An Overview of R&D in Palm Oil-Based Polyols and Polyurethanes in MPOB

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INTRODUCTION

The oil palm is one of the world's most economical oil crops. A tonne of its fresh fruit bunches (FFB) yields 200 kg crude palm oil and 40 kg palm kernels which, in turn, yield about 50% of their weight, or 20 kg, of palm kernel oil. A hectare of estate can yield 20-24 t of FFB per year, which in turn will yield 4 to 5 t of palm oil and 400-500 kg of palm kernel oil.

Palm oil is one of the 17 major oils and fats that are produced and traded in the world. Production in 2005 was 33.49 million tonnes which contributed to 24% of the total production of oils and fats. Production of palm kernel oil (PKO) in 2005 totalled 3.92 million tonnes and accounted for about 2.8% of the production of oils and fats. In 2006, palm oil trade is forecast at 27.61 million tonnes while that of PKO, 2.09 million tonnes. The total trade of oils and fats forecast for 2006 is 52.28 million tonnes compared to 50.35 million tonnes in 2005.

With the continual escalation in the petroleum price, there has been an increase in the use of renewable feedstocks for industrial products. Palm oil and its products, being renewable and readily biodegradable, are the alternative feedstocks for the production of palm oil-based polyol for polyurethane products.

MPOB has been actively involved in the R&D activities in palm oil-based polyols and their industrial applications and this paper highlights some of the R&D activities in this area.

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POLYOLS AND POLYURETHANES

A polyol is an alcohol with more than two reactive hydroxyl groups per molecule. A wide range of polyols is available, but about 90% of these used in making polyurethanes are polyethers with terminal hydroxyl groups. Hydroxyl terminated polyesters are also used to produce polyurethanes with special properties but they are usually more expensive. However, currently most of the commercial polyols are petroleum-based.

The structure, molecular weights and functional groups of the polyols play vital roles in determining the properties of the final urethane polymers. They determine the degree of cross-linking achieved in the polymer formed in the reaction with isocyanate. The degree of cross-linking has a dominant effect on the stiffness of the polyurethane polymer: for rigid foam, there must be a stiff polymer network and hence, a high degree of cross linking; for flexible foam, a lesser degree of cross-linking is needed.

Isocynate is another important component in the production of polyurethane. The most widely used isocyanates are toluene diisocyanate (TDI), methylene diphenyl diisocyanate (MDI) and their modified products. TDI is mainly used in the production of flexible foams and MDI, for rigid foams.

A blowing agent is used to generate nucleating gas bubbles in the polymerizing or gelling mixture of polyol and isocyanate. The blowing agents for polyurethane foams commonly used are water and low-boiling inert liquids /solvents. Additives also play a vital role in the preparation of polyurethane. These include catalysts, cross-linking agents, chain extending agents, surfactants, colouring materials, fillers and flame-retardants.

From a survey by Mutiara Seleras, world consumption of

TABLE 1. WORLD CONSUMPTION OF POLYURETHANES BY REGIONS (1000 t)

Region	%	2000	2002	2004	Growth (%)
Western Europe	31	2 620	2 935	3 290	6
Eastern Europe	3	255	275	300	4
North America	33	2 790	3 180	3 625	7
South America	5	425	465	510	5
Japan	6	510	550	590	4
Rest of Asia Pacific	16.5	1 395	1 560	1 750	6
Africa & Middle East	5.5	465	505	545	4
World	100	8 460	9 470	10 610	6

polyurethanes in 2004 was about 10.6 million tonnes, with the market expanding at 6% per annum (*Table 1*). The growth is driven by demands in North America, Western Europe and Asia Pacific. In Malaysia, the total polyurethane consumption is estimated at about 68 000 t. *Table 2* shows different application of polyurethene in Malaysia in different sectors.

VEGETABLE OIL-BASED POLYOLS

Currently, most of the commercially available polyols are petroleum-based. With the escalating price of crude petroleum and environmental concern, there is a search for renewable resources for use in the production of polyols with comparable properties and characteristics to those made from petroleum. One of the most interesting substitutes so far is the vegetable oils. The earliest oil used for this purpose was castor oil. Other oils which have been used are oil of tung, soyabean, rapeseed, fish and sunflower as well as palm. *Table 3* shows the fatty acid compositions of some of these oils.

Palm-Based Polyol

Figure 1 shows the simplified process for production of palm oil-based polyols and polyurethane foams. MPOB has a polyol pilot plant (*Figure 2*) of 500-800 kg per batch for all the R&D projects related to polyols and polyurethane.

Palm Oil-Based Polyols and Properties

The properties and specification of the polyols from refined, bleached and deodorized palm olein is as shown in *Table 4*.

TABLE 2. POLYURETHANE MARKET IN MALAYSIA BY SECTORS (t)

Type	Areas of applications (total No. of companies)	Present Malaysian consumption (t)
Flexible foam	Furniture/bedding (>50)	12 000
Rigid/semi-rigid foam	Construction (>70)	24 000
	Roof insulation	20 000
	Sandwich panels and pipe insulation	4 000
	Automotive	6 000
Case	Spray PU	2 000
	Adhesives	-
	Sealants	-
Total		68 000

Source: With permission from Mutiara Selaras (2001).

TABLE 3. FATTY ACID COMPOSITIONS OF SOME VEGETABLE OILS

Fatty acid	Palm oil	Soyabean oil	Rapeseed oil	Sunflower oil
C12:0	0.3	-	-	0.5
C14:0	1.1	0.1	0.1	0.2
C16:0	45.1	11.0	2.8	6.8
C16:1	0.1	0.1	0.2	0.1
C18:0	4.7	4.0	1.3	4.7
C18:1	38.8	23.4	23.8	18.6
C18:2	9.4	53.2	14.6	68.2
C18:3	0.3	7.8	7.3	0.5
C20:0	0.2	0.3	0.7	0.4
C20:1	-	-	12.1	-
C22:1	-	-	34.8	-
Others	-	0.1	2.3	-

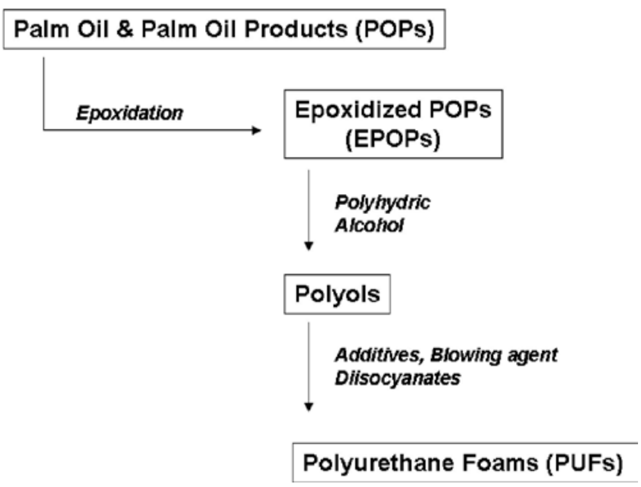


Figure 1. Process route for production of polyurethane foams.

Figure 2. Polyol pilot plant at MPOB.

APPLICATIONS OF POLYURETHANE PRODUCTS

Polyols can be used to produce various types of polyurethane products such as ceiling panels, flora foams, wall panels, cushion, flexible foams, automotive parts, *etc.*

Monier CoolBoard Ceiling Panel

The Monier CoolBoard ceiling panel has superior quality, such as better thermal insulation, three times better sound transmission class, lower water absorption, light weight and easy to install. For example, the ceiling panel in a guard house at Advanced Oleochemical Technology Division (AOTD), MPOB was made from palm oil-based polyurethane to demonstrate Monier's CoolRoof package insulation as shown in *Figure 3*.

Currently, Monier CoolBoard is being marketed by Lafarge Roofing Systems Sdn Bhd as total Monier's cooling system. The company has been installing these

TABLE 4. PROPERTIES OF PALM OIL-BASED POLYOL

Parameters	Properties	Test method
Colour	Brownish yellow	Visual
Odour	Slight /typical	Odour
Hydroxyl value, mg KOH g^{-1}	170-200	AOCS Cd 13-6
Viscosity, mPa.s @ 35°C (95°F)	3 500-4 500	ASTM D 4878
pH	6.5-7.5	pH Meter
Acid value, mg KOH g^{-1}	3.0 max	AOCS Cs 3d-63
% Water	0.30 max	AOCS Ca2e-84
Specific gravity	0.95-0.98	Gravimetric

Figure 3. A guard house at AOTD, MPOB using Monier CoolBoard system.

boards in several detached houses, link houses, laboratories and school halls as roofing.

Sandwich Panels and Laminated Boards

Palm oil-based polyurethane wall panel is a high density product with superior thermal insulation and acoustic properties. These wall panels have been used to construct a guard house at AOTD to demonstrate the performance of the Monier CoolRoof System. As palm oil-based polyurethane possesses natural bonding abilities, it can be easily laminated with medium density fibreboard (MDF), plaster board, plywood, *etc*. Palm oil-based polyurethane laminated with MDF (both sides) of different thickness (6, 9, 12 mm) and gypsum board of different thickness (6 and 9 mm) have been produced for evaluation. *Figure 4* shows some samples of sandwich laminated palm oil-based polyurethane samples.

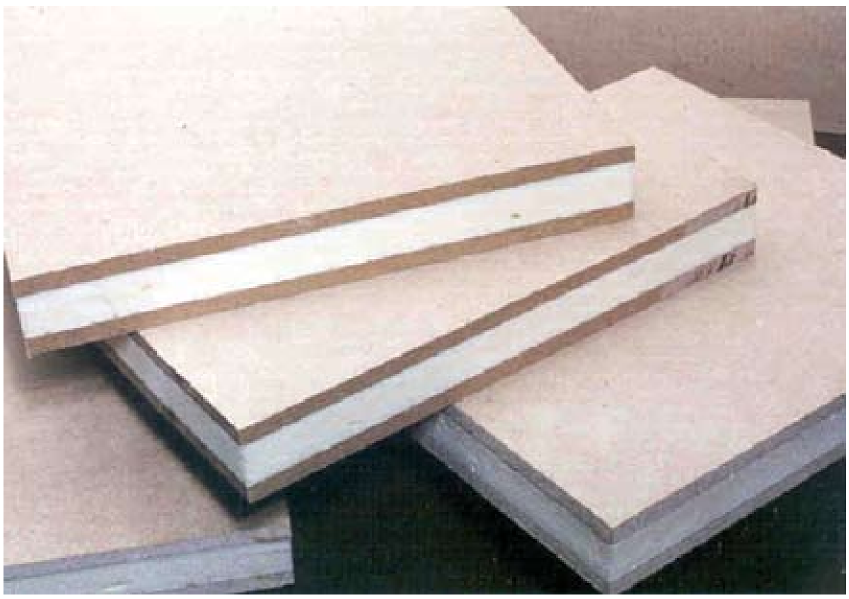


Figure 4. Sandwich laminated samples.

Polyurethane Sheets

In the production of polyurethane products, filler is usually added to the formulation to modify its physical properties as well as to reduce the cost. Some are filled with scrapped tyres to increase the strength while other with laminated gauze, aluminum paper, aluminum plastic and polyethylene plastics for a variety of applications. These polyurethane products have the potential to be applied in laying children's playground and sports track (*Figure 5*).

Flexible Polyurethane Foams

Flexible foam with lazy characteristics can also be produced from palm-based polyols. This type of foam has higher energy absorption characteristic and can also able to absorb sound and mechanical energy better. These are meant for products like furniture, cushions and mattresses. The world market for flexible polyurethane

Figure 5. Palm-based polyurethane sheets.

foams is growing at a rapid pace because of these features. Palm oil-based polyols are also suitable for the production of flexible foams. Incorporation of stannous octanoate improves the properties of polyurethane foams in terms of compressive stress, tear value, and tear strength and percentage relative energy absorption. With higher open cell content and high damping behaviour (large hysteresis area) these foams can absorb sound and mechanical energy better during compression hardness test. Because of this *lazy* behaviour, these foams can be used as packaging materials, shock absorption materials, *etc*. Commercial production trials with local companies for flexible polyurethane labstock (*Figure 6*) and some automotive parts are being carried out.

Adhesives and Coatings

MPOB and WKI have investigated a new polyol (PolyMo from glycerol and oleic acid) for use as adhesives and coatings. Two coatings were formulated, one for exterior and another for interior applications on different surfaces like wood, plastics and polyesters. The interior formulation has a great potential in the wood furniture industry. The adhesive produced by blending PolyMo with the current polyol has been evaluated and found to be suitable for use in MDF.

Slow-Release Fertilizer

Coated fertilizer has the advantage of reducing labour cost during farm application, lowering risk of root cell plasmolysis, providing uniform supply of nutrients to plants, and minimizing potential leaching which can cause environmental damage. The performance of slow-release fertilizers coated with palm-based polyurethane coating materials (*Figure 7*) developed by MPOB showed that the release of N, P and K were found to be comparable to two commercial coated fertilizers, of which one is soya-based and the other, petroleum polyurethane-based.

Automotive Parts

Polyurethane products are widely used in the automotive industry to make car seats, head rests, liners, dashboards, carpet underlay, bumpers, energy adsorption parts and sound

Figure 6. Palm oil-based flexible polyurethane slabstock.

Figure 7. Palm oil-based polyurethane coated fertilizer.

insulation. An example of palm-based polyurethane for use as carpet underlay is shown in *Figure 8*.

Palm Oil-Based Polyurethane with Palm Fibre

Oil palm plantations and palm oil mills generate large quantities of biomass such as trunks, fronds and empty fruit bunches. The chemical compositions and physical properties of the oil palm fibres are shown in *Table 5*. In Malaysia, it is estimated that the total amount generated per year is about 30 million tonnes (dry weight). Research at MPOB has found that it is technically feasible to convert them into value-added products such as fertilizer, animal feed, MDF, particle board, laminated board, pulp and paper, chemicals and mulching mat.

Rigid/semi-rigid palm oil-based polyurethane foams can be produced by incorporating palm fibre in the manufacturing process. The optimum amount of fibre for blending with palm oil-based polyols is 30% for frond and 35% for trunk and empty fruit bunch fibres. Blended polyols (palm-based: petroleum-based polyols, 50:50) showed optimal density with the inclusion of 20% frond, trunk and empty fruit bunches. The foams became very coarse and collapsed when higher percentages of fibre (>30%) were incorporated. In general, incorporation of palm-based fibres improves the foam by reducing its density and a slightly decrease its thermal conductivity. Blending palm fibres with polyols can reduce the cost of raw materials especially for the production of lighter products such as packaging materials and roof

Figure 8. Palm oil-based polyurethane carpet underlay.

insulators, which only require low compressive hardness.

UV-Curable Coating Materials

Radiation-curable systems are of increasing importance for coatings for various industrial applications due to their many advantages over the thermal and solvent-based coatings. This technology is a solvent free, fast curing process at room temperature, consuming low energy and requiring minimum working space. Currently, most radiation-curable resins in the market are petrochemical-based. Some products based on soyabean oil, tung oil and linseed oil are also available.

Two radiation curable acrylated polyester prepolymers, PEPP-1 and PEPP-2, prepared from palm oil-based polyol are found to

TABLE 5. CHEMICAL COMPOSITION OF OIL PALM FIBRES

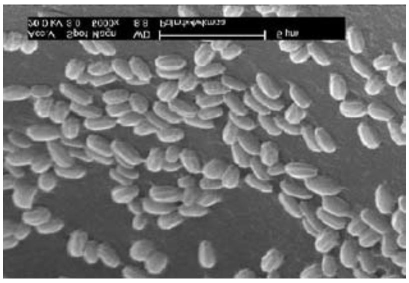
Analysis	Contents (%)		
	Empty fruit bunches	Trunks	Fronds
H cellulose	71.5	67.8	77.2
K cellulose	39.9	40.5	43.1
Lignin	15.2	14.6	13.6
Pentosans	29.0	25.1	26.8
Alcohol/benzene soluble	1.5	1.0	1.8
Hot water soluble	10.2	8.9	9.6
Alkali 1% NaOH soluble	21.4	23.6	25.3
Ash	1.0	1.5	1.2

be suitable as a main ingredient in UV-curable coatings. Various formulations have been developed with different reactive diluents, photoinitiators and curing agents. These products were cured under different UV doses and evaluated for their physical and mechanical properties such as hardness, wettability (contact angle), gel content, swelling character, tensile properties and deformation characteristics. When they are applied on rubber wood and then cured by UV radiation, the performance on gloss, adhesion, cross-cut adhesion, abrasion, solvents and chemical resistance showed that the synthesized palm-based resins are suitable coatings materials for wood.

OTHER STUDIES

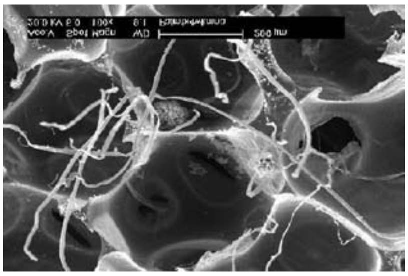
Biodegradation Studies

Some biodegradation studies have been carried out on petroleum and palm oil-based polyurethane products. Palm oil-based polyurethane was found to be more susceptible to attack by soil organisms than the petroleum-based polyurethane. The better biodegradability of palm-based polyurethane is an advantage in its disposal, thus obviating environmental problem (*Figure 9*).



On mineral salt agar

On minimal nutrient agar



Aspergillus niger: no growth

Aspergillus niger: growth 4 weeks

Figure 9. Results of biodegradability studies of palm oil-based polyurethane and petroleum-based polyurethane.

CONCLUSION

While petroleum-based polyols continue to dominate the market, the prospects of palm oil-based polyols taking a substantial market share will ultimately depend on consumers' acceptance. Currently, virtually all the polyurethanes used are made from fossil fuels, which are non-renewable, and the polyurethane industry is also concerned over the continual escalation of the petroleum price. Palm oil-based polyols, on the other hand, being derived from natural resources hold the promise of eventually replacing a substantial portion of petroleum-based polyols in the polyurethane market. Some major players in the market are already blending vegetable oil-based polyols with petroleum-based polyols in order to be more cost-effective. These developments indicate that the future for palm oil-based polyol is indeed very bright!

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