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THE EFFECT OF SILANE AS COUPLING AGENT ON THE POLYURETHANES FILLED SILICA

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ABSTRACT

Palm kernel oil –based polyol with the hydroxyl number 350-370 mg/KOH and functionality of 2.5-3.0 was used to produce rigid polyurethane foam after added with diisocyanate, surfactant and catalyst. Silica filler was mixed into the formulation of polyurethane and varied from 0, 2, 4, 6 and 8 wt.%. The concentration of silane as coupling agent were varied from 2, 2.5 and 3%. The bonding between resin and filler was investigated at various percentage of filler content. The result has shown that the compressive strength increased with the addition of silane concentration.

Keywords: *Polyurethane, filler, silica, rigid foam, palm kernel oil polyol.*

INTRODUCTION

At the present time, polyurethanes are used in various branches of industry as foams elastomers and coatings because of their unique combination of good characteristics with various special properties. Segmented polyurethanes are composed of alternating soft (low glass transition) segments and more rigid, polar urethane (hard) segments. The soft segments are generally polyester and the hard segments are formed from the extension of a diisocyanate terminated prepolymer with a low molecular weight diol [Wirspza].

Depending on the soft segment or hard segment concentration the polymer has a continuous hard phase with a dispersed soft phase, a continuous soft phase with dispersed hard phase, or a bi continuous phase [B.Bogdanov]. The polyurethane with a continuous soft phase exhibit elastomeric or thermoplastic behavior at room temperature depending on the molecular weight and crystallinity of the soft segment. Polyurethane foams can be assumed composite structures resulting by the controlled entrapment of gases that are generated during the polymerization reaction between polyfunctional alcohols and polyisocyanates to form urethane linkage [B.Bogdanov]. These foam exhibit physical and mechanical properties related to their chemical composition and density, particularly suitable for use in many applications such as seating, insulator, packaging and cushioning. The synthesis of biodegradable of polyurethanes is a relatively recent issue in polyurethane chemistry. The utilization of renewable resources to replace the petrochemicals in polyurethane has been attracting a lot of attention amongst the researchers. It is well known that polyester-based polyurethanes are much more susceptible they are too biodegradable.

In this study, polyester is derived from a renewable resource, Refined- Bleached-Deodorized (RBD) palm kernel oil in combination with alkanolamine. Direct polycondensation method were used for the synthesis. Fillers are usually finely divided solids, which take no direct part in the chemistry of foam formation [G. Wood]. They are insoluble in the foam ingredients and the polymer, causing a distinct interface between the filler particles and the polyurethanes. Filler used in polyurethane must be dry because of water-blown systems contain a known low level of water. The enhancement of properties can be achieved by inclusion of coupling agents. Coupling agent contents silane is a nonhydrolyzable organic radical that possesses functionality, which enables the coupling agent to bond with organic resin and polymer. Hence, it will improve bond strength between silica and polyurethane.

MATERIALS AND METHODS

The polyol was synthesized in accordance to K.H.Badri *et.al* method. The polyol was then used in preparation of polyurethane foam. Crude diphenyl methane diisocyanate was poured with resin based - RBD palm kernel oil polyol. The additives such as surfactant, catalyst, filler and water also added and were mixed thoroughly using a standard propeller. Then, the mixture was poured into a waxed mould, covered, and screwed tight. The foam was then demoulded just after 15 minutes. The characterization process of polyurethane foam would be done after conditioning for 16 hours at room temperature. The silane-based coupling agent was mixed with ethanol and make up to 10 wt. %. Silanol solution containing silane concentration of 2, 2.5 and 3 wt.%. The treatment of silica was carried by put it in a tumbler-mixer and silanol was sprayed continuously to obtain a uniform coating of silanol onto the surface of silica. After the mixture was left for 30 minutes, silica was coated homogeneously. It was then dried into oven at 70 °C for 2 hours to allow the condensation process of ethanol.

Fourier Transform Infrared (FTIR) spectrum of the polyol was recorded with the Perkin Elmer Paragon 500 Spectrometer. Samples were scanned between 4000 – 400 cm⁻¹ wave numbers. The selected IR peaks unique to reactants and the derivatized product were used for purpose of monitoring the reaction progress. The hydroxyl values were determined in accordance with the ASTM D4274-88 (Standard Test Method for Testing Polyurethane Raw Materials: Determination of Hydroxyl Numbers of Polyol). Water content of the polyol was determined using the Karl Fischer Titrator 702. The residual water content of polyol is an important parameter in polyurethane foam formulation because its reactivity with –NCO to generate CO₂ (blowing agent system) and it influents the final density of the foam. The viscosity of polyol at 25 °C was determined using Brookfield digital viscometer.

Polyurethane foams were characterized for apparent densities, compressive strength, dimensional stability and water absorption according to standard method BS4370: Part 1: 1988. Foam samples were cut using bone saw into cubes of 100 mm x 100 mm x 100 mm in dimensions. Foam samples were carefully weighed using an analytical balance and the exact dimensions were measured using a digital vernier caliper. Foam density was calculated according to BS4370: Part 1: 1988 Method 2. The compressive strength was evaluated on Lloyd Universal Tensile Tester in accordance to BS4370: Part 1: 1988 Method 3. The foam samples were cut into cubes of 50 mm x 50 mm x 50 mm dimensions. Rise directions of the foam were marked and a crosshead speed was set 10 mm/min. The load was applied until the foam was compressed to approximately 10% of its original thickness.

For dimensional stability, the foam samples were cut into dimensions of 100 mm x 100 mm x 2.5 mm. The exact dimensions were measured using the digital venier caliper. They were put into a controlled temperature and humidity chambers each at –15 °C and 70 °C at 95 ± 5 r.h for 24 hours in accordance with BS4370: Part 1: 1988 Method 5A. The flow of polyurethane composites containing different percentages of treated and untreated silica before cured was measured with the modified method created by K.H.Badri. Only polyurethane with a good rheological index was put into mould. The insulation value (*k*-factor or λ value) of polyurethane foam/ composite were determined using Thermal Conductivity Analyser model Anacon at testing temperature of 10 °C with sample thickness of 20-30 mm.

RESULT AND DISCUSSION

Polyol Characterization

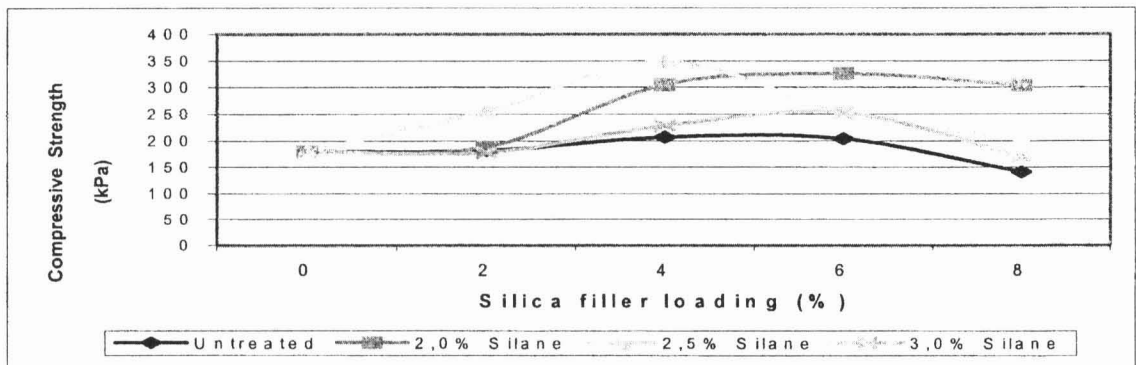
The RBD pal kernel oil has changed from a cloudy pale to clear golden yellow liquid after reaction. The others characterization of polyol is shown in Table 1.

Table 1: Characterization of RBD palm kernel oil polyol.

	Value
Viscosity, cps @ 25 ^o C	331 – 334
Moisture content (%)	0.12 – 0.14
Hydroxyl Number (mg KOH/g)	350 – 370
Molecular weight	430 – 450
Functionality	2.8 – 3.0

Figure 2 shows that the addition of silica resulted in slight increase in compressive strength for non-treated silica. However, the strength was reduced after certain percentage of filler. The inclusion of various concentration silane coupling agent showed the improved of strength. This improvement is a consequence of the creation of interaction, probably bonds between the silanol groups on silica surface and resin polymer. But, there was slightly decrease of strength for 3% silane treated silica filled PU. A large amount of silane used was not necessary for improving the bonding strength.

Figure 2: The compressive strength of sample at various filler loading and concentration of silane coupling agent.



The thermal conductivity, *k*-factor for control, untreated silica-filled PU and treated silica-filled PU with 2%, 2.5% and 3% of silane are 0.0312, 0.0326, 0.033, 0.0296 and 0.269 W/m.k respectively. The addition of untreated silica into PU formulation does not effect the cellular structure. However, the inclusion of coupling agent interfered the cellular structure due to bonding between silica and matrix. From the value given above, it decreased as the concentration of silane increased. This PU composite also showed a low absorption of water and this is good for insulation and boat making purpose.

The mechanical properties of PU composites were also obtained from stress-strain curves. Figure 3 shows the variation of the stress as a function of the strain for the composites. There is a noticeable increase in stress for strain values higher than 80% until the composite is ruptured. The curves show the similar trend accept for 3% silane-treated silica which showed quite low stress compared to others at rupture stage. This also can be seen in Table 4, which also show the elongation at break is lowest from all the samples. The composites with 2% and 2.5% silane show similar trend in compressive strength and elongation at break values (Table 4). Therefore, the addition of 3% silane treated silica has reduced in mechanical properties of PU.

Figure 3: Variation stress strain in PU composites with and without filler and at various concentration of silane.

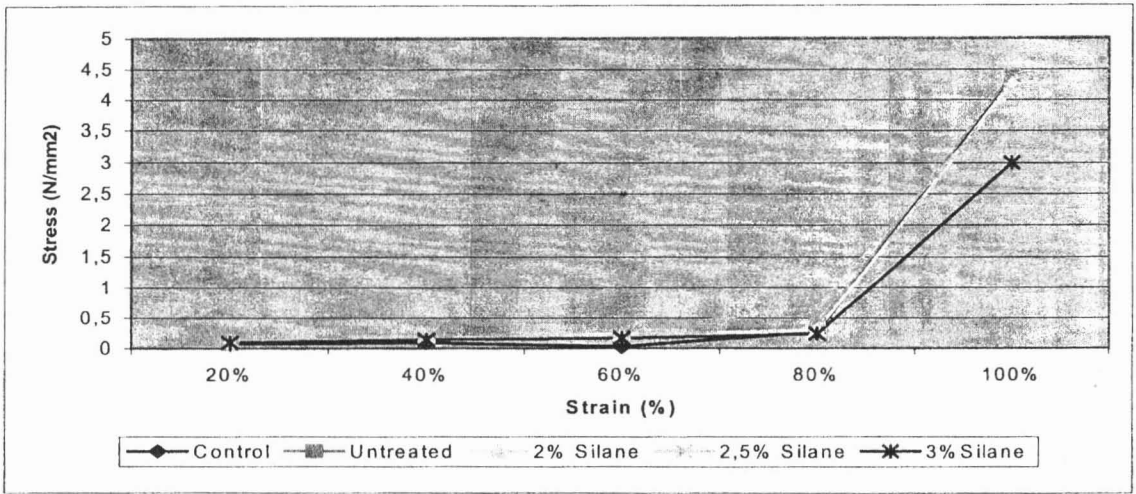


Table 4: Compressive strength and elongation at break of the PU composites with different concentration of silane coupling agents for 4% incorporation of filler.

Composite	Compressive strength (kPa)	Elongation at break (%)
Control	179.9	95.5
Non-Silane	207.302	102
2% Silane	305.096	97.5
2.5% Silane	348.66	96
3% Silane	228.03	102

CONCLUSION

The addition of silica had improved the compressive strength at certain percentages of filler loading. The compressive strength increased by two fold with the addition of 6% of silane treated filler. The mechanical properties indicate that present of silane improve the bonding between silica surface and PU.

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