

PREPARATION OF POLYURETHANE COMPOSITES WITH ACTIVATED CARBON BLACK AS THE REINFORCING FILLER

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ABSTRACT

The effect of activated carbon black (ACB) on the mechanical properties of palm-based polyurethane composites was studied. Palm-based multi-block polyurethane (PU) was prepared by reacting palm kernel oil-based (PKO-p) monoester with 4,4-diphenyl methane diisocyanate (MDI) through prepolymerization method. Poly(ethylene glycol) (PEG) was used as the chain extender while acetone was used as the solvent to control the reaction kinetics. The amount of ACB added into the PU system was varied at 0 to 8 wt% (percentage by weight). This study aimed to develop a formulation of PU-ACB composite film with excellent mechanical properties. The mechanical characterizations included tensile test, hardness test, and scratch resistance test. Fourier Transform Spectroscopy (FTIR) analysis was also conducted to identify the functional groups present in the PU composites. The incorporation of ACB as filler greatly enhanced the mechanical properties of the PU composites due to compatibility and interfacial adhesion of ACB with PU matrix. The loading of ACB at 8 wt% exhibited the optimum mechanical properties.

Keywords: biopolymer; composite film; multi-block polyurethane; prepolymerization

INTRODUCTION

Polyurethane (PU) is one of the most versatile materials used today. This polymer is widely used in daily life and has wide application in industry. PU is widely used as coatings, adhesives, and to form composites. PU is a block copolymer consists of low molecular weight polyester or polyether bonded to a urethane group (-NHCO-O) and formed via reaction of three basic materials namely hydroxyl-containing polymers (polyester or polyether polyol), polyisocyanates, and/ or chain extender, normally low molecular weight diol or diamine [1].

Most researchers focused on the production of petrochemical-based polymers such as poly(ethylene oxide) (PEO) compared to polymers based on natural resources. However, the elevation of petroleum price and awareness of environmental friendly product had resulted in intensive researches on alternative green polymers. Palm oil and its derivatives have become one of the choices in the production of polyurethane polyol [2].

Various methods have been used to form PU. These include prepolymerization, single-step polymerization, and quasi-prepolymerization. In this research, the method used for the formation of PU is through prepolymerization method. This involved the formation of urethane polymer at the initial stage of reaction between polyol and diisocyanate. Then, urethane prepolymer is chain-extended with diol or water to form polyurethane. The benefits of prepolymerization method compared to single-step polymerization method is to reduce the isocyanate vapor levels and reduced exotherm of the final reaction. The molecular weight of

urethane polymer increases with time, resulting in lower vapor pressure when diisocyanate reacts with polyol. In the single-step polymerization of PU, it gives off heat and causes shrinkage problem. However, prepolymerization method allows partial dissipation of the exotherm prior to the formation of PU [3].

It is very common that PU is reinforced by adding fillers such as carbon black, kaolin, sepiolite, and precipitated silica for industrial applications. However, these materials are inorganic in nature and therefore, are normally incompatible with organic PU matrix compared to carbon black which is organic in nature. Carbon black is one of the most important reinforcing filler used in rubber industry and about 90% of the world production of carbon black is used in tire industry to improve tear strength, modulus, and wear characteristics of tires [4]. Activated carbon black (ACB) is well-known as a porous material with large specific surface area, which is very useful in adsorption of gas and solutes. ACB can be prepared from lignocellulosic materials by physical and chemical activation. Separate and sequential application of chemical activation (with ZnCl_2) and physical activation (with CO_2) were used to produce microporous carbon [5]. For example, palm shell can be used to prepare activated carbon using potassium carbonate (K_2CO_3) and carbon dioxide (CO_2) as activating agent at carbonization temperature of 800 °C and impregnation ratio of 2 [6]. In this research, ACB was added as a reinforcing filler into the PU matrix and its mechanical properties such as tensile, scratching resistance, and hardness characteristics were determined.

EXPERIMENTAL

Materials

Palm-based polyol (PKO-p) was supplied generously by UKM Technology Sdn Bhd from the pilot plant stationed at UKM/MPOB Station, Pekan Bangi Lama, Selangor while 4,4-diphenylmethane diisocyanate (MDI) was obtained from Cosmopolyurethane (M) Sdn Bhd, Port Klang. Acetone was purchased from Systerm Sdn Bhd, Shah Alam, Selangor. Poly(ethylene glycol) (PEG) and activated carbon black (ACB) powder was purchased from Sigma Aldrich Sdn Bhd, Kuala Lumpur.

Method

Prepolymerization method was applied to produce the PU composite films. MDI prepolymer was prepared by dissolving MDI with acetone and stirred for 1 min. PKO-p/PEG prepolymer was prepared by dissolving PKO-p and PEG with acetone in a separate beaker and stirred for 2 mins. The amount of ACB added into the PU system was varied at 0 to 8 wt% (percentage by weight). The prepolymers were stirred for another 45 s before being casted into a 240 mm × 240 mm × 1 mm cavity plate. The mixture was then compressed at 50 °C at 760 kPa for 10 mins. The solid composite film was conditioned at room temperature for 24 hours prior to further characterization.

Characterization

Tensile test was performed using Instron Universal Testing Machine Model 2716 following ASTM D412 standard (Standard Test Method for Vulcanized Rubber and Thermoplastic Elastomer). Scratching resistance was conducted using pencil hardness test in accordance to ASTM D3363 standard (Standard Test Method for Film Hardness by Pencil Test). A durometer Shore A Model Techlock GS-719N was used to carry out hardness test following ASTM D2240A standard (Standard Test Method for Rubbery Property). Fourier Transform Infrared Spectroscopy (FTIR) analysis was conducted using ATR-IR technique and the spectrum was recorded by Perkin Elmer Spectrum GX spectrometer in the range of 4,000 to 600 cm^{-1} at scanning resolution of 4 cm^{-1} . Particle Size Analyzer Model Zetasizer Nano ZS was used to

determine the particle size of ACB powder. The surface area of ACB was determined by the BET N₂ adsorption at 77 K while the total pore volume was measured using ASAP 2010 (Micromeritics) at 77 K.

RESULTS AND DISCUSSION

ACB Characterization

The surface area of ACB as determined by BET N₂ adsorption at 77 K shows the value of 807.48 m²/g. The total pore volume measured is 0.44 cm³/g, confirming ACB contains pores (porous type of carbon black). The surface area and total pore volume can be increased by increasing carbonization temperature and increasing impregnation ratio during production of ACB.

Fig. 1 shows the average particle size of ACB. The average particle size of ACB is 22.28 nm (diameter in nanometer) at 90.55%. However, appearance of humps at sizes of 417.9 nm and 4507 nm present at 5.30% and 4.15% respectively, might be due to agglomeration of ACB particles. This agglomeration is due to presence of Van der Waals force and inter-particle force.

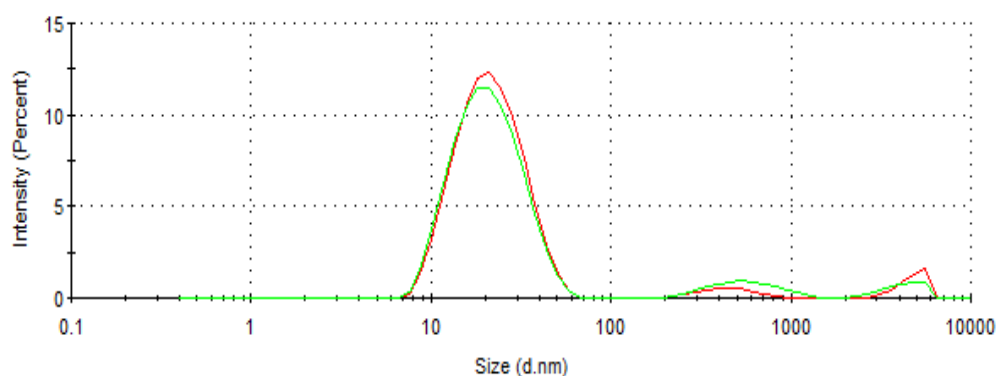


Fig. 1 Size distribution of the activated carbon black

Fig. 2 shows the FTIR spectra obtained from analysis onto the ACB. A broad O-H stretching vibration was observed in the range of 3600-3000 cm⁻¹. This band indicated the presence of hydrogen bonds. Besides, C=O moieties in carboxylic is also present in ACB, which was detected at 1738 cm⁻¹, corresponded to the studied range of 1750-1720 cm⁻¹. The peak around 2970 cm⁻¹ representing the aliphatic CH₃ or CH₂ stretching. C-O-C stretching was observed in the region of 1300-1000 cm⁻¹ [7].

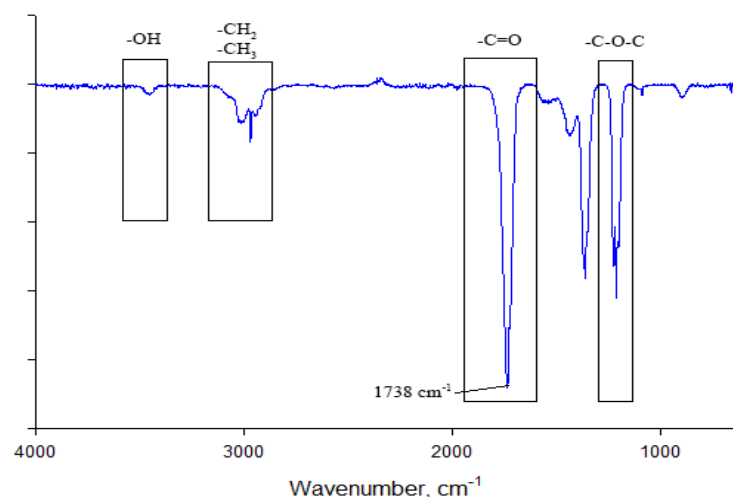


Fig. 2 FTIR spectrum of ACB

Tensile Properties

Table 1 shows data for tensile stress, tensile strain, modulus at 100%, and modulus at 300% of the PU composite film at various loading percentage of ACB. The stress of a material refers to the force applied to a certain cross-sectional area of a material. It tends to deform a material when stress is applied to the material. Strain refers to the response of a material to the applied stress, known as elongation or deformation. Modulus at 100% and modulus at 300% refers to the force at specific elongation at 100% and 300% respectively. Materials with higher modulus are normally hard and tough.

Table 1 Tensile properties of PU-ACB composite films

Samples	Amount of ACB (wt%)	Stress (MPa)	Strain (%)	Modulus at 100% (MPa)	Modulus at 300% (MPa)
PU0	0	6.48	51.0	24.5	118.0
PU2	2	6.14	56.1	18.2	70.4
PU4	4	4.86	41.9	26.2	190.0
PU6	6	4.84	31.3	39.8	154.1
PU8	8	4.68	29.7	41.7	145.7

Table 1 showed that addition of ACB up to 8 wt% decreased the tensile strength from 6.48 MPa (without ACB) to 4.68 MPa and the tensile strain decreased from 51.0% to 29.7%. Modulus at 100% showed an increment from 24.5 MPa to 41.7 MPa. The same trend was also discovered by Opera [10] and Abdul Khalil et al. and co-workers [8] when they used carbon black as reinforcing filler in the preparation of resin-based polyurethane and polyester composites. However, a sudden fall in tensile strength and modulus at 100% was observed when 2 wt% of ACB was added into the PU matrix. On the other end, an increase in tensile strain was shown. This is probably due to the disturbance in the PU system during curing process. The addition of ACB or any foreign substances in small amount will disturb the formation of crosslink and forming weak points. This is due to a slight dilation in the PU molecules adjacent to the filler particle. Tensile strain showed a decrease in value upon addition of ACB producing stiff, rigid, and non-flexible due to limited chain mobility. The addition of ACB at 4, 6, and 8 wt% decreased the tensile strain and tensile strength with increasing modulus at 100%. The addition of ACB has high potential to enhance the mechanical properties of PU composites. Based on the observation, the addition of ACB from 4 to 8 wt% showed

insignificant change in tensile strength. It is predicted that the tensile strength will continuously increase with increasing addition of ACB. In a study conducted by Sahoo and co-workers [9] the addition of carbon nanotube in PU composites increased the tensile strength and modulus, however, at 0.5 to 5.0 wt% addition of carbon nanotube, the tensile strength did not show much changes. Therefore, it is estimated that the addition of ACB at higher percentage into PU matrix will increase the tensile strength to an extent. The addition of fillers into a polymeric system leads to an improvement in the mechanical properties of the polymer matrix. The reinforcement effect is related to the properties of interphase and depends on the specific interactions between the polymer itself and the reinforcing fillers. Generally, fillers have to be dispersed homogenously into the matrix in order to achieve maximum reinforcement.

Fig. 3 shows the cross sectional area of the fractured PU composite film filled with ACB at 8 wt%. The ACB was well-dispersed with the absence of agglomeration and firmly embedded in the PU matrix due to small particle size and good compatibility with the PU matrix.

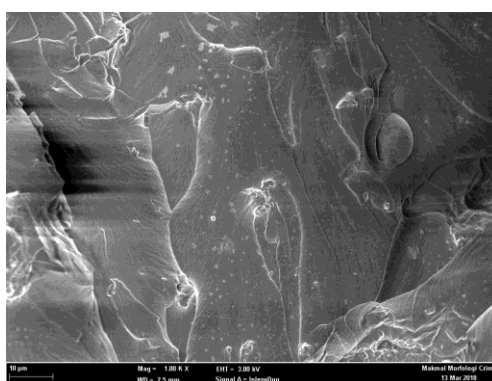


Fig. 3 FESEM cross sectional image of fractured PU composite film at 8 wt% ACB

Some microcracks were observed around the carbon particles in the PU matrix. This shows that ACB acts as a stress concentrator and promotes the formation of crack when the matrix is under stress. Excellent interfacial bonding between ACB and PU matrix can transmit stress from matrix to ACB. Besides, the porosity and surface roughness of ACB can enhance surface adhesion between ACB and PU matrix. The porosity of ACB can also act as an anchor to the PU matrix through physical adsorption and therefore, improved the properties of the PU composites [8]. Chemical adsorption was further verified in the FTIR analysis.

Scratch Resistance

The PU composite films were subjected to the scratching resistance test following ASTM D3363 standard (Standard Test Method for Film Hardness Test by Pencil Test). Pencil hardness indices range from 6H to 6B with the H end of the spectrum being the harder while B end of the spectrum being the softer. Table 2 shows the pencil hardness indices required to leave a permanent scratch on PU-ACB composites.

Table 2 Pencil hardness required to leave a permanent scratch on PU-ACB composite films

Sample	Scratch resistance indicated by the pencil hardness index
PU0	2H
PU2	3H
PU4	5H
PU6	5H
PU8	5H

Based on the observation, in order to leave a permanent scratch, PU0 left a scratch with 2H, PU2 with 3H, while PU4, PU6, and PU8 with 5H. This shows that samples of PU4, PU6, and PU8 with higher ACB loading percentage were more scratch resistance compared to PU0 and PU2. ACB formed good surface adhesion with PU matrix, increasing the scratch resistance when the amount of ACB increased.

Hardness

Fig. 4 shows the average hardness data obtained from five different points made on PU composite films using a Durometer Shore A Model Techlock GS-719N based on ASTM D2240A standard (Standard Test Method for Rubbery Property). PU8 with the highest loading percentage of ACB (at 8 wt%) showed the highest value in hardness index (48) compared to PU0, PU2, PU4, and PU6. PU8 was able to withstand higher stress and indentation was much lower. The incorporation of ACB filler into PU matrix had reduced the chain mobility and deformability.

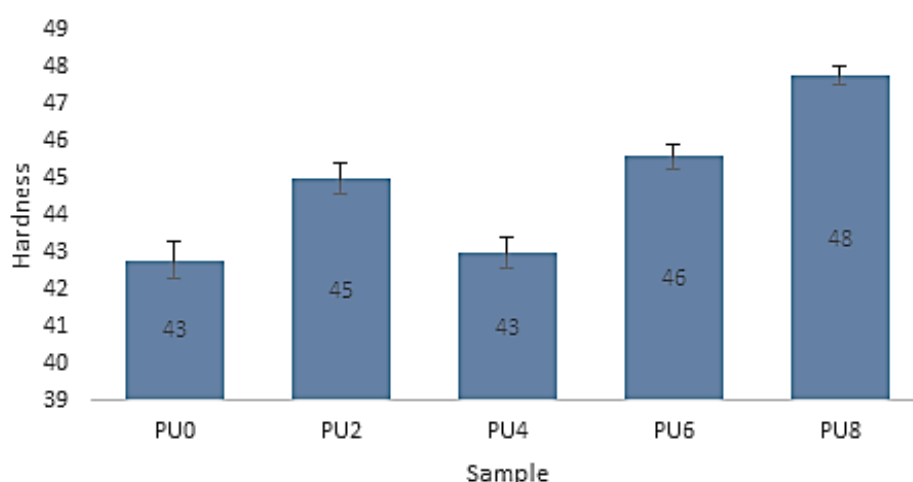


Fig. 4 Shore A hardness indices of the PU composite film

FTIR Spectrum Analysis

FTIR spectrum was used to identify the functional group present in PU composites and in determining if chemical interaction occurs between ACB and PU matrix. Fig. 5 shows the FTIR spectra obtained for comparison between PU0 and PU8.

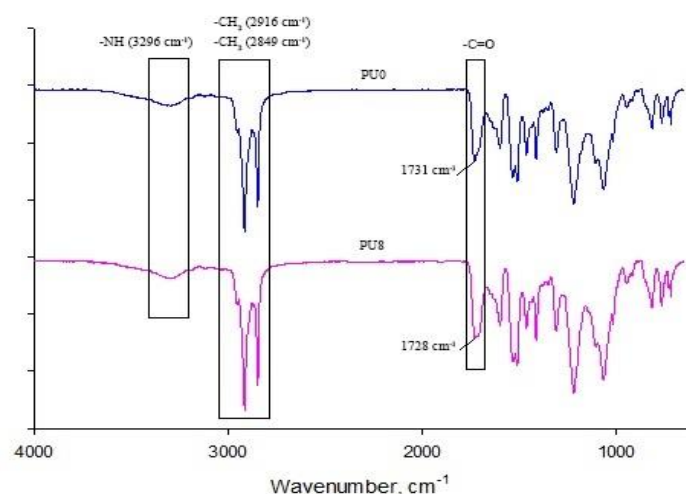


Fig. 5 FTIR spectra of PU0 and PU8 composite films

The main functional groups present in the region such as 3296 cm^{-1} represents amine peak (-NH), CH_2 peak was observed at region around $2940\text{-}2920\text{ cm}^{-1}$ and $2860\text{-}2850\text{ cm}^{-1}$, and carbonyl (-C=O) peak around 1730 cm^{-1} .

No peak was observed around $2270\text{-}2250\text{ cm}^{-1}$, confirming that no NCO group is present and all MDI had reacted with PKO-p. Besides, there is less possibility that having urea as side product as C=O peak of urea at $1690\text{-}1660\text{ cm}^{-1}$ does not exist [3].

There is possibility that ACB creates interaction with PU matrix. At 8 wt%, ACB shifting the peak 1731 cm^{-1} of pristine PU to 1728 cm^{-1} . Similar result was also obtained by Sahoo and co-workers [9] where the addition of 20 wt% carbon black functionalized with carboxylic group shift the peak from 1718 cm^{-1} to 1685 cm^{-1} . The presence of carboxylic group on ACB gives interaction between ACB and PU matrix, that is C=O group of hard segment in PU chains may form hydrogen bonding with carboxylic group of the ACB, giving a strong interaction. Fig. 6 shows possible interaction of hydrogen bonding existed between ACB and PU chains.

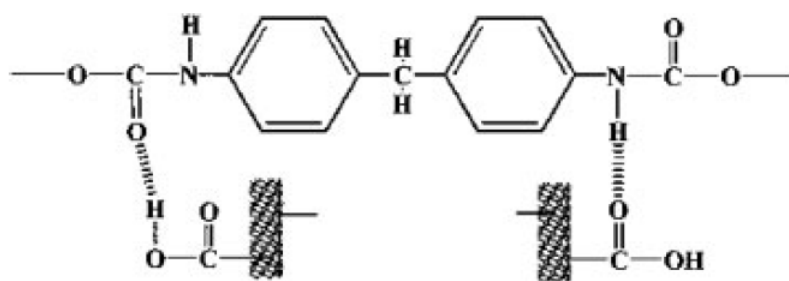


Fig. 6 A possible interaction of hydrogen bonding between ACB and PU chains [9]

CONCLUSION

Palm-based polyurethane was formed through prepolymerization method by reacting PKO-p, PEG, and MDI emulsified in acetone. The incorporation of activated carbon black as filler greatly contributed to the enhancement of the mechanical properties of the polyurethane composites. The compatibility and interfacial adhesion of activated carbon black with polyurethane matrix improved the tensile properties, scratching resistance, and hardness of the polyurethane composites. Activated carbon black at 8 wt% loading indicated the highest mechanical properties.

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