

Contact Angle Properties of Bioacrylic Palm Oil Based Polyol for Polyurethane Coating

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Abstract. Bio-acrylic palm oil based polyol was synthesized and characterized for polyurethane (PU) coating. In this project, acrylation of palm oil based polyol was done by using different amount of 2-hydroxyethyl methacrylate (HEMA) along with styrene mole ratio at 1:0.5:2, 1:1:2 and 1:1.5:2. The result shows that the increasing amount of HEMA content has increased the hydroxyl value. The characterization of bio-acrylic palm oil based polyol carried out by IR spectroscopic analysis and hydroxyl value. Coated surfaces were then characterized for the drying and gelling time, contact angle test and FTIR analysis were also reported. As the NCO/OH ratio of the coatings increased, there were progressive increased in mechanical and anticorrosive properties for all the coatings. Overall, this study showed that the material holds promise to be used as an effective surface coating compound by designing the formulation based on the desired performance.

Introduction

Polyurethanes is a polymeric material that is very easy to set up for a variety of applications. The application of polyurethane is extremely varied and diverse; polyurethane can be produced as foams, elastomers, plastics, adhesives and surface coatings for materials [1,2]. However, the increasing cost of petrochemical crude materials and diminishing stores of petroleum assets cause the expanding of the intrigued in the applications of biodegradable and renewable polymeric materials. Thus, renewable feedstock from vegetable oils for polyurethane industries get to be exceedingly alluring for both financial and natural reasons. Vegetable oils (VO) are non-toxic, non-depletable, domestically abundant, non-volatile and biodegradable resource. Other than that, petroleum-based also is non-biodegradable and lack of petroleum resources. The use of palm oil and its products, which is renewable and biodegradable, making palm oil as an alternative raw material for the production of polyurethane polyol based on palm oil [3,4]. Furthermore, there is an increased awareness of social responsibility toward the environment to meet the demand for renewable resources and environmentally friendly products [5].

Polyurethane coating on surface will provide a thin film, high gloss finish with exceptional weathering performance characteristics [6,7]. This coating is used in virtually all industrial markets to provide a smooth durable finish that has superior resistance to corrosion, abrasion, and chemical exposure. Polyurethanes are normally used to topcoat high build polymer and metal surfaces. The utmost attention is driven towards the design and development of new polyurethanes

with outstanding damage, scratch and wear resistance, the aesthetic appeal and functional performance of in-service topcoats are often compromised in short time [8,9,10]. In this study, the bioacrylic polyol was prepared using different amount of HEMA along with styrene. The effects of different amount of HEMA to palm oil polyol on curing and contact angle of PU coatings were investigated.

Materials and Methodology

Materials. 2-hydroxyethyl methacrylate (HEMA), palm oil polyol, dibenzoyl peroxide, isophorone diisocyanate (IPDI) and diethylene glycol (DEG), dibutyltin dilaurate (DBTL) and pre-treated aluminium 6016 (Al 6016) were purchased from Terra Scientific (M) Sdn. Bhd.

Synthesis of bioacrylic palm oil. Acrylation of palm oil based polyol was done by blending of palm oil polyol with various amount of HEMA added with styrene at a mole ratio of 1:0.5:2, 1:1:2 and 1:1.5:2. The mole ratio of palm oil polyol and styrene were fixed at 1 and 2 mol, respectively, mole ratio of HEMA was varied at 0.5, 1 and 1.5 mol. Palm oil based polyol, HEMA and styrene were mixed in a 250 ml three-neck flask equipped with filter funnel, thermometer and nitrogen gas inlet. Temperature was set at 60°C with a continuous stirring and purified monomers dissolved in dibenzoyl peroxide initiator (0.5 per cent by wt. of monomer) were added slowly and continuously stirred for 2 hours at 60°C. The mixture was then cooled to room temperature, sealed in a glass bottle and kept at room temperature.

Preparation of bioacrylic palm oil urethane coating. For the preparation of polyurethane coating, bioacrylic palm oil was reacted with isophorone diisocyanate (IPDI) as a hardener. IPDI and bio-acrylic polyol were mixed at different (NCO:OH) molar ratio of 1:1, 2:1 and 3:1 to obtain various coating formulations. Dibutyltin dilaurate (DBTL) as a catalyst was added drop wise in a mixture of NCO:OH. The mixture was thoroughly mixed using a spatula and then were applied using 38 mm nylon brush on the pre-treated aluminium 6016 (Al 6016). Coated Al 6016 panel was cured at room temperature for 72 hours.

Characterization. The acrylated polyols were examined using Fourier transform infrared spectroscopy (FTIR) and hydroxyl value. A coated surfaces were then characterized for the drying and gelling time, contact angle test and FTIR analysis.

Results and Discussions

Bio-acrylic Palm oil based polyol. Figure 1 shows FTIR spectrum of palm oil polyol. Figure 2, 3 and 4 show the FTIR spectrum of acrylated palm oil based polyol with different ratios. FTIR analysis reveals characteristic bands found in an acrylic polyol. Based on Figure 2 to 4, the wavenumber ranging between 3000 cm^{-1} and 3500 cm^{-1} for acrylic polyol samples A, B, and C, can be assigned to the presence of hydroxyl groups. The stretching vibration of OH band indicates the presence of hydroxyl groups of polyols in the structure. Furthermore, FTIR spectrum shows that acrylic polyol C with a ratio of 1:1.5:2 in Figure 4 has a higher of -CH stretching vibration starting from peak 2537 to 3383 cm^{-1} compared to the polyol A and polyol B. This shows that the acrylation of polyols completely occur in the acrylic polyol C. This happened due to the higher content of HEMA monomer present in acrylic polyol C which is 1.5 ratio used to enhance the acrylation occurs.

The hydroxyl value was obtained by calculating the constant value normality of NaOH as shown in Table 1. Based on the results obtained, it can be summarized that the hydroxyl value of acrylic polyol C (1:1.5:2) gives the highest hydroxyl value which is 351 with functionality obtained is 10. It indicates that the highest content of HEMA as monomer in polyol sample gives impact to the hydroxyl value and functionality obtained.

This could be due to the solubility of HEMA in water and easy to react with styrene monomer and palm oil polyol as well as absorbents for bodily fluids and lubricious coatings. It is also used as an acrylic modified polyurethane coatings and widely used for the preparation of styrene-butadiene rubber thermosetting acrylic emulsion paint modifier.

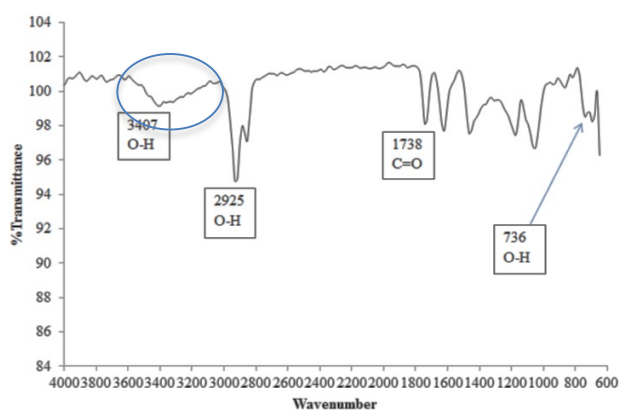


Fig. 1. FTIR analysis of palm oil polyol

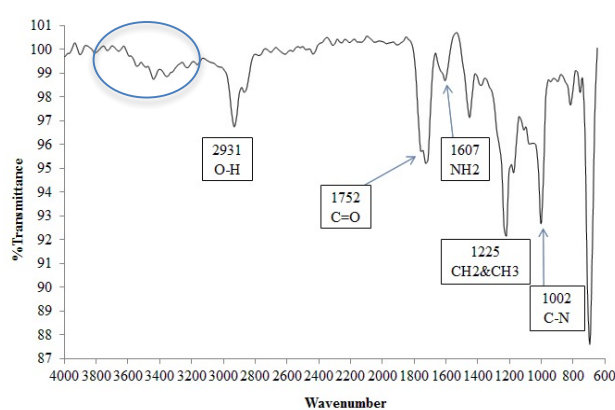


Fig. 2. FTIR analysis of acrylic polyol A (1:0.5:2)

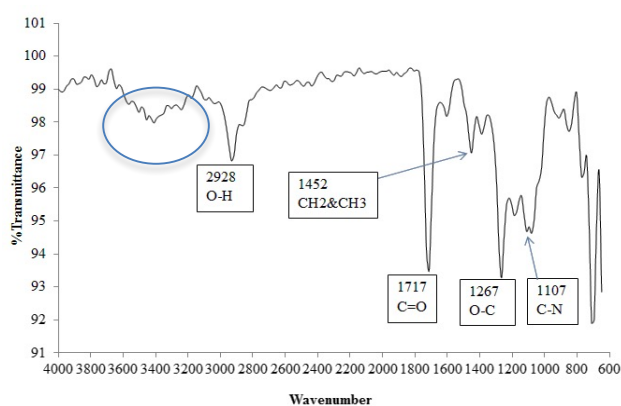


Fig. 3. FTIR analysis of acrylic polyol B (1:1:2)

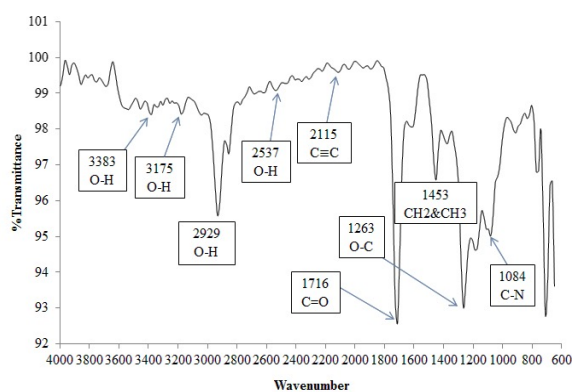


Fig. 4. FTIR analysis of acrylic polyol C (1:1.5:2)

Table 1. Specification of acrylic polyol (OH - hydroxyl value)

| Acrylic polyol | OH Value | Functionality, f(x) |
|----------------|----------|---------------------|
| A (1:0.5:2) | 157 | 4 |
| B (1:1:2) | 234 | 7 |
| C (1:1.5:2) | 351 | 10 |

Bio-acrylic Palm oil based Coating. Coating properties of polyurethanes are characterized by its drying and gel time. The results shows that the acrylic polyol B shows lowest drying time, followed by acrylic polyol A and acrylic polyol C. Coated samples were compared on the basis of rise in hydroxyl content and NCO:OH ratio 1:1, 2:1 and 3:1. For the polyurethane coating, the sample also has been characterized using drying and gelling time. The coating was cured by chemical reactions of $-NCO$ group of IPDI isocyanate with $-OH$ group of polyols.

The gelling time indicates the maximum length of time during which the system remains in fluid condition. The gel time for the formulation was found to be around one day to completely dry with addition of dibutyltin dilaurate (DBTDL) catalyst. The present of DBTDL catalyst helps to increase the drying and gelling time and the sample can dry faster on the aluminum substrate. Other than that, the addition of the DBTDL catalyst and preferring the isocyanate-polyol reaction provides to acquire greater hardness of the formed polyurethane coating. Besides, various polyol samples 1:0.5:2, 1:1:2 and 1:1.5:2 with different ratios of NCO to OH; 1:1, 2:1 and 3:1 shows the results condition obtained is different for each ratio. The condition obtained was either sticky or wet. All samples took around 24 hours to completely dry.

Furthermore, the verification hydroxyl content of polyols rising the cross-linking and the hardness of polyurethane shown by the hardness of the sample that increased with increase in hydroxyl value of acrylic polyols. Therefore, the acrylic polyols with high hydroxyl value have a tendency easy for harden than others. In further investigation of polyurethane coating, a contact angle test was performed to determine high or low of water's ability contact angle on different surfaces. Hence, the angle of the contact surface was taken immediately after the sample touch on the surfaces of glass and Teflon as shown in Table 3.

Table 3. Contact angle, θ of PU coating from two different surfaces

| Types of surface | Acrylic polyol | Ratio of PU coating | Contact angle, θ |
|------------------|----------------|---------------------|-------------------------|
| Glass | A | 1:1 | 45° |
| | | 2:1 | 30° |
| | | 3:1 | 24° |
| | B | 1:1 | 30° |
| | | 2:1 | 30° |
| | | 3:1 | 40° |
| | C | 1:1 | 21° |
| | | 2:1 | 30° |
| | | 3:1 | 22° |
| Teflon | A | 1:1 | 90° |
| | | 2:1 | 50° |
| | | 3:1 | 90° |
| | B | 1:1 | 90° |
| | | 2:1 | 90° |
| | | 3:1 | 90° |
| | C | 1:1 | 90° |
| | | 2:1 | 90° |
| | | 3:1 | 90° |

Based on the observation, the experimental results obtained is mostly the same for all the samples of polyurethane coating. The angle of the sample on the glass surface is small which is less than 90° i.e. in the range of 20-50°. This shows that the liquid spread over the glass surface as glass surface is known as hydrophilic surface. For the Teflon surface, the angle of the sample obtained is larger which is equal or bigger than 90°. The angle obtained is 50° and 90°. The liquid form looks as a bead on the surface. This type of surface is called as hydrophobic surface. The angle obtained is due to the type of characteristic surface of material and physical properties of sample whether in liquid or solid form.

FTIR results shows the reaction between isocyanate of IPDI and hydroxyl group (-OH) of acrylic polyol during the formation of polyurethane. It is revealed that the ratio acrylic polyols C (1:1) of polyurethane shows a hydroxyl of polyol band at 3287 cm^{-1} and no peak of NCO of isocyanate group found during the curing process. For polyurethane coating of ratio acrylic polyol C (2:1), it shows the band of hydroxyl polyols present at 3302 cm^{-1} and 2947 cm^{-1} and stretching vibration of NCO present at 2268 cm^{-1} . The -CH group and NCO of isocyanate group of acrylic polyol C (3:1) present at 2947 cm^{-1} and 2253 cm^{-1} . It is believed that the polyurethane coatings manufactured by utilizing acrylic polyols and IPDI had occurred between NCO and OH group get cross-linked properly to form urethane linkage. Hence, based on the circle exist on the blue line from the spectra above shows that the isocyanates completely react and there is an excess of -OH and this show that acrylic polyol C (1:1) of polyurethane is sensible for a specific end use specification in polyurethane coatings.

Conclusions

The acrylation of palm oil based polyol was successfully done by mixing palm oil polyol, styrene and HEMA using a various ratio of HEMA monomer content. The hydroxyl value of acrylic polyol C of ratio 1:1.5:2 showed the highest which is 351 with functionality obtained is 10. Based on the FTIR

test also has shown that the present of OH group of polyols mostly abundant found in acrylic polyol C with ratio 1:1.5:2 that have the highest HEMA monomer content 1.5. Furthermore, the curing time of the coating has decreased when dibutyltin dilaurate (DBTDL) was used as catalyst which helps the coating completely dry in a short time. Then, the large angle from contact angle test obtained shows that good performance and confirmation of acrylation palm oil based polyol can be applied in surface coating application.

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