two-stage reaction period. In the first stage, a fumaric acid derivation is combined with an excess of polypropylene glycol to yield bishydroxypropyl fumarate. This step can be accomplished with several materials and techniques.[14] In the second step, bishydroxypropyl fumarate is heated in the range 100–250°C *in vacuo* at approximately 1–300 mmHg in the presence or absence of a basic catalyst such as antimony trioxide. The remaining excess of PG from the first step is boiled off, and then, bishydroxypropyl fumarate goes through a transesterification reaction. Some of the aforementioned reactions are described next.

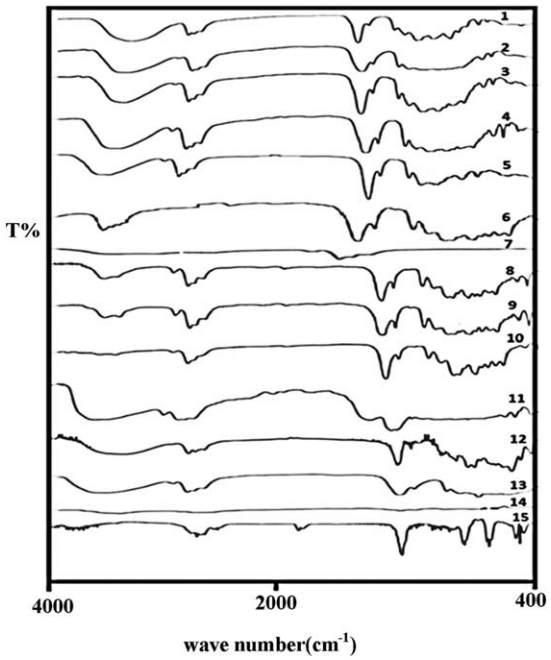

Figure 1. FTIR spectra of all prepared defined samples in Table I.

Sanderson[15] prepared PPF as a powder by a transesterification reaction between diethyl fumarate (DEF) and PG in the presence of an acid catalyst, *p*-toluene sulfonic acid, by heating it to 250°C over a period of 5 h and vacuum-drying at 220°C for 4 h.

Yaszemski et al.[16] and Peter et al.[7] also produced PPF [weight-average molecular weight (M_w) = 850, polydispersity index (PDI) = 2.0] by a two-step method. Initially, bis(2-hydroxyl propyl fumarate) was prepared by the reaction of fumaryl chloride and PG at room temperature. Then, transesterification was carried out at 160°C for 24 h *in vacuo* with an antimony trioxide as the catalyst. Szmeresanyi et al.[17] and Andreis et al.[18] synthesized PPF through a condensation reaction between maleic anhydride and PG and also their isomerization. Gresser et al.[12] produced PPF (M_w = 2600, PDI = 2.6) by the reaction of fumaric acid and PG with a *p*-toluene sulfonic acid catalyst and *t*-butyl hydroquinone as an inhibitor. Domb[19] prepared PPF by the reaction between PG and fumaric acid at 130°C for 10 h and then at 180°C for 2 h to get a viscous liquid with an M_w range of 300–2000 and a PDI of 1.5–1.7. However, none of these preparation methods has led to an optimal molecular weight and proper physical characteristics for use in biomedical applications. During synthesis, the control of molecular weight and polymer end groups in polymers will be difficult, and also, there will be some difficulties in the consistency, reproducibility, and mechanical properties of the resulting polymer.[20]

The main goal of this research was, first, to establish a functional relationship between three reaction variables [reaction temperature (T), reaction time (t), and stoichiometry of the monomers (S)] and, then, to find the responses [increasing intensity ratio of C—H/O—H peaks in Fourier transform infrared (FTIR) spectra] with a statistical technique. Response surface methodology/central composite design (CCD) was used to optimize the synthesis procedure and determine the significant factors influencing the synthesis of PPF. CCD, which is the most popular response surface method for experimental design, was applied to optimize the synthesis polymer parameters.[21–23] One of the main objectives of CCD is to optimize levels of the variables to get the best response.

To monitor the chemical structures of the synthesized samples, FTIR analysis was used. Finally, the best synthesis conditions were introduced for the synthesis of PPF, and subsequently, the product was characterized by FTIR spectroscopy (Figure 1), NMR (Figure 2), and gel permeation chromatography (GPC) analyses (Figure 3).

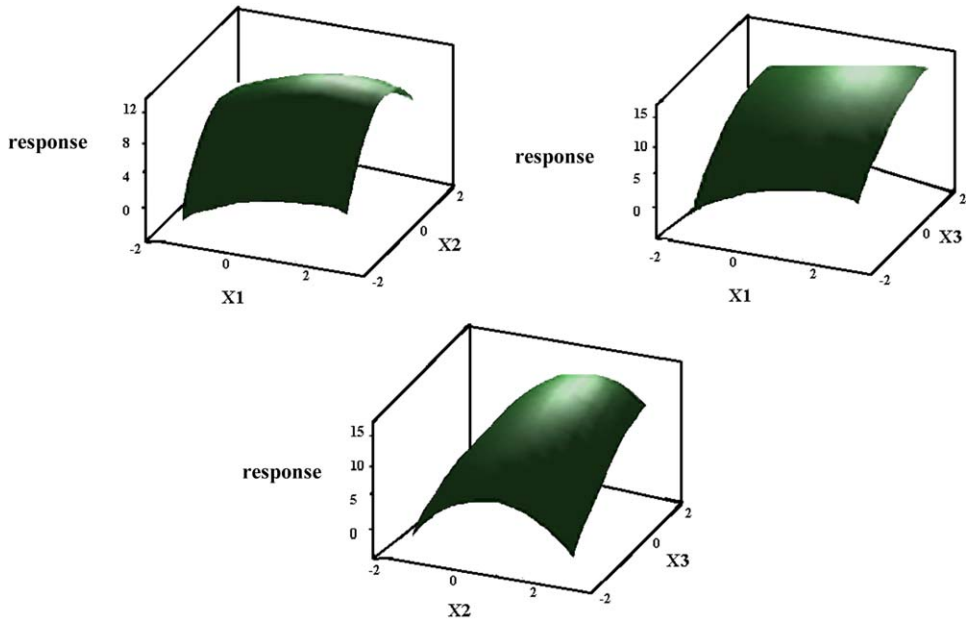

Figure 2. Surface plots of the combined effects of x_1, x_2, and x_3 variables on synthesized PPF. x_1, x_2, and x_3 variables correspond to temperature, reaction time and stoichiometry of the monomers, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

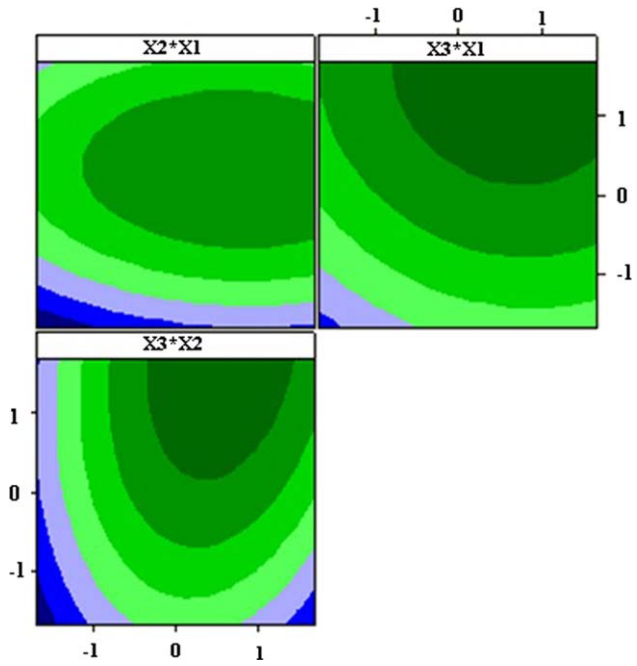

Figure 3. Contour plots of the combined effect of x_1, x_2, and x_3 variables on synthesized PPF. x_1, x_2, and x_3 variables correspond to temperature, reaction time and stoichiometry of the monomers, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

EXPERIMENTAL

Materials

DEF, PG, and zinc chloride ($ZnCl_2$) were reagent grade and were obtained from Merck. Hydroquinone was obtained from Sigma-Aldrich, and methylene chloride and hydrochloric acid were also obtained from Merck.

Experimental Design and Data Analysis

With a chemometric approach, each variable was examined and optimized in a predefined range through a series of experiments in which the values for several variables were changed at the same time.

Full uniform CCD presents the following characteristics. They require an experiment number according to the following equation:

$$N=2^f+2f+r$$

where N is the experiment number, f is the number of factors, r is the replicate number of the central point, and the α values depend on the number of variables, which can be calculated by the following equation:

$$\alpha=\pm 2^{f/4}$$

All factors must be studied in five levels.[24]

In this study, CCD was applied for three independent variables across five levels, including three replicates of the central point. The variables considered in the optimization process were *T*, *t*, and *S*. The polynomial equations, response surface, and central design for a particular response were obtained through the use of the statistical software package Minitab Release 16 (Minitab, Inc.). For an experimental design with three factors, the model includes linear, quadratic, and cross terms and can be expressed by eq. (1):

$$Y=\beta_0+\beta_1x_1+\beta_2x_2+\beta_3x_3+\beta_{11}x_{21}+\beta_{22}x_{22}+\beta_{33}x_{23}+\beta_{12}x_1x_2+\beta_{13}x_1x_3+\beta_{23}x_2x_3 \quad (1)$$

where Y is the increasing intensity of the C—H/O—H peaks in the FTIR spectra predicted response; x_1, x_2, and x_3 are the independent variables; β_0 is the intercept (constant); β_i is the linear coefficient; β_{ii} is the squared coefficient; and β_{ij} is the cross coefficient. The explained variation percentage was expressed by the coefficient of determination (R^2) at a 5% statistical significance level.

Synthesis of PPF

The synthesis of PPF was carried out by a two-stage melt polycondensation method (esterification and polycondensation), which was adapted from Kharas et al.[25] First, DEF, PG, $ZnCl_2$ as a catalyst, and hydroquinone as a radical inhibitor with different molar ratios of main reactants were added to a three-necked, round-bottomed flask. The reactants were under continuous nitrogen, submerged in an oil bath, and magnetically mixed with a stirrer. PPF was prepared through a condensation reaction through a mixed refluxing–distillation system under various temperatures and vacuum conditions at different *t* values. A refluxing–distillation system was applied for a suitable condensation and byproduct distillation, each one after another. The initial *T* was set at 90°C, and it gradually increased in each of the polymerization batches and rose to 160°C. The whole reactions were run in two distinct periods of time. In the first period, the esterification condensation occurred, and in the second step, the transesterification reaction was carried out. The *t* values of these steps were different from 2 to 18 h under the conditions of the polymer synthesis.

Consequently, the washable reaction products were dissolved in methylene chloride and were then washed with 5% aqueous HCl to remove the unreacted reactants and $ZnCl_2$. They were then purified with two washes with pure water and brine. Sodium sulfate was used as a drying agent in the organic phase. The concentrated product was then precipitated in ethyl ether twice to remove the inhibitor.[26] Finally, all of the remained solvents were removed from the product by vacuum-drying at 60–70°C for 24 h. The purified resin, as a product, was a highly viscous light brown material. The obtained resin was characterized by FTIR analysis.

Chemical and Physical Characterization

FTIR Spectra. FTIR spectra were obtained through a BOMEM (model SPG5800G). The characteristic peak at 1726 cm^{-1} corresponded to the ester linkages, that at 1646 cm^{-1} corresponded to the vinyl moiety, those at 1455 and 1375 cm^{-1} corresponded to methyl stretching, and that at 1296 cm^{-1} corresponded the secondary alcohol; these were shown in the FTIR spectrum of PPF.[27]

NMR Spectrometry. H-NMR spectrum was obtained through the use of a Bruker Avance 400-MHz NMR system (Bruker

Table I. Levels of Variables for CCD Experimental Design

Symbol	Variable	Low axial ($-\alpha = -1.68$)	Low factorial (-1)	Center (0)	High factorial ($+1$)	High axial ($+\alpha = +1.68$)
X_1	T	90	105	130	145	160
X_2	t	2.0	5.0	10.0	14.0	18.0
X_3	S[a]	1.5	2.2	3.0	3.5	4.0

[a] Here and in the text, S indicates the PG/DEF molar ratio.

Analytik GmbH, Rheinstetten, Germany) operated with a Silicon Graphics O_2 workstation (Silicon Graphics, Mountain View, CA). Proton spectra were obtained with a 30° pulse angle, 4-s acquisition time, and 3-s delay time. The samples were dissolved in $CDCl_3$ with Tetramethylsilane as a standard reference.

GPC. The PPF molecular weights were determined by a GPC technique (GPC Agilent 1100), a chromatography column (Agilent and PL gel, 3 μm, 300 × 7.5 mm) column, 50–100,000 DA range), and a refractometer index detector. Tetrahydrofuran was used as solvent with a flow rate of 1 mL/min. The molecular weights were determined from a calibration curve generated according to ASTM D 6579-11.

Viscosity Measurement. The viscosity of PPF was determined with a Brookfield viscometer (spindle no.6).

RESULTS AND DISCUSSION

Optimization by CCD

CCD was used to optimize the experimental parameters. Three independent factors, T (90–160°C, x_1), t (2–18 h, x_2), and S (DEF/G, ~1:1.5–1:4.1, x_3) were studied at five levels with three repetitions at the central point and with $\alpha = \pm 1.68$. Therefore, 17 experiments were designed. The experiments were performed according to the design matrix with coded levels of parameters, as shown in Table I. The responses of CCD for PPF syntheses are presented in Table II. The obtained coded value of each factor was obtained from Minitab Release 16 software. These coded values were transformed to the actual values to provide the optimum conditions of variable factors. The results are shown in Table III. Furthermore, Figures 4(A,B) and 5 show the surface and contour plots for the FTIR responses obtained from the 17 experiments, respectively. Therefore, the actual optimized values for T, t, and the DEF/PG molar ratio of the monomers were obtained as 140°C, 17 h, and 1:3.5, respectively. Thus, the optimized values for the simultaneous synthesis of PPF were used.

Preparation of the Sample

According to our statistical work, one sample was synthesized in our laboratory on the basis of the optimal conditions and the best molar ratio for PPF synthesis. This polymer, prepared by the aforementioned conditions, had a proper viscosity and suitable molecular weight for injection biomedical applications and was subsequently characterized by FTIR spectroscopy, NMR, and GPC analyses.

FTIR Analysis. Frequently, the characterization of the molecular weight of PPF has been done by GPC analysis.[13,28] In this study, we used the FTIR spectra to analyze the molecular weight PPF,

Table II. Production Schedule for the Three-Factor CCD and Response

Standard order	Run order	PtType	Blocks	x_1	x_2	x_3	Response
2	1	1	1	−1	−1	1	6
11	2	−1	1	−1.68179	0	0	3
7	3	1	1	1	1	−1	14
12	4	−1	1	1.68179	0	0	3
3	5	1	1	1	−1	−1	9
14	6	−1	1	0	1.68179	0	13
15	7	0	1	0	0	0	12
13	8	−1	1	0	−1.68179	0	3
10	9	−1	1	0	0	1.68179	11
17	10	0	1	0	0	0	12
4	11	1	1	1	−1	1	10
8	12	1	1	1	1	1	15
1	13	1	1	−1	−1	−1	4
6	14	1	1	−1	1	1	8
5	15	1	1	−1	1	−1	7
16	16	0	1	0	0	0	12
9	17	−1	1	0	0	−1.68179	5

Table III. Optimum Extraction Conditions for the Synthesis of PPF

Variable	Optimized value
T	140°C
t	17 h
S (molar ratio)	1:3.5 DEF/PG

check the progress of the reaction, and investigate the effective parameters on the PPF reaction synthesis.

Each functional group corresponded to a region of absorption wavelengths and, thus, allowed us to identify them through the analysis of the IR spectrum. The stretching vibrations of typical organic molecules tend to fall within the specific regions of the IR spectrum, as shown in Table IV. The results of the CCD studies show that the synthesis of the samples, including the intermediates or other substances from all of the experiments, from the FTIR spectra according to Figure 6, led us to recognize the various effective reaction parameters.

Similarly, the IR spectrum of the best synthesized product is presented in Figure 1. The intermediate diesters had a higher relative intensity in the OH region because of the terminal hydroxyl vibration at 3448 cm^{-1} because of the higher proportion of hydroxyl end groups compared to the unsaturated polyester. In the synthesized polymer, this hydroxyl peak diminished with *t* because of the decreasing relative amount of end groups present in the polymer. The ester carbonyl bonds and C═C stretching appeared at 1726 and 1646 cm^{-1}, respectively. After the transesterification of the intermediate, a noticeable decrease in the OH band at 3448 cm^{-1} was observed because of the removal of the PGs. The FTIR spectra changes strongly supported the progress of transesterification. For example, a comparison of sample number 12 with sample number 8 confirmed the reduction of the OH peak intensity, as shown in Figure 6.

The FTIR spectra emphasized that the absence of the mentioned peaks confirmed the improvement in the esterification reaction. However, according to the literature, free carbonyl groups should appear at 1690 cm^{-1}. At lower wave numbers, significant peaks, which were present around 1226 cm^{-1}, were attributed to the C—O linkages.

H-NMR Spectroscopy. ^{1}H-NMR analysis was performed to determine the results of the functional groups identified by FTIR analysis. ^{1}H-NMR spectrum of the best PPF is presented in Figure 2. As shown in Figure 2, the chemical shifts at 6.8 ppm (vinyl protons), 5.3 ppm (—CH), 4.3 ppm (—CH_2), and 1.2 ppm (—CH_3) confirmed the chemical structure of PPF.

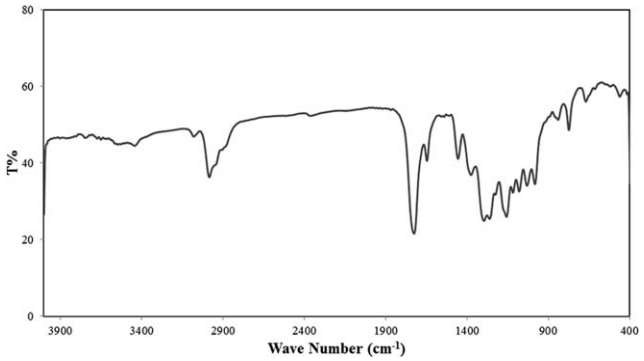

Figure 4. FTIR spectrum of poly (propylene fumarate).

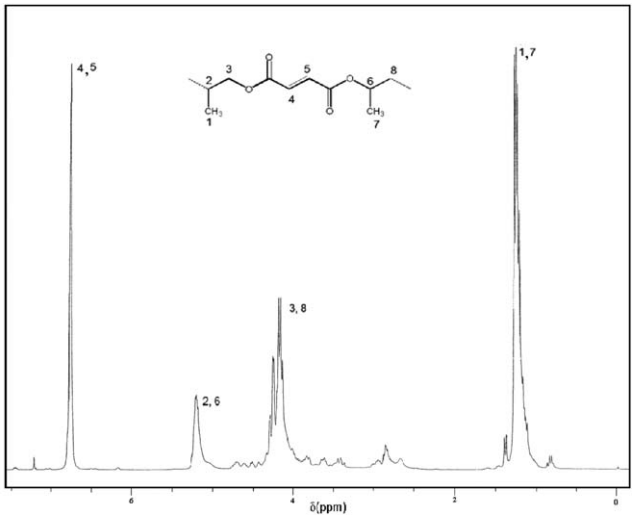

Figure 5. ^{1}HNMR (400 MHz, $CDCl_3$, ambient temperature) spectrum of PPF

GPC Analysis. The synthesis and characterization of some samples by FTIR spectroscopy and GPC showed that the best product had a number-average molecular weight (M_n) of 1167 g/mol, an M_w of 2195 g/mol, and a PDI of 2.8, as shown in Figure 3.

Given the fact that the viscosity increased logarithmically with the molecular weight, it was clear why the monitoring of viscosity was so important in the processing of the polymers. The determination of the viscosity was greatly important in processing because of the fact that for the flexible chain polymers, there is a critical molecular weight at which the entanglement begins. The molecular weight and viscosity are directly related to the type of polymer.[29]

Other poor quality substances that were defined in the matrix trough CCD were prepared in our laboratory; their FTIR spectra are presented in Figure 6.

Viscosity Measurement. The viscosity of PPF was measured, and was determined to be about 12,500 Cp. This showed that the best product was a high-viscosity material.

Table IV. Wave Numbers of Various Bands in PPF[38]

Band (cm^{-1})	Assignment
3446	OH groups
2960	Stretching frequency of CH_2
1730	Stretching frequency of acid and ester carbonyl group
1643	Unsaturation C═C in fumarate unit
1000–1300	C—O stretching vibrations

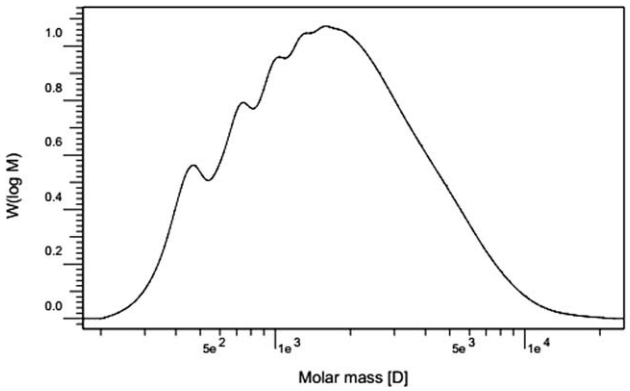

Figure 6. GPC chromatogram for molecular weight of final PPF.

Effect of the Raw Material *S*, *t*, and *T* Values on the PPF Production

Raw Material *S*. The simplest way to synthesize a polyester involves the heating of a hydroxyl–carboxylic acid or a mixture of a glycol with a dicarboxylic acid up to temperatures in the range 120–250°C, and the polycondensation process leads to the production of the polyester and water,[30] as shown in Figure 7. With the exception of the catalyst and inhibitor, the formation of a polyester will have two or more glycols in the reaction. They will be added to the polymer chain in a statistical distribution.

Therefore, careful monitoring of the ratio of ingredients is necessary to ensure that the final product contains suitable hydroxyl groups, not acidic ones.[31] The molar ratio of the diol must be more than that of the acid to ensure the completion of the esterification reaction. To obtain a high-conversion polymerization, the reactive groups should be present at all stages of the reaction to react with each other in a stoichiometric ratio.

The decrease in the PG amount caused the production of a solidlike substance similar to a solid ball or stiff material with too high a viscosity. In these products, the OH groups were blocked, and this resulted in the reaction finishing before the vacuum was applied. It seemed that the continuation of the reaction led to the crosslinking. Similarly, the solubility of the products was studied by solubility studies, which indicated they were insoluble in acetone, dichloromethane, tetrahydrofuran, and toluene as solvents of PPF. Furthermore, the FTIR spectra indicated that the hydroxyl bands appeared broadly in the 3400-cm^{-1} range, and this means that the C═C bands were opened and formed a network.

Some quantity of PG may have been lost during distillation and carried off by the gaseous stream out of the reactor in the reaction between DEF and PG (volatile).[32,33] The flow of inert nitrogen gas to the reactor may have led to the removal of the PG monomer vapors with ethanol vapors from the reactor because the boiling point of the PG–ethanol mixture was closer to the boiling point of ethanol (78°C) than to that of DEF.

However, to obtain higher degrees of polymerization, the removal of polypropylene glycol as a byproduct from the reactor was necessary in the second stage. The removal of the PG was difficult; thus, a vacuum was used to facilitate this process.[33] Obviously, the decrease in PG lead to a change in *S* of the reactants.

The *t* value was increased through an increase in the PG/DEF molar ratio from 1.5 to 4 without the application of a vacuum; this led to the development of the polymerization. So, more glycol led to the increase in *t* and made it controllable. Furthermore, a DEF/PG/$ZnCl_2$/hydroquinone molar ratio of 1:3.5:0.01:0.002 as the best formulation in the PPF synthesis was obtained.

t. To evaluate *t*, the reactant concentrations were changed with *t*, and intermediate diesters with high molecular weights were produced. According to the FTIR spectra (Figure 1), intermediate diesters or other materials had a higher relative intensity in the OH region because of terminal hydroxyl vibrations at 3400 cm^{-1} as a result of the greater proportion of hydroxyl end groups compared to the unsaturated corresponding polyesters. Theoretically, diminishing the hydroxyl peak by *t* means a decrease in the end groups present in the polymer.[34] In fact, the presence of OH terminal groups in the FTIR spectra played an important role in distinguishing the steps of PPF synthesis from each other. The reduction in the intensity of the OH region peaks indicated the development of polycondensation. The better the polycondensation development was, the higher the increase in the molecular weight was. Furthermore, the decrease in the intensity of the OH region indicated that the synthesis process was proceeding correctly.

FTIR analysis provided us with good data based on the increase in the molecular weight with time from the production of the intermediates to that of the final product. M_w increased almost linearly over time and reached fewer OH terminal groups when the reaction was finished. The FTIR spectra indicated a significant diminishing of OH groups after 13–14 h. PPF had a molecular weight values of $M_n = 1167$ g/mol and $M_w = 2195$ g/mol after17 h.

T. At the beginning of the reaction, the mixture was heated up to 90°C. At this first *T*, reflux drops occurred, and subsequently, the elimination of ethanol was fast. Furthermore, the setting point was tuned at 5–10°C/min to guarantee that the vapor temperature of reflux was not too high. *T* was continuously increased until it reached 140°C; this was the highest possible *T*. At 140°C, when the reflux stopped, we confirm that about 90% of total ethanol was distilled.[35] When no further reflux of ethanol was observed, a few grams of resin were taken to evaluate the terminal hydroxyl groups by FTIR spectroscopy after 17 h. When almost all of the ethanol was distilled, and the reflux column became free of any ethanol, the second stage of polyesterification was started.

Ethanol was removed from the reaction system through a distillation column. The distilled ethanol vapor temperature was controlled very precisely to prevent the removal of ethanol with

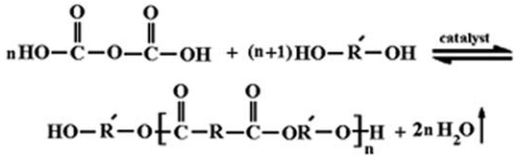

Figure 7. Formation reaction of polyester polyol.

glycols (the reflux temperature should have been 150°C at the maximum possible *T*).

Before the second stage and after the elimination of a large amount of ethanol, a vacuum was used. The pressure in the second stage decreased from 400 to 300 Pa; this was an important factor in the promotion of the reaction. Bis(2-hydroxypropyl) fumarate was then reacted at higher temperatures (140°C) and *in vacuo* to begin the step polymerization, which removed PG and continued the reaction.

We evaluated the effect of *T* on the PPF polymerization by carrying out the reaction at five different temperatures. By increasing *T*, the rate of the polymerization reaction also increased. We observed the development of polymerization by counting the decreasing terminal OH groups. The increase in *T* made the polymerization reaction fast, and also, PG was removed at a higher rate. Thereby, the polymerization reaction continued. In addition, the high temperatures lowered the product viscosity and allowed a better diffusion of the PG out of the reaction media. However, higher temperatures, above 160°C, resulted in a reversed effect on the product. The crosslinking of the reactants led to an undesirable stiff brown gel.

The reaction was run at three different *T* values: 90, 105, and 160°C. Running the reaction at low *T* led to a reduction in the possibility of crosslinking. The first reaction was run at 90°C. After 2 h, with increasing *T* up to a maximum of 160°C, a significant number of oligomers still remained in the reactor, but as the reaction progressed, the molecular weight of the product increased rapidly. Finally, the oligomers were reduced; this phenomenon was observed in the FTIR spectra, as shown in Figure 6. The molecular weights of the products showed a gradual increase with increasing *T*. At 160°C, FTIR spectroscopy showed changes in the common spectrum, especially in the fingerprint region. It seemed that a decrease in the reaction rate after distillation was the result of some reasons.

One explanation may have been that after 6 h, the majority of PG was removed. Another reason may have been that the starting material, bis(2-hydroxypropyl) fumarate, was being consumed. Higher reaction temperatures also increased PDI of the produced PPF. An increase in *T* increased the degree of polymerization; this, in turn, raised PDI.[36] For all runs at 160°C, transesterification resulted in a spontaneous crosslinking of the PPF and even increased the amount of inhibitor in some batches. In addition, over a period of 3 h at 160°C, the increased PDI indicated branched polymer formation at higher *T*s (>160°C). The resulting material was insoluble in methylene chloride and other solvents; this resulted in the crosslinking prohibition of any purification. The substance obtained at *T* values above 160°C was very stiff. Likewise, the product had a sharp odor. The FTIR spectrum confirmed that the structure of the material was degraded overall. This product was also insoluble in solvents including methylene chloride, Tetrahydrofuran, acetone, and chloroform.

As a result, the reaction occurred quickly, and higher molecular weights products were obtained at higher *T* values. In the case of lower *T* values (90–105°C), the reaction was very slow.[37] However, the products decomposed at *T* values higher than 160°C.

CONCLUSIONS

According to response surface methodology/CCD, we concluded that the *T*, *t*, and *S* values of the monomers were the main influencing factors in PPF synthesis. Unsaturated polyester polyols (i.e., PPF) were obtained through a reaction between DEF and PG. The experimental products were characterized by FTIR analysis. In this research, high-molecular-weight PPF, with low hydroxyl end groups and a viscosity of about 12,500 Cp, were obtained. The best product was obtained with a molar ratio of DEF to PG to $ZnCl_2$ to hydroquinone of 1:3.5:0.01:0.002 with a 17-h *t* at 140°C. The ceiling *T* was 150°C. The role of the amount of poly(propylene glycol) was very important in the synthesis of PPF. The conducted process of polyesterification was successfully confirmed via FTIR spectroscopy. The final spectrum of acceptable PPF showed that satisfactory results with negligible OH groups were not found. Finally, to confirm the structure of the synthesized polymer and the molecular weights of the synthesized PPF, FTIR, ^{1}H-NMR, and GPC analyses were used.

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