Optimization of Reaction Conditions for Polyurethane Foam Synthesis with Liquefied Corn Stalk by Response Surface Methodology

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ABSTRACT: Optimization of copolymerization conditions for biodegradable polyurethane foam with non-pretreated liquefied corn stalk and polymethylene polyphenylisocyanate was conducted using a quadratic regression rotational combinational design of response surface methodology. A five-level four-factor central composite design was employed to determine the maximum tensile strength at optimum levels for [NCO]/[OH] ratio, blowing agent (water), mass ratio of triethylamine (TL)/dibutyltin dilaurate (DD), and surfactant (silicone). The analysis of variance (ANOVA) of the quadratic orthogonal regression model revealed that the fit of the model was good. The model was also verified by experimentation. The maximum tensile strength of 1.64 MPa was obtained at the optimal conditions: [NCO]/[OH] ratio 0.7, blowing agent concentration 4.7 wt %, surfactant concentration 1.27 wt %, and mass ratio of TL/DD 1: 1.
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Key words: copolymerization; polyurethanes; response surface methodology; corn stalk; biodegradable

INTRODUCTION

Polyurethane foam (PUF) from the copolymerization of polyether polyol or polyester polyol and isocyanate is widely used in applications such as furniture industry, packing, coatings, decorating, building, and shoe industry. However, their undegradability results in a burden to environment when discarded. Using natural material or renewable resource to prepare bio-based materials, which are friendly to environments,[1] has received much attention. The synthesis of biodegradable PUF is one of the emphases. PUF preparation with biomass such as liquefied cashew nut shell,[2] wood,[3–5] cellulose derivatives,[6] starch,[7] corn-cobs,[8] banknote paper and pulp paper,[9] and corn stalk[10] were well documented. These works mainly focused on mechanical properties, biodegradable properties, and polymerization mechanism of the bio-based PUF.

In our earlier studies, corn stalk was liquefied with ethylene carbonate (EC) and sulfuric acid as liquefying solvent and catalyst, respectively. The liquefied products were subsequently used as biopolyol PUF preparation. The effects of [NCO]/[OH] ratio,[11] blowing agent,[12] cocatalyst (which is the mixture of triethylamine (TL) and dibutyltin dilaurate (DD)),[13] surfactant,[14] and liquefied corn stalk (LCS) from different liquefied formulations[15] on the mechanical and thermal properties and network structures of the PUF were researched in detail. The results have shown that [NCO]/[OH] ratio, blowing agent, cocatalyst (mass ratio of TL/DD), surfactant, and LCS on the PUF characteristics are important factors. Tensile strength is an important parameter for the PUF, which can suggest its application ranges. To obtain a better tensile strength, the preliminary estimation indicated blowing agent (water), surfactant (silicone), [NCO]/[OH] ratio, and mass ratio of TL/DD must be in range of 2–4.67%, 1–4%, 0.4–0.8, and 0–2, respectively.

However, it is evident that possible interaction of four factors should be sought in PUF preparation. To this end, optimization with response surface methodology (RSM) is necessary. To our knowledge, optimization of [NCO]/[OH] ratio, blowing agent (water), mass ratio of TL/DD, and surfactant

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(silicone) have not been reported. In this work, a quadratic regression rotational combinational design (QRRCD) of RSM was employed to model the copolymerization of LCS and polymethylene polyphenylisocyanate (PAPI) and to optimize the process conditions for the maximum tensile strength of PUFs. RSM is a common practice in biotechnology and chemical engineering. Various research workers have applied this technique, especially for the optimization of process conditions.[16–21] In this article, the factors selected were [NCO]/[OH] ratio, blowing agent (water), surfactant (silicone), and mass ratio of TL/DD.

MATERIALS AND METHODS

Materials and chemicals

Corn stalk from a local farm in Beijing was milled and the 20–80 mesh fraction was used for the liquefaction experiments. Chemical agents, including sulfuric acid (97%, w/w) as the catalyst, EC (99.90%, w/w) as the liquefaction solvent, the PM-200 as the PAPI, water and silicone as blowing agent and surfactant, respectively, TL and DD as the cocatalyst, are the same as those used in the literature.[11]

Preparation of LCS

The preparation methods of LCS are referred to the literature.[11] Oven-dried corn stalk flour (40 g), EC (200 g), and sulfuric acid (7.4 g) were placed in a three-neck flask (1000 mL) equipped with a reflux condenser, a thermometer, and a motor-driven stirrer and refluxed at 170°C for 90 min with continuous stirring.

The method by Kurimoto et al.[3] was employed to determine the acid number and hydroxyl number.

The moisture contents and the insoluble residues ratios (IRR) of LCS are referred to the literature.[11]

Preparation of LCS-PU foams

The foams were prepared by one-shot method. LCS (15g), water, silicone, and cocatalysts (cocatalysts mass concentration 2%, w/w) were mixed in a 150 mL polypropylene cup at 1000–1200 rpm agitation for 1 min followed by the addition of PAPI and agitated at 1400–1600 rpm agitation until a cream time was obtained (about 6–12 s) at room temperature for copolymerization. Water, silicone, cocatalysts, and [NCO]/[OH] ratio were set according to the requirement of the experimental design (Table II). The polymerized mixture was spread onto glass plates to form a uniform thin layer of PU foam. The foams obtained were cured for 7 days at room temperature, and then were conditioned for 16 h at 23°C, 50% RH (relative humidity). Each sample was experimented for three replicates. The [NCO]/[OH] ratio is given as follows:

$$[\mathrm{NCO}]/[\mathrm{OH}]\ \text{ratio} = \frac{M_{\mathrm{PAPI}} \times W_{\mathrm{PAPI}}}{M_{\mathrm{polyol}} \times W_{\mathrm{polyol}} + W_{\mathrm{Water}} \times 1000/9} \quad (1)$$

where M_{PAPI} is the content of the isocyanate group in PAPI (6.745 mmol/g), M_{polyol} is the content of the hydroxyl group in LCS (hydroxyl number/56.1, in mmol/g), W_{PAPI}, W_{polyol}, and W_{water} are the weights (g) of PAPI, LCS, and water, respectively.

Measurement of the tensile strength

The tensile strength of the foams as the response was measured with a universal tensile tester (INSTRON-4411) according to the literature.[11]

Experimental design

A QRRCD was applied to optimize the four significant factors ([NCO]/[OH] ratio, blowing agent, surfactant, and mass ratio of TL/DD) for the tensile strength of LCS-PUF as the response. A total of 36 runs were conducted. To simplify the recording of experimental data, the independent variable x_i was coded as Z_i by the following equation:

$$Z_i = \frac{x_i - x_{0i}}{\Delta_i} \quad (2)$$

Where Z_i is the coded value of x_i; x_{0i} is the center point of x_i; Δ_i is the step change.

The tensile strength of LCS-PU foams was fitted by the following second-order degree equation:

$$\hat{y} = b_0 + \sum_{j=1}^{p} b_j Z_j + \sum_{k=1}^{p-1} \sum_{j=k+1}^{p} b_{jk} Z_j Z_k + \sum_{j-1}^{p} b_{jj} Z_j' \quad (3)$$

where $\hat{y}$ is the predicted response, the tensile strength, MPa; b_0 is the constant term; b_j is the linear coefficient; b_{jk} is the interaction coefficient; b_{jj} is the squared coefficient; p is the number of independent variables, 4.

SAS software, Version 9.0 (SAS Institute, Cary, North Carolina) was used for the experimental design and statistical analysis of the experimental data. Design-Expert software, Version 8.0.2, was used for analyzing the interaction effects of factors. The determination coefficient R^2 and adjusted R^2 were employed to check the goodness of the fit of the model. An F-test was used to determine the statistical significance and the significance of the regression coefficients.

RESULTS AND DISCUSSION

Characteristics of LCS

The characteristics of the LCS were: acid number, 19.2 mg KOH/g; hydroxyl number, 137.3 mg KOH/g; moisture content, 1.48 wt %, and IRR 1.98 wt %.

Quadratic regression rotational combinational designs and response surface analysis

RSM using QRRCD was employed to determine the optimal levels of the four selected variables ([NCO]/[OH] ratio, blowing agent, surfactant, and mass ratio of TL/DD) which influenced remarkably the tensile strength of LCS-PUF. The four independent factors were studied at five different levels. The following five levels were tested for each independent variable: two star levels, two factorial levels, and a center level. To limit the boundaries of the experimental space, the ranges for the four variables were chosen: water 2–4.67%, silicone 1–4%, and [NCO]/[OH] ratio 0.4–0.8, mass ratio of TL/DD 0–2. These ranges have been proved effectively in our previous studies illuminated in Introduction section. The respective uncoded and coded values of the four independent variables are defined in Table I. A total of 36 experimental runs with different combinations of [NCO]/[OH] ratio, blowing agent, surfactant, and mass ratio of TL/DD were conducted including 12 replicates at the center point according to the design in Table II. The regression coefficients estimated (code factors) were shown in Table III. From Table III and eq. (2), the second-order polynomial regression equation in terms of coded factors was obtained:

$$\begin{aligned}\hat{y} = {} & 1.06889 + 0.19875Z_1 + 0.17958Z_2 - 0.06542Z_3 \\ & - 0.10042Z_4 + 0.07938Z_1Z_2 - 0.02938Z_1Z_3 \\ & - 0.08438Z_1Z_4 + 0.00188Z_2Z_3 + 0.00188Z_2Z_4 \\ & - 0.07688Z_3Z_4 - 0.14635Z_1' - 0.04885Z_2' \\ & - 0.04510Z_3' - 0.00010Z_4' \end{aligned} \quad (4)$$

To eliminate the interaction effect of the regression coefficients between constant term and squared term, the squared term in eq. (4) needs to be modified based on the following equation:

$$Z'j = Z_j^2 - 0.667 \quad j = 1, 2, 3, 4 \quad (5)$$

Therefore, eq. (4) was changed to:

$$\begin{aligned}\hat{y} = {} & 1.2292 + 0.19875Z_1 + 0.17958Z_2 - 0.06542Z_3 \\ & - 0.10042Z_4 + 0.07938Z_1Z_2 - 0.02938Z_1Z_3 \\ & - 0.08438Z_1Z_4 + 0.00188Z_2Z_3 + 0.00188Z_2Z_4 \\ & - 0.07688Z_3Z_4 - 0.14635Z_1^2 - 0.04885Z_2^2 \\ & - 0.04510Z_3^2 - 0.00010Z_4^2 \end{aligned} \quad (6)$$

TABLE I
Coded Values of Factor and Level on Quadratic Regression Orthogonal Rotating Design

Coded values	[NCO]/[OH] ratio, x_1	Water, x_2 (g)	Silicone, x_3 (%[a])	Mass ratio of catalysts, x_4
2	0.8	0.7	4.0	2
1	0.7	0.6	3.0	1.5
0	0.6	0.5	2.0	1
−1	0.5	0.4	1.0	0.5
−2	0.4	0.3	0	0

[a] "%"is the result of silicone weight/LCS weight, g/g.

The coefficients of determination R^2 and adjusted R^2 were used to evaluate the fit of the models and calculated to be 87.87% and 79.78%, respectively, which showed that 87.87% of the variability in the response could be explained by the model. An analysis of variance (ANOVA) at 99% confidence level was listed in Table IV. *F*-test was employed to test the significance of the model. *F*-statistics for the regression equation is the result of [mean of square (MS) for regression]/(MS for residual error), which is $17.48264 > F_{0.01}(f_1, f_2) = F_{0.01}(10, 25) = 3.13$. *F*-statistics for the lack-of-fit is the result of (MS for lack-of-fit)/ (MS for pure error), which is calculated to be $3.90670 < F_{0.01}(f_1, f_2) = F_{0.01}(14, 11) = 4.29$. The two *F*-statistic results suggest that the model has a goodness-of-fit.

The significance of each coefficient could be determined by *F*-test (listed in Table III). The larger the *F*-value, the more significant is the corresponding coefficient. [NCO]/[OH] ratio, blowing agent (water), mass ratio of TL/DD, and surfactant (silicone) showed the significant linear main effects. The LCS-PU foam was also significantly affected by quadratic term of [NCO]/[OH] ratio.

According to eq. (1), in terms of actual factors, the regression model was:

$$\begin{aligned}\hat{y} = {} & -5.93764 + 17.2681x_1 + 1.918x_2 + 0.26874x_3 \\ & + 1.11924x_4 + 7.938x_1x_2 - 1.6876x_1x_4 \\ & - 0.15376x_3x_4 - 14.635x_1^2 - 4.885x_2^2 - 0.0451x_3^2 \end{aligned} \quad (7)$$

Subjected to: $0.4 \le x_1 \le 0.8; 0.3\text{g} \le x_2 \le 0.7\text{g}; 0\% \le x_3 \le 4\%; 0 \le x_4 \le 2$

In our earlier studies, it has been testified that with an increase of [NCO]/[OH] ratio, blowing agent content, and mass ratio of TL/DD in the copolymerization formulation, the tensile strength of LCS-PU foam increased and then decreased; with an increase of surfactant content, the tensile strength increased. The response surface curves can be used to explain the interaction effects of the variables as described by the model eq. (7), shown in Figures 1–3. Each figure demonstrates the interaction effect of two factors under the other factors at zero level. From Figure 1, the tensile strength is enhanced at low mass

TABLE II
Experimental Design and Results

Run no.	Z_1	Z_2	Z_3	Z_4	Z_1Z_2	Z_1Z_3	Z_1Z_4	Z_2Z_3	Z_2Z_4	Z_3Z_4	Z'_1	Z'_2	Z'_3	Z'_4	$\hat{y}$ (MPa)
1	−1	−1	−1	−1	1	1	1	1	1	1	0.333	0.333	0.333	0.333	0.54
2	−1	−1	−1	1	1	1	−1	1	−1	−1	0.333	0.333	0.333	0.333	0.59
3	−1	−1	1	−1	1	−1	1	−1	1	−1	0.333	0.333	0.333	0.333	0.58
4	−1	−1	1	1	1	−1	−1	−1	−1	1	0.333	0.333	0.333	0.333	0.59
5	−1	1	−1	−1	−1	1	1	−1	−1	1	0.333	0.333	0.333	0.333	0.88
6	−1	1	−1	1	−1	1	−1	−1	1	−1	0.333	0.333	0.333	0.333	0.86
7	−1	1	1	−1	−1	−1	1	1	−1	−1	0.333	0.333	0.333	0.333	0.86
8	−1	1	1	1	−1	−1	−1	1	1	1	0.333	0.333	0.333	0.333	0.65
9	1	−1	−1	−1	−1	−1	−1	1	1	1	0.333	0.333	0.333	0.333	1.13
10	1	−1	−1	1	−1	−1	1	1	−1	−1	0.333	0.333	0.333	0.333	0.86
11	1	−1	1	−1	−1	1	−1	−1	1	−1	0.333	0.333	0.333	0.333	1.08
12	1	−1	1	1	−1	1	1	−1	−1	1	0.333	0.333	0.333	0.333	0.43
13	1	1	−1	−1	1	−1	−1	−1	−1	1	0.333	0.333	0.333	0.333	1.47
14	1	1	−1	1	1	−1	1	−1	1	−1	0.333	0.333	0.333	0.333	1.48
15	1	1	1	−1	1	1	−1	1	−1	−1	0.333	0.333	0.333	0.333	1.69
16	1	1	1	1	1	1	1	1	1	1	0.333	0.333	0.333	0.333	1.08
17	−2	0	0	0	0	0	0	0	0	0	3.333	−0.667	−0.667	−0.667	0.50
18	2	0	0	0	0	0	0	0	0	0	3.333	−0.667	−0.667	−0.667	1.05
19	0	−2	0	0	0	0	0	0	0	0	−0.667	3.333	−0.667	−0.667	0.88
20	0	2	0	0	0	0	0	0	0	0	−0.667	3.333	−0.667	−0.667	1.45
21	0	0	−2	0	0	0	0	0	0	0	−0.667	−0.667	3.333	−0.667	1.36
22	0	0	2	0	0	0	0	0	0	0	−0.667	−0.667	3.333	−0.667	1.00
23	0	0	0	−2	0	0	0	0	0	0	−0.667	−0.667	−0.667	3.333	1.54
24	0	0	0	2	0	0	0	0	0	0	−0.667	−0.667	−0.667	3.333	1.18
25	0	0	0	0	0	0	0	0	0	0	−0.667	−0.667	−0.667	−0.667	1.23
26	0	0	0	0	0	0	0	0	0	0	−0.667	−0.667	−0.667	−0.667	1.26
27	0	0	0	0	0	0	0	0	0	0	−0.667	−0.667	−0.667	−0.667	1.32
28	0	0	0	0	0	0	0	0	0	0	−0.667	−0.667	−0.667	−0.667	1.24
29	0	0	0	0	0	0	0	0	0	0	−0.667	−0.667	−0.667	−0.667	1.26
30	0	0	0	0	0	0	0	0	0	0	−0.667	−0.667	−0.667	−0.667	1.25
31	0	0	0	0	0	0	0	0	0	0	−0.667	−0.667	−0.667	−0.667	1.28
32	0	0	0	0	0	0	0	0	0	0	−0.667	−0.667	−0.667	−0.667	1.27
33	0	0	0	0	0	0	0	0	0	0	−0.667	−0.667	−0.667	−0.667	1.23
34	0	0	0	0	0	0	0	0	0	0	−0.667	−0.667	−0.667	−0.667	1.29
35	0	0	0	0	0	0	0	0	0	0	−0.667	−0.667	−0.667	−0.667	1.04
36	0	0	0	0	0	0	0	0	0	0	−0.667	−0.667	−0.667	−0.667	1.08

ratio of TL/DD and high [NCO]/[OH] ratio. However, the tensile strength decreases with the decreasing mass ratio of TL/DD when [NCO]/[OH] ratio Z_1 exceeds 1.0. Both high [NCO]/[OH] ratio and water content could facilitate the improvement of the tensile strength as shown in Figure 2. However, an increase of water content contributes to the decreasing of tensile strength when [NCO]/[OH] ratio Z_1 is over 1.0. From Figure 3, it is observed that high mass ratio of TL/DD can enhance the tensile strength when surfactant content (silicone) Z_3 is lower than −1.0. However, an increase of mass ratio of TL/DD results in a decrease of the tensile strength at Z_3 over −1.0.

The optimal concentrations for the four components obtained from the maximum point of the

TABLE III
Model Coefficients Estimated by the Multiple Linear Regression

Factor	Coefficient	Standard error	*F*-value	*P*-value
Z_0	1.0689			
Z_1	0.19875	0.029685	44.8278	0.0001
Z_2	0.17958	0.029685	36.5986	0.0001
Z_3	−0.06542	0.029685	4.8564	0.0388
Z_4	−0.10042	0.02968	11.4431	0.0028
Z_1Z_2	0.07938	0.036356	4.7666	0.0405
Z_1Z_3	−0.02938	0.036356	0.6528	0.4282
Z_1Z_4	−0.08438	0.036356	5.3860	0.0304
Z_2Z_3	0.00188	0.036356	0.0027	0.9594
Z_2Z_4	0.00188	0.036356	0.0027	0.9594
Z_3Z_4	−0.0769	0.036356	4.4711	0.0466
Z'_1	−0.1464	0.025708	32.4002	0.0001
Z'_2	−0.0488	0.025708	3.6114	0.0712
Z'_3	−0.0451	0.025708	3.0783	0.0939
Z'_4	−0.0001	0.025708	0.0000	0.9968

TABLE IV
ANOVN of the Regression Equation After Insignificant Model Terms Removed

Source	DF	SS	MS	*F*-value
Regression U	10	3.202939	0.3202939	17.48264
Residual error Q_{e2}	25	0.458017	0.01832068	
Lack-of-fit Q_{Lf}	14	0.381325	0.0272375	3.90670
Pure error Q_e	11	0.076692	0.006972	
Total	35	4.0213		

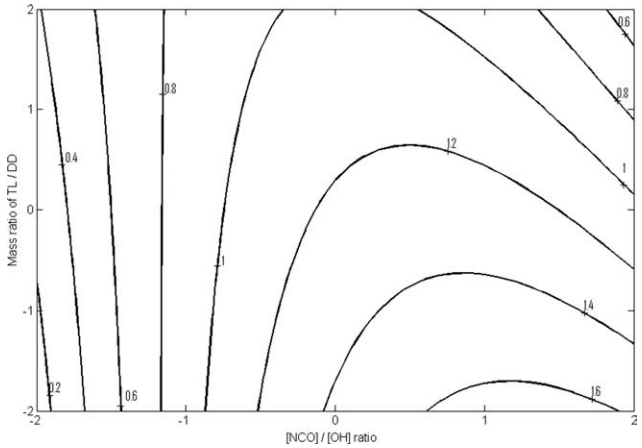

Figure 1 Response surface curves for the effects of [NCO]/[OH] ratio and mass ratio of TL/DD.

model were calculated by the SAS software to be $Z_1 = 1.22$, $Z_2 = 2.00$, $Z_3 = -0.73$, $Z_4 = 0.00$. The uncoded values of [NCO]/[OH], blowing agent, silicone, and mass ratio of TL/DD were 0.72, 0.70 g (correspondingly to 4.67 wt %), 1.27 wt %, and 1: 1, respectively. The maximum tensile strength of LCS-PU foams predicted was 1.64 MPa.

Verification of the results

In order to confirm the model, three additional experiments were performed under the predicted conditions. The mean value (average of three repeats) of the tensile strength was 1.62 MPa, which is agreed well with the predicted value. This also suggests the validity of the response model.

CONCLUSION

The RSM showed effectiveness in optimizing the synthesis conditions of the LCS-PU foams based on the LCS for maximal tensile strength. The optimized culture conditions to synthesize LCS-PU foams was NCO]/[OH] 0.72, blowing agent 4.7 wt %, silicone1.27 wt %, and ratio between cocatalysts 1: 1. The maximum tensile strength of LCS-PU foams predicted was 1.64 MPa.

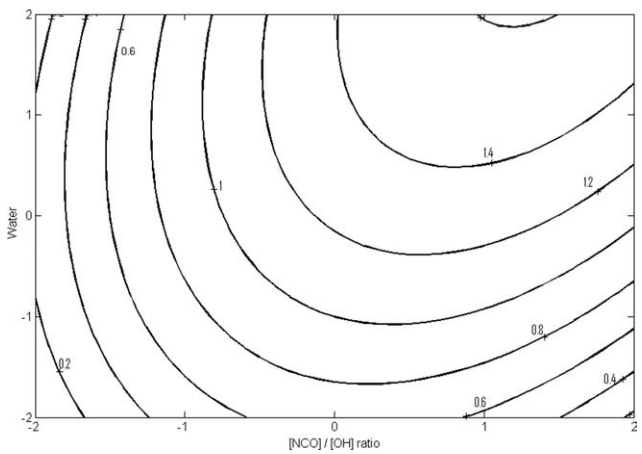

Figure 2 Response surface curves for the effects of [NCO]/[OH] ratio and water.

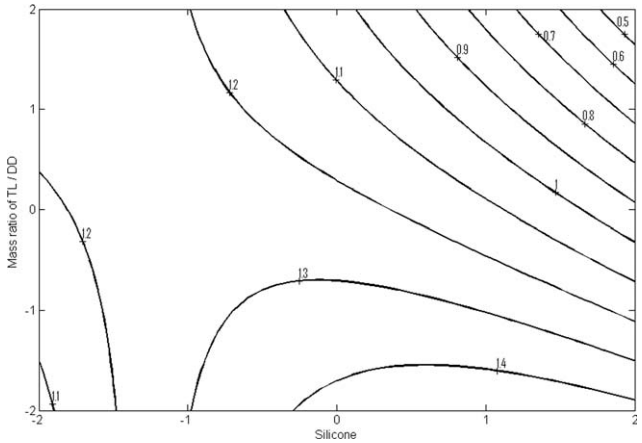

Figure 3 Response surface curves for the effects of silicone and mass ratio of TL/DD.

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