



ارائه شده توسط:

سایت ترجمه فا

مرجع جدیدترین مقالات ترجمه شده

از نشریات معتبر

POLYVINYL BUTYRAL AND POLYVINYL FORMAL

Polyvinyl butyral (PVB) and polyvinyl formal (PVF) are two commercially important polyvinyl acetals at present. The name polyvinyl acetal is generally applied to a group of resins derived from the reaction of polyvinyl alcohol with aldehydes. The first preparation of polyvinyl acetal was made in 1924 by Herrmann and Haehnel, who reacted polyvinyl alcohol with benzaldehyde. Commercial methods of polyvinyl acetal manufacture were developed in subsequent years.

CHEMISTRY

The kinetics of the condensation reaction of polyvinyl alcohol and aldehyde have been studied in the past. The following mechanism is generally applied to that reaction:

As clearly indicated, the overall reaction is controlled by the second step reaction between polyvinyl alcohol and protonated aldehyde. The rate of reaction was found to be first order with respect to the concentrations of polyvinyl alcohol and aldehyde, and the acidity of the solution.

In the presence of dilute acid, Smets and Petit found that the reaction became more complicated. In addition to the overall alcohol concentration, the unreacted hydroxyl group adjacent to the acetal functional group enhanced the reversed reaction, hydrolysis of acetal, a phenomenon similar to that described in section 6 for the hydrolysis of polyvinyl acetate. Commercially available polyvinyl alcohols are in atactic form, which is a mixture of syndiotactic and isotactic structures. The structurally different position of the hydroxyl groups have different effects on the acetalization. Shibatani et al. found that the rate of formalization to form a cis-formal at the isotactic part of PVAL was four times greater than that to form a trans-formal at the syndiotactic part and that the migration of formal rings from syndiotactic portions occurred when the reaction was allowed to continue for a long period of time. The reaction of PVAL with aldehyde occurs not only in the intramolecular hydroxyl groups but also in the intermolecular ones. Matsuzawa et al. found that crosslinking, or intermolecular reaction, occurred in the precipitation method (i.e. reaction in a heterogeneous phase, to be described in a later section) with formalization starting from PVAL aqueous solution. Similar results are also reported in the case of polyvinyl butyral. The intrinsic viscosity of PVB increases sharply with the degree of butyralization when the precipitation method is used. However, when the dissolution method is used, the intrinsic viscosity remains essentially constant. Ogasawara et al. in their study on heterogeneous formalization, found that the crosslinking reaction occurred more easily in syndiotacticity-rich PVAL than in atactic PVAL, and that the rate of the crosslinking reaction increased with increasing formaldehyde concentration under constant acid concentration. The presence of polymeric formaldehyde, which is a result of high formaldehyde concentration, and the degree of swelling of PVAL film during the formalization are the two important factors in the crosslinking reaction considered by Ogasawara et al.

Review of Processes

Acetalization Processes

Commercial exploitation has been directed largely to polyvinyl butyral and polyvinyl formal and to a much less extent to other polyvinyl acetals. Selective lists of patents for the preparation of polyvinyl butyral and polyvinyl formal are summarized in Table 7.1 and 7.2 respectively. Mineral acids, particularly sulfuric acid and hydrochloric acid, are claimed in most patents. In addition, methylol sulfonic acid. Prepared by absorbing SO_2 in aqueous solution of formaldehyde and mixtures of sulfuric acid and paratoluene sulfonic acid are also used in patent examples. In a patent assigned to Sekisui Chemical an H-type ion exchange resin is used such that PVB solution produced needs no caustic neutralization. The subsequent wash of PVB resin is therefore not necessary. The process, however, produces only partially butyralized PVB with low degree of butyralization at 20-30 mol%. The processes summarized in Table 7.1 and 7.2 can be classified into one-step processes involving simultaneous hydrolysis of PVAc and acetalization of PVAL (sometimes in consecutive stages without intermediate separation of PVAL), and two-step processes involving alcoholysis of PVAc as the first step and the condensation of PVAL with aldehyde as the second step. The one-step preparation of PVB or PVF is conducted for the most part as a solution process in organic solvents such as acetic acid, methanol, methyl acetate, and ethyl acetate. The process can also be effected in dispersion systems, which permit the handling of higher solids content in the reaction mixture. In the two-step process, preformed PVAL in solution or suspension form reacts with aldehyde in the presence of an acidic catalyst. Examples of organic solvents used are methanol (or methanol/water mixture), isopropanol, and toluene.

Work-up Processes

In processes using the dissolution method or homogeneous reaction method, the final PVB or PVF is generally precipitated by adding water or a dilute aqueous solution of the organic solvent used in the process. In a Unitika patent, alcohol-soluble salts such as sodium acetate and calcium chloride are used to precipitate PVB. The salt is added at 0.1-3 parts per one part of PVB. Purification of PVB is an important procedure in the PVB process, particularly for products used as safety glass interlayers. Processes for purification and stabilization of PVB resin have been patented by Du Pont and Monsanto. In the Monsanto patent, polyvinyl butyral (in organic solvents such as methanol, ethanol, and acetic acid) is neutralized with an alkali or alkaline salt. The resin solution may be filtered either before or after the treatment to remove dirt or other foreign substances. The resin is then precipitated by diluting the solution with a non-solvent, generally water. The precipitated PVB is suspended again in a dilute alcohol solution containing alkali salt at 0.2% of the weight of the batch. The mixture is heated at 176°F (80°C) for several hours, then washed to remove alkali or any free salts. After washing, the resin is given a final stabilization treatment in 10 wt% methanol solution at about 450 parts of solution, containing about 0.1 part of KOH per 100 parts of resin. The resin is then centrifuged and dried at 122-176°F (50-80°C). In the Du Pont patent, the crude polyvinyl acetal resin as precipitated from the organic medium is treated in a steeping liquid composed of a mixture of water and water-miscible solvent for the resin. Alkaline

substances, such as alkali metal hydroxides and tertiary amines (e.g. triethanol amine, diethyl cyclohexyl amine, dimethyl cyclohexyl amine), are added in an amount to keep the pH of the steeping liquid at 9-10. Ammonium hydroxide is not desirable because of its volatility and its effect on the color of the resin. Alkaline earth metal hydroxides are also undesirable because of their formation of insoluble salts with sulfuric acid which is commonly present in the crude resin as catalyst for the condensation reaction. The treatment of the steeping liquid is maintained at 122°F (50°C) for 1-1/2 to 2 hours to leach out residual aldehyde and the salts formed by neutralization. After the steeping treatment, the steeping liquid is drained off, and the resin is rinsed by the use of weaker mixtures of the solvent with water and finally by the use of water until the percentage of methanol in the wash liquid has been reduced to not more than 5% by weight. The resin is then filtered and dried at temperatures not in excess of 167°F (75°C). The use of urea in the last rinse is claimed in a Du Pont patent as an aldehyde-binding reagent which combines with aldehyde in the formation of a compound which is either leached out by water or remains as an innocuous impurity in the resin. A small amount of alkaline substance, generally alkali metal hydroxide, is preferably added in the last rinse to impart a specified alkalinity titer to the final PVB resin. Safety glass interlayers made from this product have improved impact resistance.

Process Description

Figure 7.1 illustrates a process for manufacturing polyvinyl butyral at an annual capacity of 25 million pounds. In this process vinyl acetate is polymerized in methanol solution polyvinyl acetate is then hydrolysed to polyvinyl alcohol with caustic catalyst in methanol solution, followed by a condensation reaction with butyraldehyde in the presence of sulfuric acid as catalyst. The conditions of vinyl acetate polymerization and of polyvinyl acetate hydrolysis are the same as those described in section 6. The condition for the polyvinyl alcohol condensation reaction, selected from those described in the patents assigned to Wacker Chemie, Celanese, and Unitika are listed as follows:

Overall yield is assumed at 1.4 pounds of vinyl acetate per pound of PVB product. The process comprises five sections - (100) Raw Material Storage and Purification, (200) Polymerization, Hydrolysis, and Condensation, (300) Product Washing and Drying, (400) Bulk Handling, and (500) Solvent and By-Product Recovery. A list of major equipment and a utilities summary are given in Table 7.3. Stream flows are shown in Table 7.4. In Table 7.5, a summary of waste streams is listed.

Raw Material Storage and Purification

The operation of this section is essentially the same as that in the polyvinyl alcohol process described in Section 6. Purified vinyl acetate from the inhibitor stripping column, C-101, is stored in the daytank, T-101, ready for charging along with the initiator solution from the initiator solution feed tank, V-103, to the polymerization reactor. In addition, streams of butyraldehyde, ethyl acetate, and methanol are charged to appropriate parts of the process.

Polymerization, Hydrolysis, and Condensation

Polymerization and hydrolysis reactions are conducted in the same manner as those in the PVAL process. Neutralized polyvinyl alcohol slurry from the surge tank, V-208, is, however, charged batchwise for half an hour into the centrifuge, S-201, where PVAL is separated from the mother liquor and washed with methanol from the recovered methanol surge tank, T-503. This operation is performed every three hours, and the amount is therefore three times that of the stream shown in Table 7.4. Solvent-separated PVAL is then charged into the condensation reactor, R-204A or 204B, along with methanol, butyraldehyde and sulfuric acid in methanol solution. The initial charge of methanol is about 58% of the total charge from methanol tank, T-302. The reaction mixture is then refluxed for one hour before the remaining methanol is charged. Reaction is continued for an additional 4 hours with reaction temperature controlled at 140°F(60°C) by a reflux condenser (E-205A; E-205B for Reactor R204B) and jacket cooling.

Product Washing and Drying

At the end of the batch, a methanol solution of polyvinyl butyral is discharged through a press filter to remove any solid contaminants. The filtered PVB solution is then fed into the precipitator, V-301, where the solution is neutralized with caustic solution from the tank, V-304, and agitated for half an hour. Water is then added to precipitate PVB from the diluted methanol solution. Precipitation is conducted at 100°F(38°C) for one hour with sufficient agitation to produce uniform particles of PVB resin. The PVB slurry is then transferred into two of the four Washer, V-302A and V-302B (V-302C are for an alternative batch) for half an hour. The washers are jacketed and equipped with agitators inserted from the top and filter plates fitted near the bottoms of the vessels. Part of the methanol solution is drained through the filter plate until the solid content of the remaining slurry reaches 15 wt%. Water is then added to the PVB slurry to dilute the solid content from 15 wt% to 5 wt%. Caustic solution is introduced if needed to keep the Ph to a steady value of between 9 and 10. The PVB slurry is now maintained at a temperature of

122°F(50°C) for three hours to leach out residual aldehyde and salt from neutralization. The liquid in the PVB slurry is drained for the second time until 15 wt% solid slurry is again reached in the washer. The PVB resin is then washed and drained twice again, the same amount of water being used for each washing and the pH kept at 8-9. Streams of the first three drains, containing dilute methanol, are transferred to the dilute methanol surge tank, T-301, while about 45% of the last drain is sent to the drained water tank, T-501, supplying water for ester hydrolysis in the hydrolyzer, C-502. The remaining drained water is discharged to waste treatment. PVB slurry in the washers is diluted with water to 10 wt% solid content. Caustic solution is added in an amount of 0.1 part of caustic per 100 parts of PVB. The resulting PVB slurry is then discharged into the PVB slurry surge tank T-303. The total cycle time for neutralization and precipitation is assumed at 2-1/2 hours, and that for washing at 6 hours. PVB slurry from the surge tank, T-303, is continuously fed into the product centrifuge, S-301, where the resin is separated from the mother liquor and washing water. Wet PVB resin is then dried with 180°F(82°C) drying air in the rotary dryer, PAC-301.

Bulk Handling

Dried PVB from the rotary dryer, PAC-301, is collected in the product collector, PAC-302. The resin is then transferred pneumatically to storage bins PAC-402 to 404, after passing through the product screen, PAC-401. A 15-day production volume has been provided by these storage bins. PVB product from the storage bins is loaded into railroad cars or trucks for transport to sales.

Solvent and By-Product Recovery

The stream from the crude solvent storage tank contains methanol, methyl acetate, some sodium acetate, and water. The recovery of methanol, the hydrolysis of methyl acetate to methanol and acetic acid, and the conversion of sodium acetate to acetic acid and sodium sulfate are essentially the same as described in section 6 for the PVAL process.

Process Discussion

Methanol is used in the present process for the polymerization, the alcoholysis, and the condensation reaction. This is different from the Shawinigan PVB process described in the literature, where ethanol is used as solvent. As a result of alcoholysis, methanol used in the present process is converted to methyl acetate, which is then converted by ester hydrolysis to methanol and acetic acid. The conversion of methyl acetate to methanol and acetic acid is important because 1-methyl acetate forms an azeotrope with methanol at 81.3 wt% methyl acetate, which prevents further purification by conventional distillation, and 2-methyl acetate does not have as much market value as acetic acid. In the case of

ethanol used as solvent for PVAC alcoholysis, ethyl acetate which is the product of the alcoholysis, has a market value about the same as, or better than, the market value for acetic acid. It appears that further conversion of ethyl acetate to acetic acid is not necessary. Thus the operation of ester hydrolysis can be eliminated. However, purification of ethyl acetate from the alcoholysis mother liquor, which contains ethyl acetate, ethanol, sodium acetate, and water, is difficult because of the existence of azeotropes among these components. An extractive distillation system similar to the one used in section 500 (solvent and By-Product Recovery) may be necessary to recover ethyl acetate. Furthermore, ethanol is too expensive to be used as solvent for this process. The recovery of methanol is conducted in two separate distillation columns—one for the mother liquor of PVAL slurry and the other for the crude dilute methanol from PVB precipitation and washing operations. This is to prevent any residual butyraldehyde from getting into methanol used for vinyl acetate polymerization. As described in section 6, the presence of aldehyde could cause a low degree of polymerization.

Cost Estimates

Capital Costs

Table 7.6 summarizes the capital cost estimates for a polyvinyl butyral resin plant with a flow sheet shown in Figure 7.1. The resin plant, having an annual production capacity of 25 million pounds, requires a total fixed capital of 21 million, of \$21 million, of which about 71% is the cost of battery limits equipment. The costs of utilities and tankage investment amount to 16% of the total fixed capital. With the addition of interest on the construction loan, start-up cost, and working capital, the total capital investment reaches \$27.2 million. As in the PVAL process described in section 6, the costs of equipment for the recovery of solvent and by-product are the highest in the process, estimated at \$4.08 million. The facilities for the polymerization, the alcoholysis, and the condensation reaction, and for the product washing and drying are also high, estimated at \$5.10 million and \$4.65 million respectively. The capital costs were estimated without the investment for land, facilities for waste treatment, shelter for the polymerization equipment, and buildings for product work-up and loading facilities. Figure 7.2 illustrates the effect of plant capacity on the total fixed capital. In this figure, the curve shows that the total fixed capital for a 100 million 1 lb/yr PVB plant will be \$57.4 million, which is \$18.1 million higher than that of the PVAL plant shown in Table 6.8. The higher costs for the PVB plant can be attributed to 1—the additional equipment required for the condensation reaction and 2—the operations of product precipitation and washing.

Production costs

Itemized in Table 7.7 are the estimated production costs for the PVB process. The net production cost, not including freight allowance and packaging cost, is calculated at 81.5¢/lb, of which 38% is from the cost of VAM and more than 12% from the cost of butyraldehyde. A credit for the by-product, acetic acid, may reduce the production cost. Assuming that acetic acid credited at 15 ¢/lb, the net production cost is estimated at 67.6¢/lb. The significant effect, of the VAM price is further depicted in Figure 7.3. Also affecting the production cost are the plant capacity and the operating level of the plant. This is shown in Figure 7.4. Figure 7.5 expresses the effect of acetic acid credit on production cost as well as on the total capital investment. The selling price of PVB, after by-product credit of 15¢ per pound of acetic acid, is also estimated with the usual procedure. Based on a linear sales build-up from 50% in five years and 10% (after taxes) return on the fixed capital investment, an average price of 84.0¢/lb is required. This price may be reduced to 77.7¢/lb if the capacity production can be attained from the outset.



این مقاله، از سری مقالات ترجمه شده رایگان سایت ترجمه فا میباشد که با فرمت PDF در اختیار شما عزیزان قرار گرفته است. در صورت تمایل میتوانید با کلیک بر روی دکمه های زیر از سایر مقالات نیز استفاده نمایید:

لیست مقالات ترجمه شده ✓

لیست مقالات ترجمه شده رایگان ✓

لیست جدیدترین مقالات انگلیسی ISI ✓

سایت ترجمه فا ؛ مرجع جدیدترین مقالات ترجمه شده از نشریات معتبر خارجی