



# Preliminary study on bio-based polyurethane adhesive/aluminum laminated composites for automotive applications



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## ABSTRACT

Composite materials that are offered for real applications in the automotive industry vary from thermoplastics to laminated structures. This study focuses on a preliminary study on the processing and characterization of bio-based polyurethane (PU) adhesive/aluminum-laminated composites. Five different formulations of PU adhesives were prepared from five different formulations of polycaprolactone (PCL) polyols. The PCL polyols were synthesized by a ring opening polymerization of  $\epsilon$ -caprolactone initiated by a blend of palm kernel oil polyesteramide (PPKO) and 1,6-hexanediol (HDO) with various weight ratios of PPKO:HDO (0:100, 25:75, 50:50, 75:25, and 100:0). The PCL polyols were reacted with a mixture of aromatic and cycloaliphatic diisocyanate. Physical and chemical analyses of PCL polyols such as viscosity, OH number, molecular weight, and proton nuclear magnetic resonance (<sup>1</sup>H-NMR) were carried out. The swelling and mechanical testing were performed to explore the correlation between the structure of PU network and its properties. The adhesion strength of bio-based PU/aluminum-laminated composites was found to be influenced by the structure of the PU network system. The ratio of 75:25 (PPKO:HDO) was found to be the optimum based on the mechanical strength of laminated composites and the thermal stability of the PU adhesive.

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## 1. Introduction

The automotive industry faces many challenges, including increased global competition, the need for higher performance vehicles, and tighter environmental and safety requirements. One of the major challenges that the automotive sector will face in both the near- and long-term future is the need for higher fuel efficiency. This challenge is being driven by international requirements targeting reduced fuel consumption and carbon emissions, in the quest for sustainability. One of the most important methods by which fuel economy can be achieved is reducing the weight of the vehicle, or light weighting the car. Composite materials, with their high strength-to-weight ratio, provide an excellent platform upon which to develop the next generation of lightweight vehicles [1].

Laminated composite materials contribute a broad range of applications in structural design, especially for light-weight structures that have severe stiffness and strength requirements [2]. The combination of thermoset polymer and metal sheets, so-

called metal-laminated polymer/metal composites have played important roles as structural components. These materials have been increasingly employed as advanced materials in the automobile, aerospace, and electric industries [3], especially for exterior and interior building panels and vehicle body panels.

Laminated composites provide excellent in-plane mechanical properties: high in-plane Young's moduli, shear modulus, and in-plane ultimate strength. However, composite laminates are prone to delamination and inter-laminar shear. The high dependency of the mechanical properties of the composite on the performance of the adhesive layer and core material demands proper characterization of their properties [4]. Thus, it is necessary to do a preliminary investigation on the adhesion strength of the adhesive system. The selection of raw materials and formulation of the adhesive are the most appropriate parameters to get an adhesive with excellent adhesion strength.

Polyurethane is one of the thermoset polymers that possess excellent properties. It can be tailor-made for various applications. Because of its easy processing [5] and superior properties, this class of polymers is used in a wide range of applications, from home appliances and furniture to engineering applications, including as an adhesive layer in laminated composites.

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This paper focuses on the synthesis of PU adhesives based on a PCL polyol that is derived from renewable resources, i.e. palm kernel oil polyesteramide (PPKO). This paper also deals with the study of the influence of the different PPKO:HDO ratios on the strength of the PU adhesive. This paper also highlights the correlation between the structure of the PU network and the adhesion strength of laminated composites. The thermal degradation of the PU adhesives was also analyzed.

## 2. Materials and methods

### 2.1. Materials

$\epsilon$ -caprolactone (high purity), 1,6 hexanediol (HDO), stannous octoate, and diethylene glycol (DEG) were purchased from Sigma-Aldrich Malaysia. Palm kernel oil (PPKO) based polyesteramide was supplied by Polymer Laboratory, Polymer Research Center, Universiti Kebangsaan Malaysia. 2,4-diphenyl methylene diisocyanate (MDI) with an NCO content of 31% was obtained from Maskimi Polyols Sdn. Bhd. and bis(4-isocyanatocyclohexyl) methane (H12MDI) with an NCO content of 32%, propylene carbonate (PC) were purchased from Sigma-Aldrich.

### 2.2. Synthesis of polycaprolactone polyols

The polycaprolactone (PCL) polyols were synthesized by ring opening polymerization of  $\epsilon$ -caprolactone ( $\epsilon$ -CL), as described in the previous work [6]. The monomer  $\epsilon$ -CL was reacted with two different initiators, PPKO and HDO, and catalyzed by stannous octoate (Sn(II)Oct). Five types of polyol, labeled as PCL0, PCL25, PCL50, PCL75, and PCL100, were prepared with PPKO:HDO ratios of 0:100, 25:75, 50:50, 75:25, and 100:0, respectively.

### 2.3. Characterization of polyols

The standard method, ASTM E1899-97 (Standard Test Method for Hydroxyl Groups Using Reaction with p-Toluenesulfonyl Isocyanate (TSI) and Potentiometric Titration with Tetra-butylammonium Hydroxide) was used to determine the hydroxyl values (OHVs) of the polyol. Moisture content was determined using KF Titrator 700. Molecular weight was determined by gel permeation chromatography (GPC) using a Water 2410 refractometer with tetrahydrofuran (THF) and a set of columns (50 A, 100 A, and 500 A). The correlation between the functionality ( $f$ ) and number average molecular weight ( $M_n$ ) is as follows [7]:

$$f = \frac{M_n \times \text{OHV}}{56,100} \quad (1)$$

The viscosities of the polyols were determined using a modular compact rheometer model MCR300. The measurements were performed at room temperature on a measuring plate CP50-1 (50 mm diameter, 1°).

<sup>1</sup>H-NMR spectra were recorded at room temperature using a Bruker FT-NMR 600 MHz cryoprobe spectrometer. The polyol samples were diluted in 600  $\mu$ l chloroform-d ( $\text{CDCl}_3$ ) prior to test.

### 2.4. Preparation of polyurethane adhesives

The PU samples were equipped with a clean, dry paper cup. Two types of isocyanate, namely MDI and H<sub>12</sub>MDI, with a ratio of 65:35 were mixed prior to adding the requisite amount of polyol resin. The ratio of NCO:OH was 1.3. The samples of PU were labeled PU0, PU25, PU50, PU75, and PU100 for the reaction of isocyanates and polyols PCL0, PCL25, PCL50, PCL75, and PCL100, respectively. The mixture was mixed well using a mechanical stirrer at

1000 rpm for about 15 s, upon which the adhesive mixture was ready to be applied or tested.

### 2.5. Swelling test

The crosslink densities of PU films were determined by swelling test, in which the specimens were immersed in toluene for 48 h. The swollen samples were then removed from the solvent. The specimens were weighed after excess solvent was gently wiped off the surface. The crosslink densities ( $n$ ) were obtained using Flory–Rehner theory, as discussed in detail by Zain et al. [8].

### 2.6. Mechanical testing of PU/aluminum laminated composite

Two mechanical tests (single lap shear and T-peel) were performed to investigate the influence of different formulations of polyols on the adhesion strength of PU/aluminum-laminated composites. Single lap shear tests were carried out according to ASTM D1002-72, as described in detail in our previous work [9].

T-peel tests were performed according to the standard method ASTM D1876-01. The test specimens were cut into the dimensions of 25.4 mm  $\times$  305 mm. The bonded area is approximately 241 mm  $\times$  25.4 mm. The 76 mm-long unbonded ends were bent apart, perpendicular to the glue line, for clamping in the grips of the testing machine. The configuration of the T-peel test specimen is shown in Fig. 1 [10]. The unbonded ends of the specimen were clamped in the test grips of the tension testing machine. The load was applied at a constant head speed of 254 mm min<sup>-1</sup>. Mittal [11] reported that the fracture energy,  $G_c$ , can be determined from the average peel load by using the formula in Eq. (2):

$$G_c = \frac{F_c}{b}(1 - \cos \beta) \quad (2)$$

where  $F_c$  is the peeling load,  $b$  is the width of the specimen, and  $\beta$  is the peeling angle (180°).

### 2.7. Thermogravimetric analysis of PU adhesive

PU samples (10–15 mg) were tested in a thermogravimetric analyzer (Mettler Toledo TGA/DSC) at a programmed rate of 10 °C min<sup>-1</sup> in the temperature range from 25 °C to 900 °C under nitrogen gas at a flow rate of 200 ml min<sup>-1</sup>.

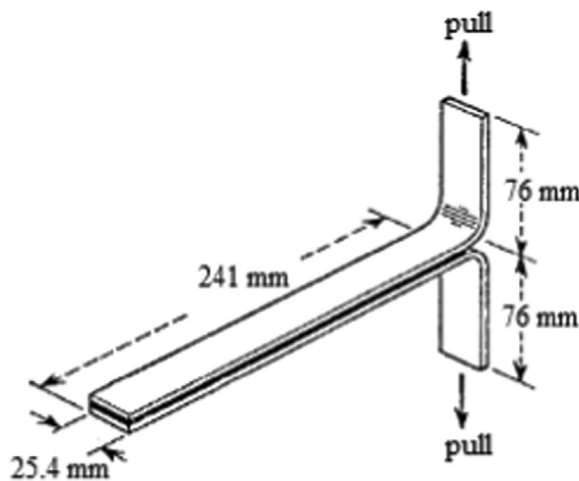


Fig. 1. Schematic view of the T-peel test specimen.

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