

Scratch Hardness Properties of Waste Palm Cooking Oil based Polycaprolactone Urethane Coatings

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Abstract. Polyurethane has been widely used in various coating industries due to its good weathering resistance, promising appearance, excellent elasticity and good mechanical properties. The present work reports the development of polycaprolactone urethane coatings based on waste palm cooking oil (WPCO). WPCO was recycled to synthesis polycaprolactone (PCL) polyol using two-steps methods; transesterification and ring opening polymerization with various ratios of ϵ -CL to WPCO based polyesteramide. The WPCO based PCL polyols were reacted with isophorone diisocyanate (IPDI) to produce polycaprolactone urethane coatings. FTIR analyses were employed to confirm the formation of polyols and the scratch resistance properties of coatings were characterized by scratch hardness testing. The results revealed that the scratch resistance of polycaprolactone urethane coatings increased by increasing the ϵ -CL composition in the formulation.

Introduction

Polyurethane (PU) coating industry having a unique combination of performance and application properties. The major concern of restriction of commercial exploitation of PU are largely related to the cost of raw material is too high. Various countermeasures have been made to cut down the cost of PU production, such as the use of bio-materials resources for the synthesis of polyol. Recycling of waste materials is also one of the most important issues in the research and development for reducing the production cost and protection of global environment.

Waste palm cooking oil (WPCO) is waste materials from food industry resulted from degradation reaction during frying due to presence of heat, air and water. The degradation reaction reduced the quality of oil and caused adverse effect to human if it is consumed as food. Uncontrolled dumping of WPCO to the drainage system without proper treatment can lead to severe environmental problems. WPCO has potential as raw material for PU production due to its physical and chemical properties. Waste cooking oils have been exploited especially in bio-fuel and polymer productions [1, 2]. Moreover, waste cooking oil is considered as biodegradable and renewable resource that would reduce the environmental pollution and disposal problem.

The application of organic and hybrid clear coats has increasingly gained reputation for protection purposes aesthetic value added in several manufacturing domains [3]. Topcoats is an outermost layer of coating with variable thicknesses. A wide variety of substrates can be used such as electronics and biomedical devices, automotive body parts and components, and sporting goods. During the daily usage, many of the aforesaid basic products are subject to a broad range of loading conditions, including impacts, rubs and scratches of diverse magnitudes. These issues further complicate the extrapolation of the coatings response to external loads and, therefore, a proper strategies to prevent damage is crucial. In this respect, many of the investigations reported in the literature regard the definition of relatively novel polyurethane-based formulations [4-6]. The utmost attention is driven towards the design and development of new polyurethanes with outstanding damage, scratch and

wear resistance, the aesthetic apparel and functional performance of in-service topcoats are often compromised in short time.

For the development on innovative PU coatings whilst respecting the environment, in the present study, the PCL polyol was prepared by ring opening polymerization of ϵ -caprolactone initiated by WPCO based polyesteramide. The effect of different ratios of ϵ -CL to WPCO based polyesteramide (PEA) on scratch hardness properties of PU coatings was investigated.

Materials and Methods

Materials. ϵ -caprolactone (high purity), 2-(dimethylamino)-ethanol (DMEA), 1,8-diazabicyclo 5.4.0 undec-7-ene (DBU), isophorone diisocyanate (IPDI) and diethylene glycol (DEG) were purchased from Terra Scientific (M) Sdn. Bhd. Waste palm cooking oil (WPCO) was collected from restaurants in Klang valley, Malaysia.

Synthesis of Waste Palm Cooking Oil (WPCO) based Polyol. There are two-steps involved in the synthesis of WPCO based polyol. First step, WPCO based polyol was synthesized by using transesterification process by mixing a polyhydric solution with WPCO and 1,8-diazabicyclo 5.4.0 undec-7-ene (DBU) as a catalyst. The transesterification was performed in a chemical reactor at a temperature of 90°C for about 1 hour under vacuum and inert condition. In the second step, the synthesis was continued by using the ring opening polymerization by adding the ϵ -caprolactone (CL) into the mixture and it was continuously stirred and maintained at the same temperature for another 2 hours. Nine types of polyol, labeled as PCL10, PCL20, PCL30, PCL40, PCL50, PCL60, PCL70, PCL80, PCL90 were prepared with different ratios of CL to WPCO based polyesteramide varied from 90:10, 80:20, 70:30, 60:40, 50:50, 40:60, 30:70, 20:80 and 10:90, respectively.

Preparation of Polycaprolactone Urethane Coatings. For the preparation of polycaprolactone urethane coating, PCL polyol based on WPCO was reacted with isophorone diisocyanate (IPDI) with isocyanate to polyol (NCO:OH) ratio is 1:1. AA 6061 was used as a substrate to test the performance of the coating produced. The PU coating was applied on the metal surface by using nylon brush and the samples were left at room temperature for complete curing (72 hours) before testing their performance properties.

Characterization. WPCO based polyol samples were analyzed using Fourier Transform Infrared (FTIR) Spectroscopy to confirm the formation of polyol. A scratch hardness test was carried out for all PU coated substrates according to ASTM D3363. A coated substrate was placed on a firm horizontal surface. The pencil was held firmly against the film at a 45° angle and pushed away from the operator in a 6.5 mm (1/4 in.) stroke. The process was started with the hardest pencil and continued down the scale of hardness until the pencil that will not cut into or gouge the film. The scale used in the scratch hardness test is shown in Fig. 1.



Fig. 1: Scratch Hardness Scale

Results and Discussion

FTIR Analyses. The spectra of WPCO, ϵ -CL and derivative PCL polyols with different ratios of ϵ -CL: WPCO based polyesteramide are revealed in Fig.2. FTIR spectrum for a sample of WPCO and ϵ -CL are used as a reference to observe any changes in the formation of the essential peaks for the production of polyol i.e. hydroxyl (OH) and carbonyl (C = O) peak. The stretching peak at frequency 1736 cm^{-1} the spectrum of ϵ -CL specifies the presence of C = O group in the cyclic lactone. WPCO samples also showed the presence of C=O group in its structure. The C=O peak was also observed at 1727 cm^{-1} for WPCO based polyesteramide (PEA) and all the PCL polyols samples (PCL10, PCL50 and PCL90) including the samples which are not revealed (PCL20, PCL30, PCL40, PCL60, PCL70

and PCL80). The shifted of carbonyl band designates the formation of a linear ester linkage and ring opening polymerization of lactone had occurred [7]. The presence of broad peak around the frequency 3500-3200 cm^{-1} indicates the formation of free hydroxyl (OH) group in the PCL polyols. This also supported the phenomena that the C=C bond had reacted and converted to C-OH bonding or forming oligomer with other compounds. The presence of free OH group is essential in the polyol production because this functional group will react with isocyanate to form polyurethane structures.

Furthermore, band at 2930 cm^{-1} and 2857 cm^{-1} are synchronous reflections of asymmetric methylene (CH_2). The band observed at 730 cm^{-1} is due to the rocking CH_2 ($n>3$) vibration indicates the presence of a long linear chain aliphatic structure [8]. Another change was in the appearance of the peak of C-N stretch for tertiary amide from WPCO based polyesteramide at around 1631 cm^{-1} according to the addition of WPCO based as starting material.

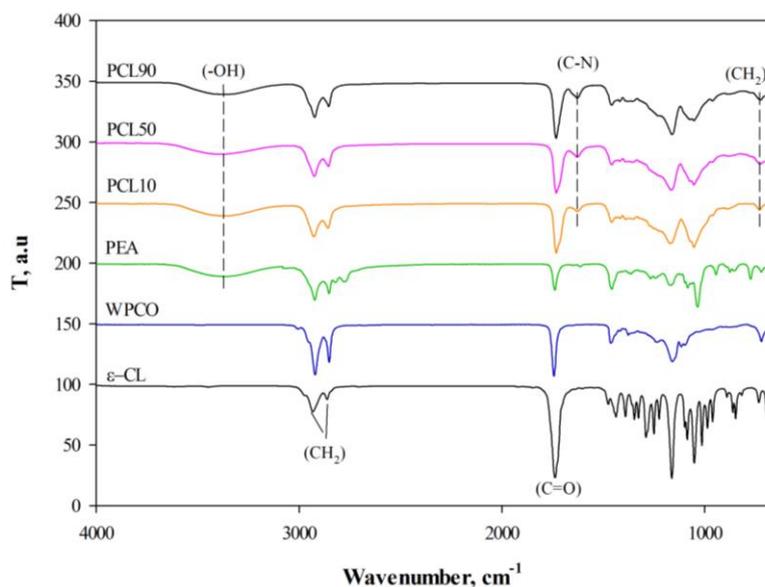


Fig.2: FTIR spectra

Scratch Hardness Behaviour of Polyurethane Coatings. Fig. 3 shows scratch resistance behavior of the PU coatings. It is clearly seen that the scratch resistance of PU coating showed significance dependences on ϵ -CL composition. As the ϵ -CL composition increases in the PCL polyols the scratch resistance of PU coatings was also increased. The surface of PU10 – PU40 samples were displayed too softs due to their scratch hardness fell in B scale. PU50 and PU60 show intermediate values of hardness scale (HB and H). The samples scratched at lower scale of hardness due to the lower amount of entanglements in the polymer. Meanwhile, PU90 sample that composed of 90% of ϵ -CL shows the highest scratch resistance (4H). This might be due to the formation of phase-separated hard domains acting as physical cross-links, thus hindering the crystallization process [9]. While the increased hardness might be explained by the increasing the degree of PCL phase crystallinity of these samples, this should also lead to increased resistance to scratch. This argument agreed by Flores et al. [10] and Batista et al. [11] which increasing the degree of crystallinity increases hardness and density of a material. The dissolved hard segments likely decrease the deformability of the soft phase as well. The dependences of hardness properties on the polyols composition are shown in Fig.4.

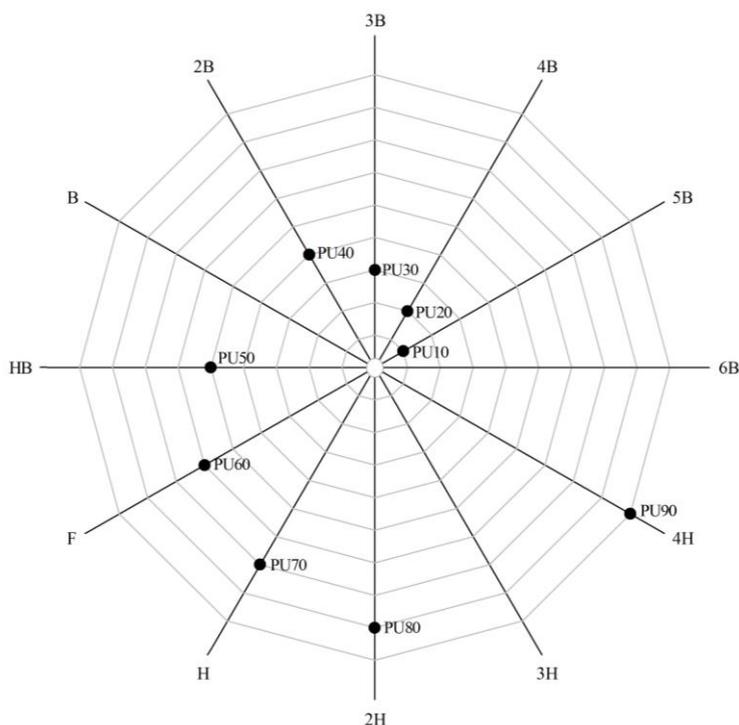


Fig.3: Scratch behavior of PU coatings with various types of PCL polyols

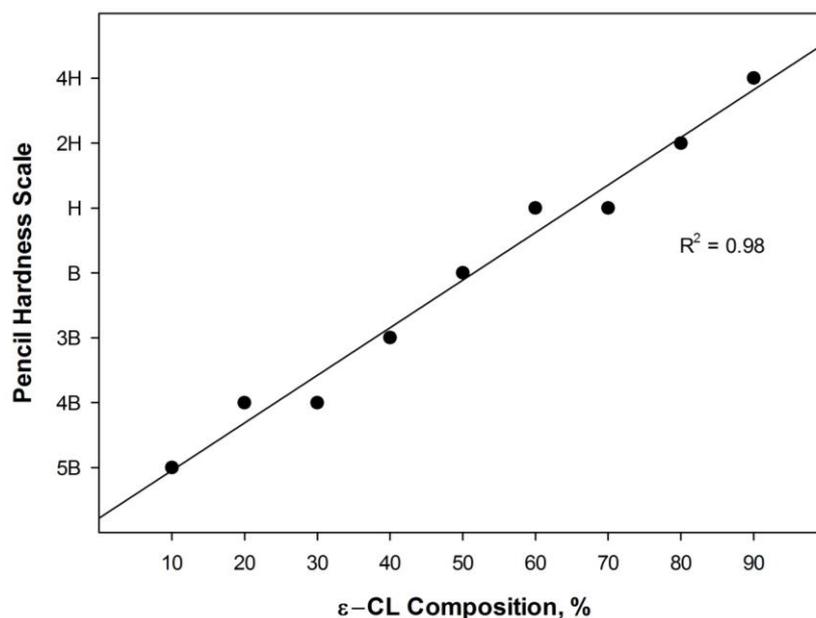


Fig.4: Dependences of hardness behavior on ε-CL composition

Conclusion

In conclusion, WPCO has great potential in replacing petroleum and vegetable oils as starting raw material for polyurethane coatings. FTIR established the WPCO-based PCL polyols have been successfully synthesized using transesterification followed by ring opening polymerization. A series of WPCO based polycaprolactone urethane coatings was successfully. These PU coatings displayed significant dependences of scratch resistance on ε-CL composition. The higher the ratio ε-CL to WPCO based polyesteramide increases the scratch resistance and hardness of PU coating.

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