Investigation of Factors Affecting Synthesis of Polyvinyl Butyral by Taguchi Method

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ABSTRACT: Polyvinyl butyral (PVB) was prepared by condensation reaction of butyral with polyvinyl alcohol (PVA) in aqueous phase containing an acid as a catalyst and an emulsifying agent. Properties of the polymer were a function of the relative amounts of the three randomly distributed units of acetal, acetate and vinyl alcohol groups, and the molecular weight. In this work, some effective factors in synthesis of PVB have been investigated by Taguchi method. The percent of the acetalization has been determined according to the ASTM D1396, and the polymer was characterized by IR, TG, and DTG techniques. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 3592–3597, 2010

Key words: modification; polycondensation; synthesis; thermogravimetric analysis (TGA)

INTRODUCTION

PVB was made in 1944 by Robert Bryce and Co. Pty Ltd, USA.[1] PVB is a resin usually used for applications that requires strong binding, optical clarity, adhesion to many surfaces, toughness, and flexibility. So, it has been widely used in laminated safety glasses, paints, adhesives, primers, and binders. The main properties and applications of this polymer are shown in Table I. This industrially important random copolymer of vinyl alcohol and vinyl butyral units is synthesized by condensation reaction of PVA with butyraldehyde in an acid medium in the presence of an effective emulsifying agent. Although the product of this reaction is generally termed "polyvinyl butyral," some amounts of unreacted vinyl alcohol groups remain in the polymer chains. The acetalization reaction requires the presence of two adjacent hydroxyl groups on the PVA chains (Scheme 1). PVB resin can be produced by either a solvent process or an aqueous process.[2–5] In the aqueous process, PVA was dispersed in water or an aqueous solution containing acetic acid, and then the solution is acidified with a mineral acid and reacted with butyraldehyde. During acetalization reaction, PVB precipitates from the aqueous reaction mixture.

In this work, some effective factors containing time, temperature, and portion of PVA in the mixture of water and an organic solvent containing different ratio have been investigated by Taguchi method. The percent of acetalization has been determined according to the ASTM D1396. The polymer was also characterized by IR and thermal analysis methods.

EXPERIMENTAL

Materials

Polyvinyl alcohol with molecular weight 72,000 g/mol with degree of hydrolysis 98%, butanal, sodium dodesylsulfate (SDS), concentrated sulfuric acid (95-98%), potassium hydroxide, 1,2- dichloroethane, pyridine, and acetic anhydride were of analytical grade supplied from Merck Co. Industrial acetic acid with purity 98% was supplied from Arak Petrochemical Co.

Instruments

Infrared spectrums were recorded by IR spectrophotometer model IR-435 made by Shimadzu co in the region 4000 to 400 cm^{-1} at room temperature.

Differential thermal analysis and thermogravimetry analysis (DTA/TGA) were carried out using a Mettler TG5 in nitrogen atmosphere at a heating rate of 10°C / min.

Synthesis of polyvinyl butyral: general procedure

Polyvinyl alcohol (7 g, $M_W = 72{,}000$, residual vinyl acetate content = 1%) was dispersed in a solution of water, acetic acid, and a few drops of sulfuric acid according to Table II. To this mixture, 0.1 g of SDS

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TABLE I
Some Important Properties and Applications of PVB

Properties	Applications
Crosslinkable with other resins	Coatings with improved hardness and chemical resistance
Good dispersing properties	Pigment preparations
Excellent barrier properties	Stain blocking primers
Combustion without residue at 300–550°C, under air or nitrogen	Temporary binders (e.g., for ceramics)
Thermoplastic properties	Heat-sealing lacquers, thermotransfer printing
Clear and light resistant films	Interlayer in reflecting materials textile coatings
Good elasticity	Cobinder to elastify brittle resins (e.g., phenolic, epoxies) in coatings and adhesives
Excellent adhesion on many substrates, especially on metal and glass	Binder for lacquers, primers, adhesives, printing inks, and safety glass

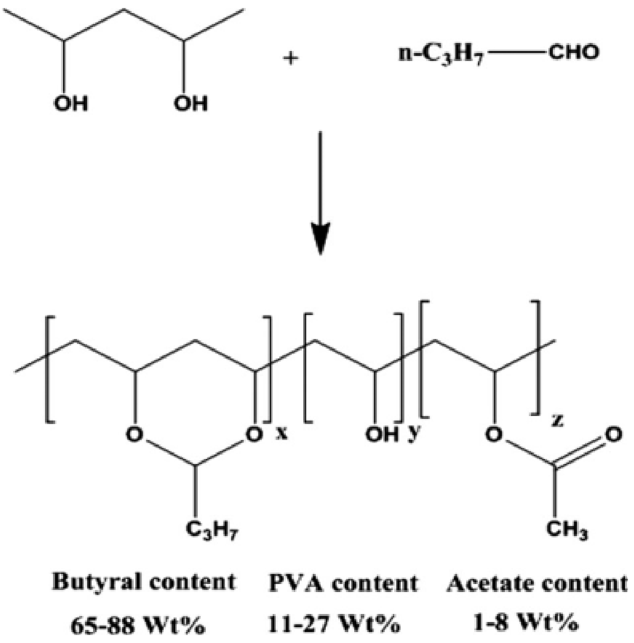
was added. The mixture was stirred at 10°C, and butyraldehyde (4.06 g) was added to the mixture. The reaction was carried out for a constant time according to the Table II. The temperature was then raised to 70°C. The reaction time at this temperature was according to Table II. Mixture was then washed with distilled water and neutralized with KOH (50% solution) to a PH of 10–11. The PH was kept constant for 45 min and then washed again with distilled water to a final PH of 7.5–8. The product was then filtered and dried at 50°C in an oven until a constant weight.

IR (PVB, casting solution, cm^{-1}): 3409 (OH stretching), 2947 (aliphatic CH stretching), 1431 (CH_2 bending), 1377 (CH_3 bending), 1136 (C—O—C stretching), 999 (CO stretching).

IR (PVA, casting solution, cm^{-1}): 3350 (OH stretching), 2931 (aliphatic CH stretching), 1423 (CH_2 bending), 1087 (CO stretching).

Analysis of vinyl alcohol content

The vinyl alcohol content was determined by a chemical method (ASTM D1396) in which the residual hydroxyl was acetylated with acetic anhydride in pyridine, followed by titration of the liberated acid.



Scheme 1 Acetalization of PVA.

TAGUCHI METHODOLOGY

A full fractional design of experiments identifies all possible combinations for a given set of factors. Because most industrial experiments usually involve a significant number of factors, a full fractional design results in a large number of experiments. To reduce the number of experiments to a partial level, only a small set from all the possibilities is selected. The method of selecting a limited number of experiments, which produces the most formation, is known as a partial fraction experiment. Taguchi analysis provides a special set of general design guideline for fractional experiments that cover many applications. It investigates how different parameters affect the mean and variance of a process performance characteristic that defines how well the process is functioning. The experimental design by Taguchi method involves orthogonal arrays to organize the parameter affecting the process and the levels at which they should be varied. It determines the factors that affect product quality the most with a minimum amount of experimentation, thus saving time and resources. The major steps required for the experimental design

TABLE II
Factors and Levels

	Levels		
Factors	1	2	3
Acetic acid/water volume ratio = factor A	10 : 90	30 : 70	50 : 50
Time at low temperature (t_1) = factor B	55	122.5	190
Time at high temperature (t_2) = factor C	90	195	300
Weight percent of PVA in solvent = factor D	5	11	17

TABLE III
The L_9 Orthogonal Array

Experiment number	Factors			
	A	B	C	D
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	2	3
5	2	2	3	1
6	2	3	1	2
7	3	1	3	2
8	3	2	1	3
9	3	3	2	1

using Taguchi method are (1) establishment of objective function, (2) identification of the factors and their levels, (3) selection of an appropriate orthogonal array (OA), (4) experimentation, (5) analysis of the data and determination of the optimal levels, and (6) the confirmation experimentation.

Establishment of objective function

The overall objective of the Taguchi method is to produce high-quality product at low cost to the manufacturer. The objective of the present work is synthesis of polyvinyl butyral with improved properties for laminated safety glass that result in 20–25 wt % of vinyl alcohol group. There are three possible categories of the quality characteristics. They are (1) smaller is better; (2) nominal is better; and (3) larger is better. In this investigation, the objective is to minimize the vinyl alcohol group; therefore, "smaller is better" quality characteristics are selected.

Determination of controllable factors and their levels

In Taguchi's methodology, all factors affecting the process quality can be divided into two types: control factors and noise factors. Control factors are those set by the manufacture and are easily adjustable. The noise is usually due to the uncontrollable factors, which exist in the environment that often cannot be eliminated, and which cause variations in the output. Noise factors are difficult, impossible, or expensive to control. Control factors are the most important in determining the quality of product characteristics. In this work, control factors include acetic acid/water volume ratio, time at low temperature, time at high temperature and weight percent of PVA in solvent. Control factors levels according to the present data in articles and patents were determined as Table II.[6–10]

Design of Taguchi orthogonal array layout

The Taguchi orthogonal array layout stipulates the way of conducting the minimal number of experiments, which could give the full information of all the factors that affect the performance parameter. It consists of an inner array and an outer array. The inner array is made up of the orthogonal array (OA) selected from all the possible combinations of the controllable factors. The outer array contains the combinations of the uncontrollable factors. L_9 orthogonal array is selected for the present investigation. The experimentation is conducted to understand the influence of four independent variables each at three levels. Table III shows L9 orthogonal array layout.

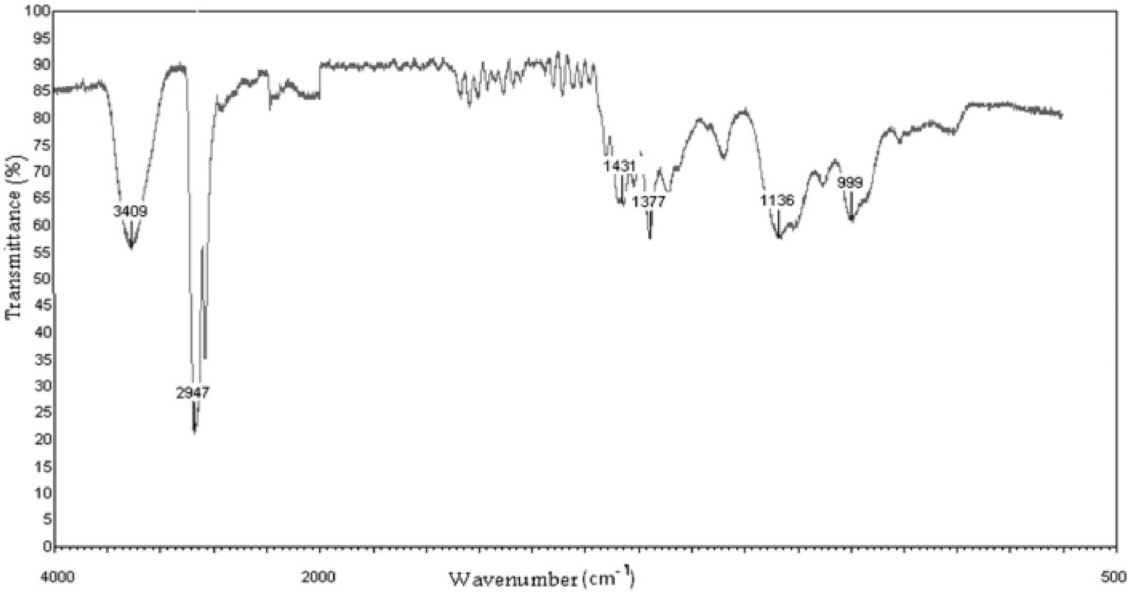


Figure 1 Infrared spectrum of PVB at room temperature.

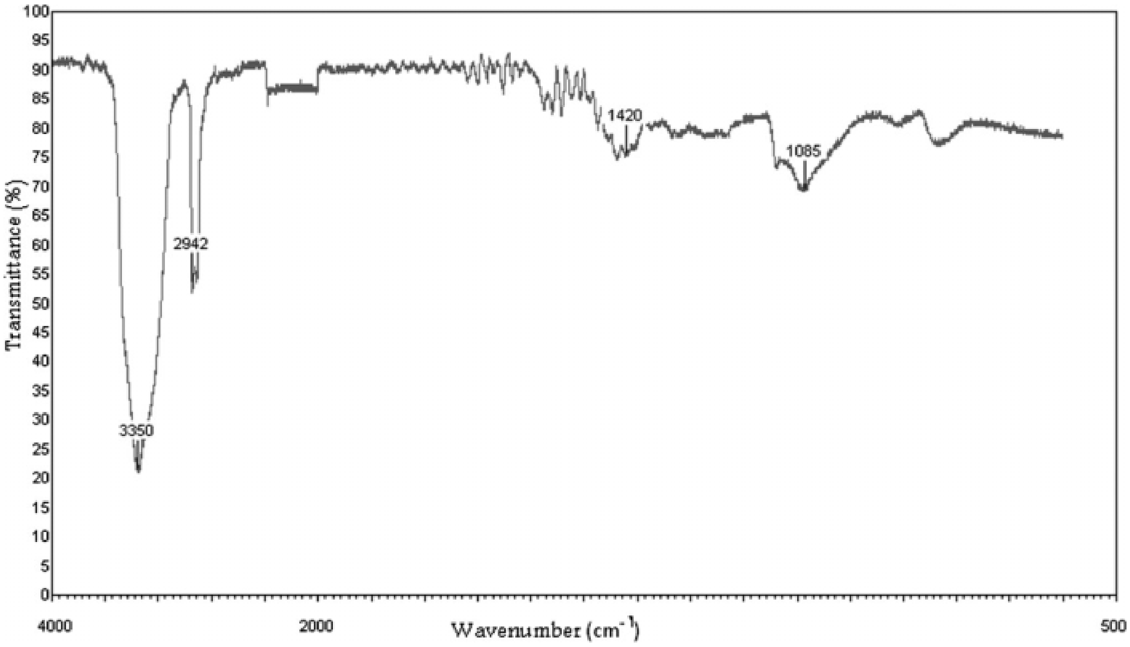


Figure 2 Infrared spectrum of PVA at room temperature.

The tests were done according to the Table III. Samples of every test were dried after neutralization and washing.

RESULTS AND DISCUSSION

Characterization of polyvinyl butyral

Formation of butyral ring containing C—O—C and other significant groups by acetalization of PVA was confirmed by IR spectroscopy (Figs. 1 and 2).

Thermal behavior of both PVA and PVB were investigated that in thermogram of PVA, decomposition at 285°C is related to vinyl alcohol that in the thermogram of PVB this peak considerably decreased and decomposition of butyral group was shown at 373°C (Fig. 3).[11]

Measurement and analysis

Percent of vinyl alcohol group in the samples or reaction progress that were considered as the results

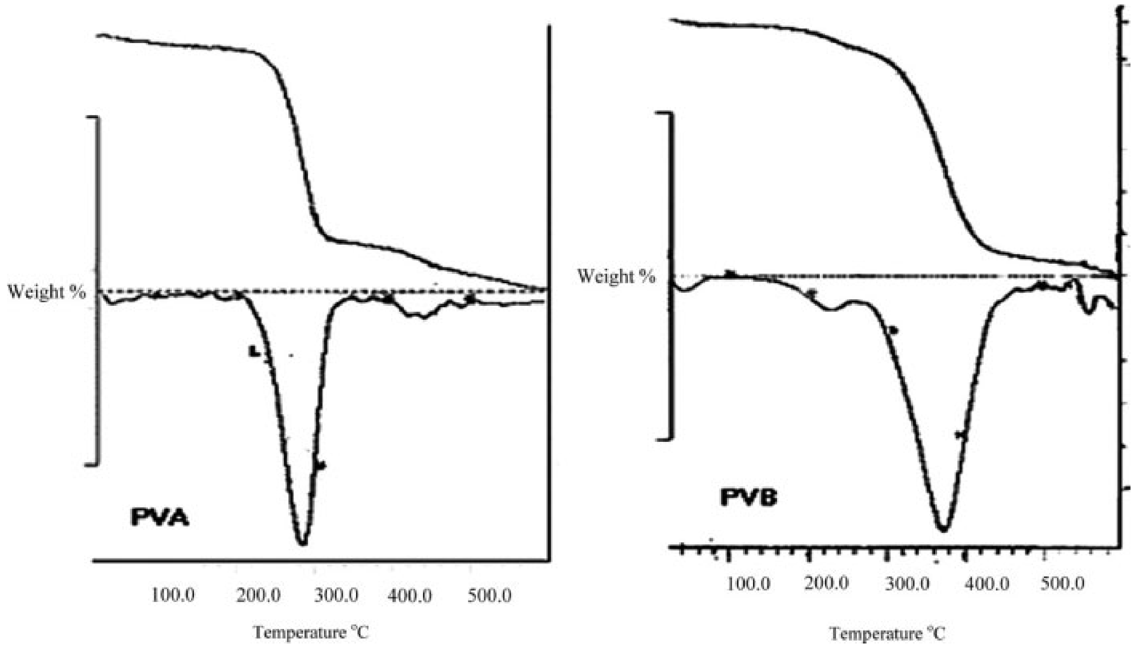


Figure 3 TG and DTG curves of polyvinyl alcohol and polyvinyl butyral.

TABLE IV
Analytical Results for PVB

Test number	Vinyl alcohol group percent
1	32.48
2	33.6
3	36.7
4	35.6
5	31
6	32.64
7	34.26
8	31.24
9	29.8

of tests were determined by chemical method. The obtained results are shown in the Table IV.

The response refers to the values of performance characteristics for each parameter at different levels. In this study, all the analysis based on the Taguchi method is done by software Qualitek-4 (Nutec Inc.) to determine the main effect of the process parameters, to perform the analysis of variance (ANOVA), and to establish the optimum conditions.

Main effects of factors were obtained and are given in Table V. The main effects analysis is used to study the trend of the effects of each of the factors, as shown in Figure 1. It is clear from Figure 1 that parameter values at levels A_3, B_2, C_1, and D_1 are best choice in terms of vinyl alcohol group content. After completing the experiments, the next step in data analysis is to estimate the optimum level of each control factor and to perform ANOVA. The ANOVA predicts the relative significance of the process parameters along with estimating the experimental errors. It gives the percentage of contribution of each factor and provides a better feel for the relative effect of the different factors on experimental responses.[12] Precision of a parameter estimate is based on the number of independent samples of information, which can be determined by degree of freedom (DOF). In the ANOVA table, DOF equals to the number of experiments minus the number of additional parameters estimated for the calculation. The sum of squares value represents deviation of the data from the average value. The variance for a factor is computed by dividing sum of squares by the DOF. The percent of contribution (P %) represents contribution effect of each factor for the response. The ANOVA of raw data (Table VI) indicates that all the selected process parameters significantly affect the vinyl alcohol group of the samples.

TABLE V
Main Effects of Factors

	Level 1	Level 2	Level 3
Factor A	34.259	33.079	31.766
Factor B	34.112	31.946	33.046
Factor C	32.119	33	33.986
Factor D	31.093	33.5	34.513

TABLE VI
Analysis of Variance (ANOVA)

No.	Factors	DOF	SS	v	P^a (%)
1	A	2	9.330	4.665	23.254
2	B	2	7.038	3.519	17.542
3	C	2	5.234	2.617	13.044
4	D	2	18.519	9.259	46.254
Total		8	40.124		100%

DOF, degree of freedom; SS, sum of squares; V, variance; *P* (%), percent of contribution

[a] Significant at 95% confidence level.

Relationship between reaction progress and acetic acid/water volume ratio

Reaction progress with volume of acetic acid/water ratio is a linear relation. This line shows with increase of acetic acid, percent of remained vinyl alcohol group decreases. With increase of acetic acid volume, solubility of polyvinyl butyral increases that causes the product precipitates later from the system; so, reaction progress will be more.

Relationship between reaction progress and time at low temperature

Reaction progress against time of reaction at low temperature in a limit range shows an optimum condition. With increasing the time, the reaction first shifts to the right and percent of remained vinyl alcohol group decreases, and after a definite time, because of the conversion reaction, percent of vinyl alcohol group increases.

Relationship between reaction progress and time of reaction at high temperature

Reaction progress versus time of reaction shows a linear relationship. High temperature is necessary for the cyclic formation and completion of the reaction, but continuation of the reaction at this temperature for long time causes the opening of the acetal ring in the presence of an acid.

TABLE VII
Optimum Condition in a Limited Range

No.	Factors	Level description	Level	Contribution
1	A	50	3	−1.269
2	B	122.5	2	−1.089
3	C	90	1	−0.916
4	D	5	1	−1.943

Total contribution from all factors −5.217.
Current grand average of performance 33.035.
Expected result at optimum condition 27.818.

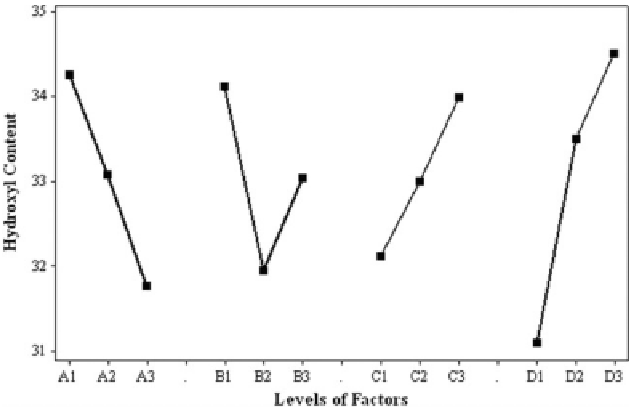


Figure 4 Effects of process parameters.

Relationship between reaction progress and weight percent of polyvinyl alcohol

Reaction progress versus weight percent of polyvinyl alcohol first shows a linear relation and after Level 2 increases slightly. As weight percent of polyvinyl alcohol decreases, viscosity of the reaction increases and probability of contacts decreases, so, reaction progress decreases. Effect of concentration on progress of the reaction was decreased after Level 2.

Estimation of optimum quality characteristics

A major benefit of conducting Taguchi's methodology is to determine the near optimum or the range of process parameter levels, where global optimum resides. The optimum level for a factor is the level that gives the minimum value of vinyl alcohol group. The significant factors selected for the vinyl alcohol group are A_3, B_2, C_1, and D_1. Optimum condition in a limited range was shown in Table VII.

Confirmation of optimum runs

The reaction was taken at optimum level of factors and percent of vinyl alcohol group was determined (24 wt %) that shows that butyral content is about 75% wt.

CONCLUSIONS

In this work, uncrosslinked PVB was synthesized by condensation reaction and was characterized by IR, differential thermal analysis, and thermogravimetry analysis techniques. Some effective factors in the synthesis of PVB containing time, temperature, and portion of PVA in the mixture of water and acetic acid containing different ratio have been investigated by Taguchi method. The percent of acetalization or the vinyl alcohol group has been determined according to the ASTM D1396. Main effects of factors were obtained and plotted in Figure 4. The ANOVA of raw data (Table VI) indicates that all the selected process parameters significantly affect the vinyl alcohol group of the samples. The optimum level for each factor was determined that are A_3, B_2, $C_{1,}$ and $D_{1.}$ The synthesis of PVB was taken at optimum level of factors and percent of vinyl alcohol group was determined (25 wt %) that shows that butyral content is about 75% wt.

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