



Polyvinyl Butyral Synthesis Process Based on Deep Eutectic Solvent as a Catalyst

Po Li¹, Weilan Xue^{1*}, Zuoxiang Zeng¹, Li Sun¹ and Yu Bai²

¹School of Chemical Engineering, East China University of Science and Technology, 200237 Shanghai, China.

²Sinopec Shanghai Research Institute of Petrochemical Technology, 201208 Shanghai, China.

Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/AJOCS/2021/v10i319095

Editor(s):

(1) Prof. Pradip K. Bhowmik, University of Nevada Las Vegas, USA.

Reviewers:

(1) Meryem Hrimla, Cadi Ayyad University, Morocco.

(2) Ashraf M. El-Shamy, National Research Centre, Egypt.

Complete Peer review History: <https://www.sdiarticle4.com/review-history/74060>

Original Research Article

Received 14 July 2021

Accepted 24 September 2021

Published 27 September 2021

ABSTRACT

Polyvinyl butyral (PVB) was prepared by the condensation reaction of polyvinyl alcohol (PVA) with n-butylaldehyde using a catalyst which is a kind of deep eutectic solvent (DES) made of dodecyltrimethylammonium chloride and p-toluenesulfonic acid. The raw materials and products were characterized by Fourier transform infrared spectroscopy (FT-IR). The effects of the following reaction conditions on the degree of PVB acetal, yield and agglomeration of the products were investigated: the mass ratio of n-butylaldehyde to PVA (m_{BA}/m_{PVA}) of 0.48-0.96, the mass ratio of catalyst to PVA (m_{cat}/m_{PVA}) of 0.16-0.64, the low temperature reaction temperature (5-20°C), and the low temperature reaction time (1-3h). The results showed that at $m_{BA}/m_{PVA} = 0.8$, $m_{cat}/m_{PVA} = 0.32$, low temperature reaction temperature of 15°C and low temperature reaction time of 2 hours, the obtained PVB was a homogeneous powder with the highest acetal degree of 73.85%.

Keywords: Polyvinyl butyral; catalyst; synthesis.

*Corresponding author: E-mail: wlxue@ecust.edu.cn;

1. INTRODUCTION

Polyvinyl butyral (PVB) resin is a terpolymer composed of hydroxyl, acetoxy and butyraldehyde groups, which are randomly distributed in the long molecular chain. These three groups also affect the physicochemical properties of PVB, such as viscosity, solubility, water resistance and phase solubility, and their interrelationships can be seen in Fig. 1 [1-3]. PVB with higher hydroxyl value has higher water solubility and can be used to prepare hydrophilic separation membranes [4]; PVB with higher acetoxy value has better water resistance and can be used to prepare ceramic flower paper; butyraldehyde group value increases, phase solubility and water resistance both increase. In the actual production process, the ratio of the three differs due to the different raw materials and production processes, and thus the performance of the products also differs. PVB resin has high mechanical transparency, good mechanical properties, and good adhesion to glass, ceramics, metals and other materials [5-7], so it is mainly made into films used in safety glass, photovoltaic battery interlayer materials [6], in addition to widely used in coatings, aluminum foil paper and other aspects [9-11]. Due to the expansion of the automotive industry, the demand for PVB films with sound insulation, UV resistance, high impact strength, transparency, and high and low temperature resistance will continue to increase [12-15].

Polyvinyl butyral (PVB) is a resin formed by the condensation of polyvinyl alcohol (PVA) and n-butylaldehyde under the catalytic effect of acid. The current synthesis process often uses hydrochloric acid [16] as the catalyst, and the concentration of reactants is high at the beginning of the reaction, in order to prevent the products from agglomeration, a lower reaction temperature is required to slow down the reaction, as the reaction proceeds, the concentration of reactants in the system gradually decreases, and the temperature needs to be gradually increased to speed up the reaction and make the raw materials fully react. At the same time, in order to make the long-chain PVA molecules in solution to stretch and stretch to better combine butyraldehyde molecules, most common PVB synthesis processes add surfactants as emulsifiers, such as SDS, sodium dodecyl sulfate, sodium dioctyl sulfosuccinate, etc. [17-18]. The emulsifier generates a large amount of foam during filtration, which requires repeated washing with large amounts of water to remove, which undoubtedly increases the operational process and production costs, and also puts pressure on the wastewater treatment system [19]. Some studies have shown that NMP [20], ethanol [21], and dimethyl sulfoxide [22] can be used as solvents to increase the solubility of PVA and PVB to improve product quality, but this can also bring about increased production costs, safety hazards, environmental pollution, and other problems.

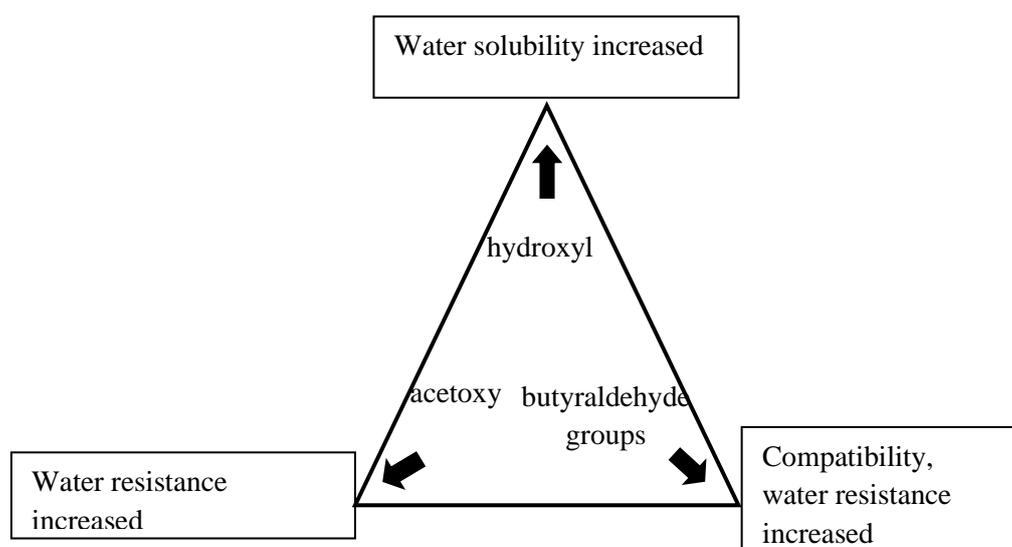


Fig. 1. The relationship between PVB structure and characteristic

Deep eutectic solvent (DES) is a new type of green solvent, which has similar properties to ionic liquids and has the advantages of easy synthesis, low cost, safety and non-toxicity [23-25], and is usually formed by a certain proportion of hydrogen bond acceptors (HBA) such as quaternary ammonium salts and quaternary phosphonium salts and hydrogen bond donors (HBD) such as amides, carboxylic acids and alcohols by hydrogen bonding [26]. In this paper, a new PVB synthesis method without the addition of emulsifier was found by studying the condensation process of PVB with 05-88 PVA (polymerization degree of 500 and alcohol resolution of 88) and n-butyraldehyde, i.e., the deep eutectic solvent of dodecyltrimethylammonium chloride-p-toluenesulfonic acid was used as a catalyst to solve the problem of spreading the long chain of PVA in solution and large amount of foam generated in filtration. The effects of catalyst dosage, butyraldehyde dosage, reaction temperature and time on butyraldehyde dosage of PVB were also investigated in this paper.

2. EXPERIMENT

2.1 Reagents

The chemicals involved in this experiment include polyvinyl alcohol (05-88, Shanghai yuanye Bio-Technology Co., Ltd), n-butyl aldehyde (Shanghai Macklin Biochemical Co., Ltd), dodecyltrimethylammonium chloride (Shanghai Titan Scientific Co., Ltd), p-toluenesulfonic acid (Shanghai Ltd.), sodium hydroxide (Tianjin Jiani Chemical Co., Ltd.), hydroxylamine hydrochloride (Shanghai Titan Scientific Co., Ltd.), ethanol (95% wt%) (Shanghai Titan Scientific Co., Ltd.). All of them are AR grade.

2.2 Preparation of DES

The appropriate amounts of dodecyltrimethylammonium chloride and p-toluenesulfonic acid were weighed separately according to the molar ratio of 1:0.9, and both were placed in an oven at 55°C for 2h. After drying, the two were mixed and poured into a flask, stirred at 80 °C under the heat of the water bath until completely dissolved, the solution was clarified and transparent, and the resulting product was dodecyltrimethylammonium chloride-p-toluenesulfonic acid deep eutectic solvent. The product was sealed and kept in a silica gel oven for storage.

2.3 Preparation of PVB

Add some (about 60mL) water to the three-mouth flask, weigh some (about 5g) PVA into the three-mouth flask and stir continuously, wait for a period of time so that the PVA absorbs water and dissolves, in order to prevent the dissolution of heating into a lump. Heat to 80 °C so that PVA completely dissolved, the solution is a homogeneous transparent liquid, no obvious undissolved material. Weigh a certain amount of DES, dissolve it in 10 ml of water and add it to the flask.

The completely dissolved PVA solution was cooled to a certain temperature, and a certain amount of n-butyraldehyde was gradually added to the PVA solution at a rate of 10ml/h. After 10min of complete addition of n-butyraldehyde, PVB gradually precipitated and formed a white suspension. After holding the reaction at low temperature for a period of time, the temperature was gradually increased to 35°C at a rate of 40°C/h, and then held at 35°C for 0.5h. After holding, the temperature was increased to 60°C at a rate of 40°C/h and held for 0.5h.

After the reaction solution is cooled to room temperature, the PVB resin pellets and the recovery solution are filtered out and washed 2-3 times with pure water PVB pellets. The particles obtained by filtration were crushed and dried in a vacuum oven at 50°C to obtain the sample.

2.4 PVB Synthesis Principle

PVB is produced from PVA and n-butyraldehyde by hydroxyl aldol condensation reaction. Under acid catalysis, n-butyraldehyde combines with a hydroxyl group to form a hemiacetal and removes a molecule of water; the resulting hemiacetal is unstable and further combines with another molecule of hydroxyl group to produce a condensed butyral group. The reaction process is shown in Fig. 2 [27-28].

2.5 Performance Tests

2.5.1 Determination of acetal degree of PVB

The acetal group in PVB reacts with hydroxylamine hydrochloride to produce hydrochloric acid, and the degree of acetal can be calculated by titration with standard NaOH solution using methyl orange as indicator, according to the amount of base, the formula is as follows

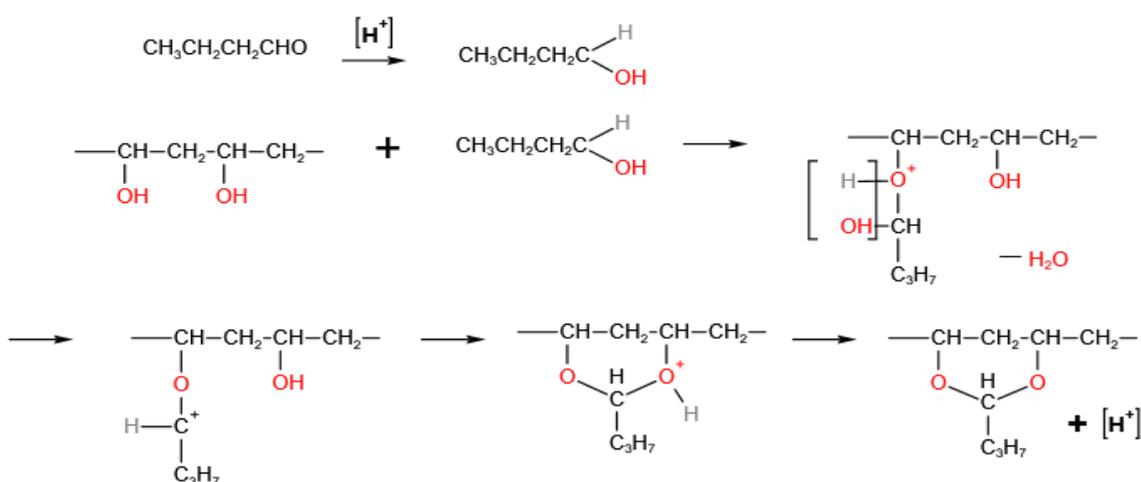


Fig. 2. PVB synthesis reaction principle

$$AD = \frac{0.141 \times (V - V_0) \times c}{m} \times 100\%$$

- AD acetal degree of the sample, %
 V volume of NaOH solution consumed to titrate the sample, mL
 V_0 : volume of NaOH solution consumed for titration of blank, mL
 c: concentration of standard NaOH solution, mol/L
 m: mass of the sample, g

3. RESULTS AND DISCUSSION

3.1 Characterization of PVA and PVB

The reaction between PVA and n-butyraldehyde involves the formation of a chemical bond

between the -OH group of PVA and the -COH of n-butyraldehyde, resulting in a C-O-C group. Two samples of PVA and PVB were characterized by Fourier infrared transform spectroscopy (FT-IR) using KBr compression technique, respectively. The corresponding FT-IR spectra are shown in Fig. 1. In Fig. 1, the IR spectra of PVA and PVB samples share some common vibrational absorption peaks: both have absorption peaks in the region near 1745 cm^{-1} , indicating the presence of -COOC- in both molecules, and both have absorption peaks near 2960 cm^{-1} , indicating the presence of -CH₂ in both molecules. In comparison with the IR spectrum of PVA, two new peaks of 1004 cm^{-1} and 1142 cm^{-1} appeared in the PVB spectrum, both due to the stretching vibration absorption of the C-O-C structure. Therefore, we can assume that the reaction of PVA with n-butyraldehyde occurred successfully.

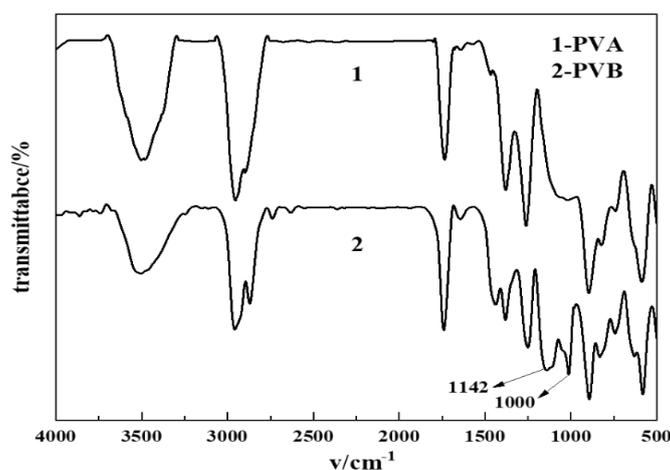


Fig. 3. FTIR spectra of PVA and PVB

3.2 Effect of Butyraldehyde Dosage

The effects of butyraldehyde concentration on product quality, acetal degree and agglomeration were investigated by varying the mass ratio of n-butylaldehyde to PVA (m_{BA}/m_{PVA}) in the range of 0.48-0.96 at a low temperature of 15°C, a low temperature reaction time of 2h and the mass ratio of catalyst to PVA (m_{cat}/m_{PVA}) in the range of 0.16-0.64, and the results are shown in Fig. 4. As can be seen from the figure, the degree of acetal increases with the increase of n-butylaldehyde dosage, and the degree of acetal is 73.85% when m_{BA}/m_{PVA} is 0.8, at which time the PVB is a homogeneous powder. This is due to the higher concentration of butyraldehyde increases the chance of n-butylaldehyde reacting with hydroxyl group, which is conducive to the positive reaction. When m_{BA}/m_{PVA} reached 0.8, the rate of increase of the acetal degree slowed down and the degree of agglomeration of the product started to increase, which may be due to the too fast reaction rate making it difficult for the generated PVB to be fully dispersed and thus cross-linked into clusters with each other. Therefore, the appropriate value of m_{BA}/m_{PVA} is 0.8 in terms of economy and product quality, i.e., the mass ratio of PVA to n-butylaldehyde is 1:0.8.

3.3 Effect of Catalyst Dosage

The catalyst used in this reaction is DES composed of dodecyltrimethylammonium chloride and p-toluenesulfonic acid, which is an

important controlling factor of the reaction. On the one hand, under the catalytic effect of p-toluenesulfonic acid, one molecule of aldehyde reacts with two molecules of alcohol to produce stable acetal; on the other hand, dodecyltrimethylammonium chloride has hydrophilic amino group and hydrophobic long carbon chain, which can stretch the long chain of PVA in the solution and expose the hydroxyl group to react with butyraldehyde to improve the acetal degree and inhibit the generated PVB cross-linked blocks.

The effect of catalyst dosage on the degree of acetal and agglomeration was investigated by changing m_{cat}/m_{PVA} at 0.16-0.64 under the conditions of low temperature 15°C, low temperature reaction time 2h, and m_{BA}/m_{PVA} of 0.8, and the results are shown in Fig. 5. As can be seen from the figure, the yield and degree of acetal increased continuously with the increase of catalyst dosage when m_{cat}/m_{PVA} was less than 0.32g; when m_{cat}/m_{PVA} was greater than 0.32, the increase of degree of acetal was not obvious. Therefore, from the viewpoint of cost, m_{cat}/m_{PVA} of 0.32, i.e., the mass ratio of PVA to DES is 1:0.32 is more appropriate.

3.4 Effect of Low Reaction Temperature

The acetal reaction includes two parts: low temperature and high temperature. At the early stage of the reaction, the reaction is more violent due to the high concentration of n-butylaldehyde and hydroxyl group, and the reaction is controlled

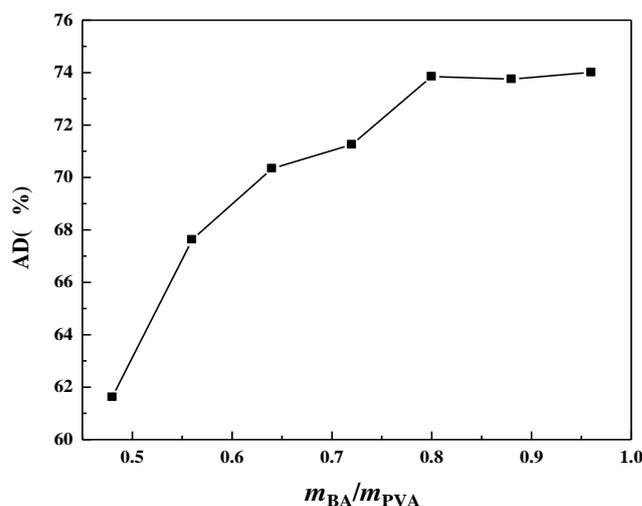


Fig. 4. Effect of butyraldehyde dosage on the degree of PVB acetal

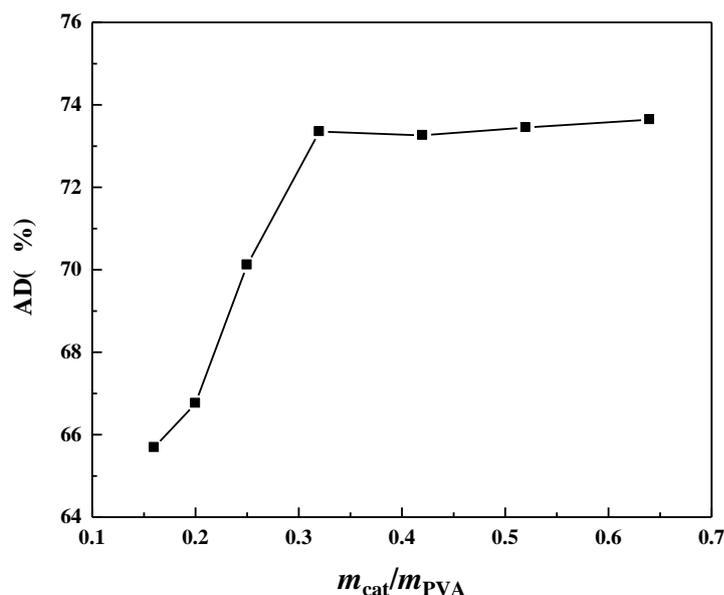


Fig. 5. Effect of catalyst dosage on the degree of PVB acetal

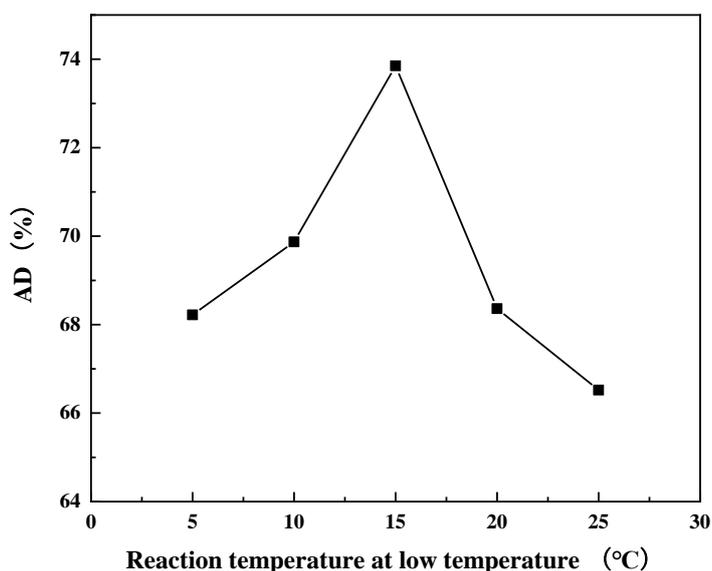


Fig. 6. Effect of low reaction temperature on the degree of PVB acetal

at low temperature to reduce the reaction rate; at the later stage of the reaction, the concentration of n-butyraldehyde and hydroxyl group is low, and the reaction is controlled at high temperature to accelerate the reaction rate and increase the degree of acetal.

The effect of low temperature reaction temperature on the degree of acetal and agglomeration was investigated by varying the

low temperature reaction temperature from 5 to 20°C under the conditions of low temperature reaction time of 2h, m_{BA}/m_{PVA} of 0.8 and m_{cat}/m_{PVA} of 0.32, and the results are shown in Fig. 6. When the temperature was lower than 15 °C, the mass and degree of acetal of the product increased with the increase of the reaction temperature, while the agglomeration of the product gradually improved. This may be due to the slower reaction rate when the reaction

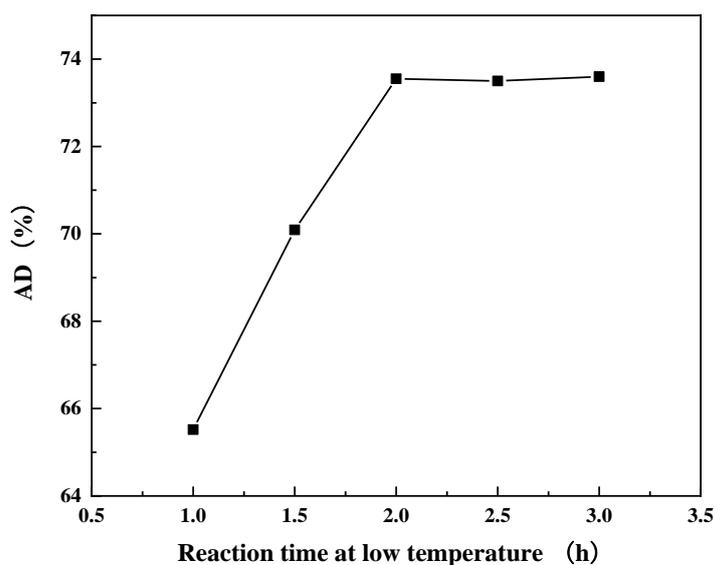


Fig. 7. Effect of low reaction time on the degree of PVB acetal

temperature is low and there are still more butyraldehyde and hydroxyl groups in the solution at high temperature reaction. When the temperature was increased, the reaction was more intense and the resulting PVB solids were cross-linked with each other leading to product agglomeration, while the unreacted hydroxyl groups were wrapped and thus could not continue the reaction, resulting in a lower degree of product acetal. Similarly, when the low temperature reaction temperature is higher than 15°C, the degree of acetalization starts to decrease and the degree of agglomeration increases. Therefore, the suitable temperature for low temperature reaction is 15°C.

3.5 Effect of Low Reaction Time

The effect of low temperature reaction time on the degree of acetal and agglomeration was investigated by changing the low temperature reaction time to 1-3h under the conditions of low temperature reaction temperature of 15°C, m_{BA}/m_{PVA} of 0.8 and m_{cat}/m_{PVA} of 0.32, and the results are shown in Fig. 7. When the low-temperature reaction time reached 2h, the degree of acetal had reached a high value and the product was a homogeneous powder, and the increase of the degree of acetal was not obvious when the reaction time continued to be increased. Therefore, extending the reaction time could not effectively improve the product quality and significantly increase the energy consumption of production, so the low

temperature reaction time was chosen to be 2h.

4. CONCLUSION

In this experiment, PVB was synthesized from PVA and n-butyraldehyde using a deep eutectic solvent (DES) made from dodecyltrimethylammonium chloride and p-toluenesulfonic acid as the catalyst. The qualitative analysis of the raw materials and products by Fourier transform infrared spectroscopy (FT-IR) showed that the product contained a large number of C-O-C groups, indicating that it was the target product. The effects of the reaction conditions such as the mass ratio of n-butyraldehyde to PVA m_{BA}/m_{PVA} at 0.48-0.96, the mass ratio of catalyst to PVA m_{cat}/m_{PVA} at 0.16-0.64, the low temperature reaction temperature (5-20°C) and the low temperature reaction time (1-3h) on the degree of acetalization, yield and agglomeration of the product PVB were investigated. The results showed that under the conditions of $m_{BA}/m_{PVA}=0.8$, $m_{cat}/m_{PVA}=0.32$ and 2h low temperature reaction at 15°C, the obtained PVB was a homogeneous powder with the highest degree of acetalization of 73.85%.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

- Li GD, Zhang Y. Study and application of polyvinyl butyral resin [J]. China Adhesives. 2006;15(6):27-32.
- Iwasaki R, Sato C. The influence of strain rate on the interfacial fracture toughness between PVB and laminated glass[J]. Phys. IV. 2006;134:1153-1158.
- Fernandez MD, Fernandez MJ, Hoces P. Synthesis of poly(vinyl butyral)s in homogeneous phase and their thermal properties [J]. Appl. Polym. Sci. 2006; 102(5):5007-5017.
- Liu JL. Application of PVB in Separation Membrane Materials [J]. Anhui Chemical Industry, 2021;47(1):17-19.
- Liu BH, Sun YT, Li YB. Systematic experimental study on mechanical behavior of PVB material under various loading conditions [J]. Polymer Engineering and Science. 2012;10:1137-1148.
- Chetri P, Dass NN. Preparation of poly (vinyl butyral) with high acetalization rate [J]. Journal of Applied Polymer Science. 2010;81(5):1182-1186.
- Sun TY, Shen ZX. The market status and development analysis of polyvinyl butyral [J]. Guangdong Chemical Industr. 2013; 40(6):87-74.
- Liu BH, Sun YT, Li YB, Wang Y, Ge DY, Xu J. Systematic experimental study on mechanical behavior of PVB (polyvinyl butyral) material under various loading conditions [J]. Polym. Eng. Sci. 2012;52(5):1137-1147.
- Gao G. Synthesis and application of polyvinyl [J]. Chemical Engineering Design Communications. 2018;44(9):12.
- Hajian M, Koohmareh GA, Rastgoo M. Investigation of factors affecting synthesis of polyvinyl butyral by taguchi method [J]. Journal of Applied Polymer Science. 2010;115(6):3592-3597.
- Zhou BY. Technology for an energy-saving and fast synthesis of polyvinyl butyral in a microreactor system [J]. Industrial & Engineering Chemistry Research. 2017; 56(49):14463-14470.
- Ji SH. Market analysis on PVB and PVB membrane (2009-2016) [J]. China Synthetic Resin and Plastics, 2017, 34(4): 98-102.
- Lin XY, Yan S, Zhou BY, Wang K, Zhang JS, Luo GS. Highly efficient synthesis of polyvinyl butyral (PVB) using a membrane dispersion microreactor system and recycling reaction technology. Green Chem. 2017;19(9):2155-2163.
- Zhou BY, Lin XY, Wang K, Luo GS. Technology for an energy-saving and fast synthesis of polyvinyl butyral in a microreactor system. Ind. Eng. Chem. Res. 2017;56(49):14463-14470.
- Liu BH, Wang Y, Xu XQ et al. Experimental research on energy absorption characteristic of PVB laminated windshield subjected to headform low-speed impact [J]. Journal of Mechanical Engineering. 2013;49(22):128-136.
- Wang JW, Jiang WW, Zhu YM et al. Study on new process of synthesizing polyvinyl butyral[J]. China Adhesives. 2016; 25(03):13-17.
- Liu XF, Wu GD, Zhang DP. Preparation and application of surfactant-catalyzed polyvinyl butyral[J]. China Adhesives. 2014;23(02):11-14.
- Li F. Exploratory research on poly (vinyl butyral)[J]. Thermosetting Resin. 2005;20(5):48-50.
- Li Y. Research on the Preparation of PVB Resin by Novel Soap-free Polymerization Technology and Its Application[D]. Changchun University of Technology; 2020.
- Fernández MD, Fernández MJ, Hoces P. Synthesis of poly(vinyl butyral)s in homogeneous phase and their thermal properties[J]. Journal of Applied Polymer Science. 2006;102(5):5007–5017.
- Liang H. Synthesis of polyvinyl butyral with high acetal degree [J]. Chemistry and Adhesion. 2019;41(4):316-318.
- Ding L, Qing JN. PVB production in dimethyl sub-sulphone[J]. Contemporary Chemical Industry. 2008;37(5):453-455.
- Sorouraddin Saeed Mohammad et al. Development of an air-assisted liquid-liquid microextraction method based on a ternary solidified deep eutectic solvent in extraction and preconcentration of Cd(II) and Zn(II) ions[J]. International Journal of Environmental Analytical Chemistry. 2021;101(11):1567-1580.
- Xu H, Peng J, Kong Y, et al. Key process parameters for deep eutectic solvents pretreatment of lignocellulosic biomass materials: A review [J]. Bioresource Technology. 2020;310.
- Liu Q, Sun W, Yuan T, et al. Green and cost-effective synthesis of flexible, highly

- conductive cellulose nanofiber/reduced graphene oxide composite film with deep eutectic solvent [J]. Carbohydrate Polymers. 2021;272:118514-118514.
26. Cheng HY, Qi ZW. Research progress of deep eutectic solvent for extractive separation [J]. Chemical Industry and Engineering Progress. 2020;39(12):4896-4907.
27. Wang LG, Zheng YB, Shang HZ. New synthesis technology for polyvinyl butyral [J]. China Adhesives. 2008;17(8):15-18.

© 2021 Li et al.; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Peer-review history:

The peer review history for this paper can be accessed here:
<https://www.sdiarticle4.com/review-history/74060>