

Preparation of polyester polyols by modifying the ricinoleic acid chains of castor oil with dibasic fatty acids

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Abstract:

Polyurethanes are used in a wide range of industrial applications due to their chemical versatility, high performance and low cost. They find use in building and construction, consumer products, furniture and fixtures, transportation and in industrial applications. Polyurethane manufacturers are looking for alternatives so as to reduce carbon footprint, and at the same time positively impact the product quality and economics of production. Thermoplastic polyurethane manufacturers in particular are more inclined towards adopting bio based alternatives and increasing the bio based content in their product by using polyester polyols made from natural and renewable raw materials. The most common sources of natural oil polyols are castor oil, soy oil, peanut oil and canola oil. Castor oil accounts for the majority of natural oil polyol as it contains a ready hydroxyl group unlike the others, where hydroxyl group needs to be introduced by prior processes. Series of experiments were carried out taking castor oil as one of the reactant for making polyester polyols. Castor oil was reacted with different dibasic fatty acids in presence of acidic catalyst at elevated temperature. The progress of reaction was measured by measuring the acid value of the reaction media. Different types of acid catalyst were used to evaluate the progress of reaction. Further, the series of experiments were conducted with different amount of catalyst. It was found that the tin based catalyst showed more rate of reaction than the conventional acid catalyst. 0.15% by wt. of tin based catalyst showed more rate of reaction than 0.015% by wt. polyester polyols prepared from castor oil. Resulting polyester polyols were characterized for physical properties like density, viscosity, color and moisture content.

Key words: Polyester polyols, Castor oil, Dibasic fatty acids, Succinic acid, Adipic acid, Sebacic acid

1. INTRODUCTION

Polyurethanes are used in a wide range of industrial applications due to their chemical versatility, high performance and low cost [1]. They find use in building and construction, consumer products, furniture and fixtures, transportation and in industrial applications [2-5]. Polyurethane is traditionally a downstream derivative of crude oil, rendering it susceptible to the crude oil market fluctuations. Moreover in this age of the consumers, and the global inclination towards green products and sustainable development, bio based alternative for crude oil is the need of the day.

Polyurethane manufacturers are looking for alternatives so as to reduce carbon footprint, and at the same time positively impact the product quality and economics of production. Thermoplastic polyurethane manufacturers in particular are more inclined towards adopting bio based alternatives and increase the bio based content in their product by using polyester polyols made from natural and renewable raw materials. The main demand for bio based polyurethane is derived from application segments such as automotive, footwear and apparel. Uses in applications such as electronics, carpets, and furniture among others are also gaining momentum.

Petroleum based product, and some other di-acids are the conventional raw materials for manufacturing polyurethanes. However, natural oil polyols (NOP) or biopolyols, which are derived from vegetable oils by different methods, are used in the production of bio based polyurethane. The most common sources of natural oil polyols are castor oil, soy oil, peanut oil and canola oil. No. of publications had been reported for natural oil based polyester polyols for preparation of polyurethane [6-16].

Castor oil accounts for the majority of natural oil polyol as it contains a ready hydroxyl group unlike the others, where hydroxyl group needs to be introduced by prior processes. Natural oil polyols have similar origins and applications but the materials are different depending on their manufacturing process. In order to meet the global challenges for specific properties of polyester polyols used in polyurethane, modifications in the raw bio product is necessary. In case of castor oil, modifications can be made by modifying the long carbon chain of ricinoleic acid by reacting it with different types of fatty acids.

2. CHEMICALS USED

In house FSG castor oil was used as bio source for polyester polyols having free fatty acid content and moisture content less than 1% and 0.25% respectively. Dibasic fatty acids, like succinic acid, adipic acid and sebacic acid, were purchased from Finar Chemicals with 99% purity. Tin catalyst (92.5-100% pure) was purchased from Sigma-Aldrich. Diethylene glycol was purchased from Sigma-Aldrich with 99% purity. Extra pure sulfuric acid (99% purity) was purchased from Finar Chemicals.

3. EXPERIMENTAL

Castor oil was reacted with dibasic fatty acids e.g. succinic acid, adipic acid and sebacic acid in presence of acidic catalyst. Molar ratio of castor oil to dibasic fatty acid was taken as 1. The reaction mixture was heated to temperature range of 230-250°C in a stepwise manner. Nitrogen gas was used to provide inert atmosphere and to prevent oxidation as it might lead to degradation of the product. Series of experiment was designed with different dibasic fatty acids and different catalyst and different amount of the catalyst. Decrease in acid value of the reaction mixture was taken as a control parameter to ensure the progress of esterification and transesterification process. Once the acid value dropped down below 10, reaction mixture was capped with the calculated amount of diethylene glycol followed by cooling to room temperature. Prepared polyester polyols were characterized for physical properties such as density, viscosity, moisture content and colour. Schematic diagram of reaction is shown in figure 1.

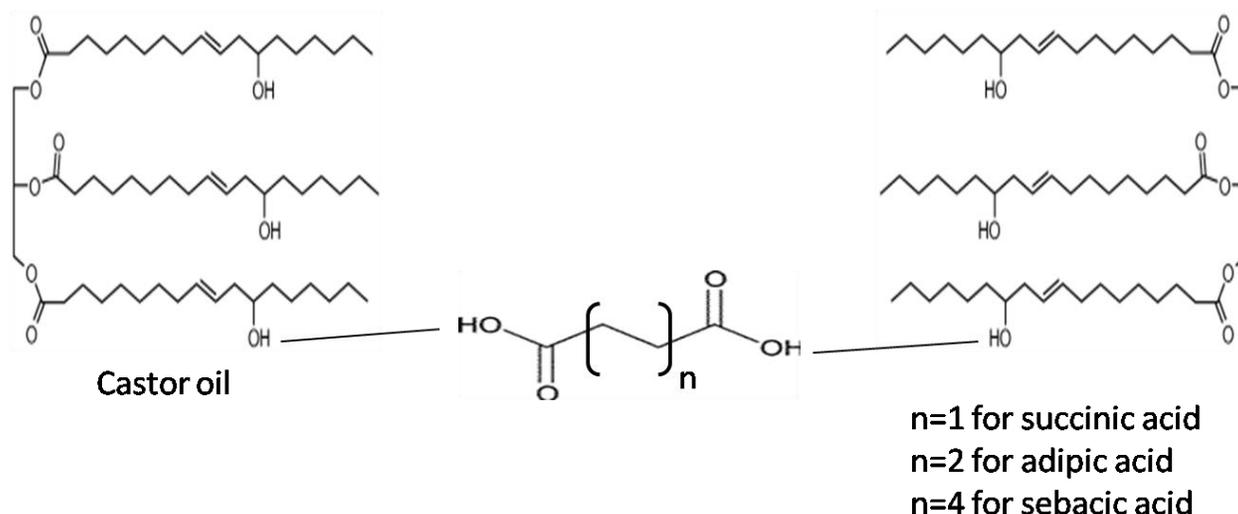


Figure-1: schematic diagram of reaction between castor oil and dibasic fatty acids

4. RESULTS AND DISCUSSION

When sulfuric acid was used as a catalyst, process of the esterification reaction was slow compared to that with the tin based catalyst. Use of sulfuric acid lead to darken the colour of the reaction mixture and final product also. In the temperature range of 230-250°C, it caused charring of some fraction of the reaction mixture and product. The effect of catalyst on color of product is shown in figure 2. Approximately 40%, 49% and 44% of increase in color of polyester polyols was observed in case of

polyester polyols prepared from Castor oil and Succinic acid, adipic acid and sebacic acid respectively. Two different amount of the tin catalyst, 0.015 and 0.15%, were tried to determine the progress of esterification reaction. It was observed that the reaction went fast with the higher amount of catalyst. Colour of final polyester polyols wasn't affected by higher amount of catalyst. Figure 3 shows the effect of amount of tin catalyst on the process time. Physical properties of polyester polyols is shown in table 1.

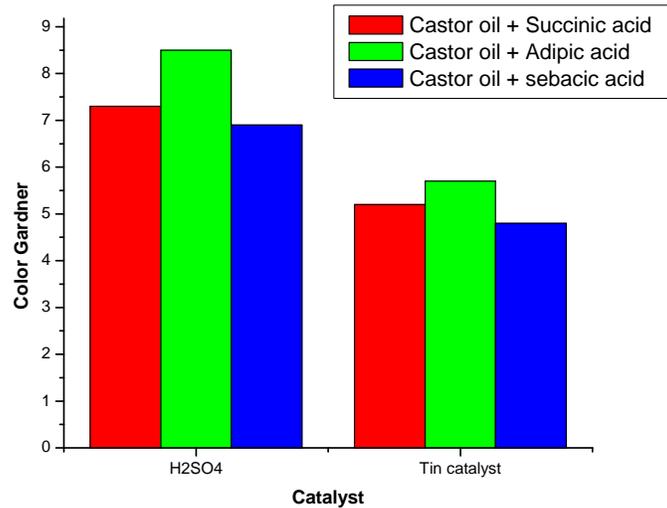


Figure 2 Effect of catalyst on color of polyester polyols

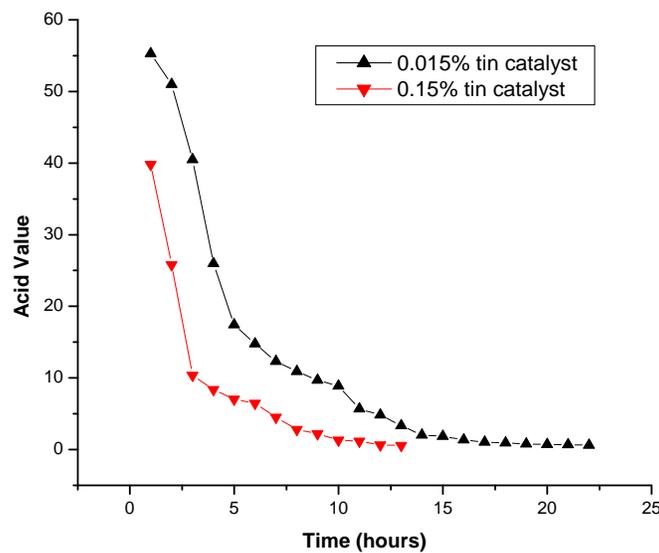


Figure 3 Effect of amount of catalyst on reaction time

Table-1: Physical properties of castor oil based polyester polyols

Sr. No.	Polyester polyol	Reactant		Physical properties			
				Density (g/cc)	Viscosity (cp)	Colour gardner	Moisture content (%)
1	CSU101YA	Castor oil	Succinic acid	0.96	8920	5.2	0.27
2	CAD101YA	Castor oil	Adipic acid	0.96	6588	5.7	0.29
3	CSE101YA	Castor oil	Sebacic acid	0.96	8600	4.8	0.26

Prepared polyester polyols has density less than 1 and high viscosity. Colour of polyester polyols are light brown to light redish. It was also observed that with time the viscosity of polyester polyols increases due to extent of post ploymerisation of the same. Addition of diethylene glycol to polyester polyols help to prevent the post polymerization and controls the viscosity of prepared polyester polyols.

5. CONCLUSION

Polyester polyols can be synthesized using castor oil as a biosource. Reaction temperature depends on the type of fatty acid being reacted to castor oil. Use of tin based catalysts showed effectiveness in progress of esterification process. It was also found that the amount of catalyst used have profound effect on the rate of progrees of esterification reaction. Higher the catalytic amount, higher will be the rate of reaction. Therefoere, amount of catalyst can be taken as one important control point for the reaction in order to control any exothermic reaction in case if happens. Polyester polyols prepared showed post polymerization resulting in increase of viscosity. Capping with diethylene glycol showed profound decrease in the rate of increae in viscosity.

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REFERENCE

- [1] D. K. Chattopadhyay, K. V. S. N. Raju, Progress in Polymer Science, Vol. 32, 2007, pp. 352– 418.
- [2] "The Socio-Economic Impact of Polyurethanes in the United States from the American Chemistry Council" (PDF). The Polyurethanes Recycle and Recovery Council (PURRC), a committee of the Center for the Polyurethanes Industry. February 2004. Retrieved 2007-09-28
- [3] "What's That Stuff?", Chemical & Engineering News, Vol. 77, 1999, pp. 7.
- [4] "Polyurethane Applications in Heavy Duty Industrial Casters and Heavy Duty Industrial Wheels", Caster Concepts, 2014
- [5] M. Desroches, M. Escouvois, R. Auvergne, S. Caillol, B. Boutevin, Polymer Reviews, Vol. 52 (1), 2012, pp. 38–79.
- [6] G. Lligadas, J. C. Ronda, M. Galia, V. Cadiz, Biomacromolecules, Vol. 11, 2010, pp. 2825– 2835.
- [7] Z. S. Petrović, Polymer Reviews, Vol. 48, 2008, pp. 109-155.
- [8] D. P. Pfister, Y. Xia, Chem. Sus. Chem., Vol. 4(6), 2011, pp. 703-717.

- [9] O. S. Ogunfeyitimi, A. O. Okewale and P. K. Igbokwe, *Inter. J. Multi. Sci. and eng.*, Vol. 3 (10), 2012, pp. 10-14.
- [10] C. K. Lyon and V. H. Garrett, *J. Amer. Oil Chem. Soc.*, Vol. 51, 1974, pp. 331-333.
- [11] C. K. Lyon, V. H. Garrett and L. A. Goldblatt, *J. Amer. Oil Chem. Soc.*, Vol 41, 1964, pp. 23-25.
- [12] S. S. Narine, X. Kong, L. Bouzidi and P. Sporns, *J. Am. Oil. Chem. Soc.*, Vol. 84, 2007, pp. 65-72.
- [13] A. Guo, D. Demydov, W. Zhang and Z. S. Petrovic, *J. Polym. & Environ.*, Vol 10, 2002, pp. 49-52.
- [14] A. Guo, I. Javni and Z. Petrovic, *J. Appl. Polym. Sci.*, Vol. 77, 2000, pp. 467-473.
- [15] Z. S. Petrovic, W. Zhang, A. Zlatanovic, C. C. Lava and M. Ilavsky, *J. Polym. & Environ.*, Vol. 10, 2002, pp. 5-12.
- [16] A. Guo, W. Zhang and Z. S. Petrovic, *J. Mater. Sci.*, Vol. 41, 2006, pp. 4914-4920.