

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO	
RAD: 11-130078- -19	FECHA: 2015-11-19 13:59:22
DEP: 2020 DIRECCION DE NUEVAS CREACIONES	EVE: 1 REGISTRO/DEPOSITO/CONCESION/DEPOSITO
TRA: 2 PATENTES DE INVENCION	FOLIOS: 8
ACT: 519 TRASLADOINFORME	

DIRECCIÓN DE NUEVAS CREACIONES

2020
Bogotá, D.C.,

Abogado(a)/Señor(a)
LUZ CLEMENCIA DE PÁEZ

Asunto: Radicación: 11-130078- -19
 Trámite: 2
 Evento: 1
 Actuación: 519
 Oficio: 13742
 Folios: 8

Patente de Invención	X			Patente de Modelo de Utilidad	
Vía Nacional	X				
Vía PCT (Fase Nacional)		Capítulo I		Capítulo II	
No. Solicitud Internacional					
Fecha de Presentación Internacional					

Como resultado del examen de fondo realizado, con fundamento en el Artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se comunica:

1. Documentos estudiados

Descripción:	Rad. N° 11-130078-00000-0000	8/Octubre/2011
Reivindicaciones:	Rad. N° 11-130078-00018-0000	14/Octubre/2015
Dibujos:	Rad. N° 11-130078-00000-0000	8/Octubre/2011

2. Objeto de la invención

De acuerdo con lo establecido en el numeral 1.2.2.2 del Capítulo Primero del Título X de la Circular Única para efectos del examen de patentabilidad, se tendrá en cuenta la tasa pagada por el solicitante al momento de comenzar el examen para las reivindicaciones adicionales; esto es que cuando la solicitud contenga más de diez (10) reivindicaciones y no se haya pagado la tasa complementaria, sólo se estudiarán las cubiertas por la tasa pagada. Por lo tanto, se estudiaran las reivindicaciones 1 a 5.

Título de la solicitud: “Procesos para la obtención de un poliol a partir de aceite de palma, polioles obtenidos a partir de dichos procesos, productos derivados de dicho poliol y su método de preparación” (Ver página 1 del radicado N° 11-130078-00000-0000).

El problema planteado en esta solicitud consiste en la necesidad de suministrar

espumas de poliuretano a partir de aceite de palma y con características deseables.

Para resolver este problema técnico, la solicitud en estudio proporciona un método de obtención de polioles a partir de aceite de palma, para su posterior polimerización a poliuretano.

El objeto de la presente solicitud se relaciona con la Clasificación Internacional de Patentes (CIP): C08G 18/36, 18/00, C07C 29/00.

3. De la solicitud de patente

Reivindicaciones (Art 30 D 486, Art 22 PCT)

Durante la evaluación de claridad y concisión de las reivindicaciones, esta Oficina encontró que:

- La reivindicación 1, no es clara porque presenta términos generales “*surfactante*”, el cual, aunque corresponde a un término conocido, abarcan una extensa gama de posibilidades, de tal manera que sugieren de forma imprecisa que la protección se extiende a otras posibles variaciones o modificaciones. Se sugiere sustituirlas por un término preciso o un rango concreto.
- La reivindicación 3, no es clara porque presenta resultados a obtener “*tiene una densidad entre 0,120 g/cm³ y 0,158 g/cm³, “módulo de Young entre 0,78727MPa y 1,54311MPa y esfuerzo máximo entre 0,07012 MPa y 0,09753 MPa*”, lo cual no es permitido, puesto que las citadas reivindicaciones incluirían no sólo la solución propuesta por el solicitante, sino todas las alternativas presentes o futuras que lleguen a ese resultado.

Descripción (Art 28 D 486)

Durante la evaluación de claridad y suficiencia de la descripción, esta Oficina encontró que:

- A partir de los ejemplos de la descripción se muestra que en el experimento No. 26 el poliuretano que presenta un módulo de Young de 1,32276 Mpa y esfuerzo máximo de 0,08760 Mpa se obtiene preparando el poliol por epoxidación y glicerólisis a partir de la fase Oleína de aceite de palma, por lo cual, no se evidencia que a partir de la preparación del poliol por maleinización se obtenga un poliuretano flexible con las características de densidad, módulo de Young y esfuerzo máximo como se reivindica.
- Además no se muestra mediante los ejemplos presentados un efecto técnico sorprendente e inesperado que evidencie el aporte de la invención al estado de la técnica.

4. Determinación del Estado de la Técnica

El estado de la técnica se determinó con base en la fecha de presentación de la solicitud de patente nacional, es decir, 8 de octubre de 2011.

Consultadas las fuentes de información con que se cuenta, se encontraron los siguientes documentos que anticipan el objeto de esta solicitud:

Ítem	Documento	Título	Fecha de Publicación*
D1	US 2009/0209441	“Maleated vegetable oils and derivatives, as self-emulsifying lubricants in metalworking”	20/Agosto/2009
D3	Artículo 1	“Water-borne and air-drying oil-based resins”	2004

El documento D1¹ divulga la modificación de triglicéridos insaturados como el aceite de palma con anhídrido maléico (Pág. 2, Párr. 26 a Párr. 29).

El documento D3² divulga un método para la maleinización de triglicéridos y su posterior uso para la formación de barniz de poliuretano (Pág. 260, Col. 2, Párr. 2 y Párr. 3, Pág. 261, Tabla 1, Pág. 261, Col. 2, Párr. 5 a Pág. 262, Párr. 5).

5. Examen de Patentabilidad (Art 14 D486)

El siguiente examen de patentabilidad se realizó teniendo en cuenta las objeciones señaladas en el numeral 3 de la presente comunicación.

Nivel inventivo (Art18 D486)

La reivindicación 1 consiste en “Proceso para la obtención de poliuretanos a partir de aceite de palma (...)” (Ver página 11 del radicado N° 11-130078-000006-0000).

Comparación de las características técnicas esenciales, con las del estado de la técnica:

Características esenciales	D3	D1
Proceso para la obtención de poliuretanos a partir de aceite de palma caracterizado porque consta de los siguientes pasos	No menciona.	Reacción entre el anhídrido maléico y triglicéridos de origen vegetal que contienen ácidos grasos insaturados, el triglicérido puede ser aceite de palma (Pág. 1, Párr. 10, Pág. 1, Párr. 12, Pág. 2, Párr. 26).
a. Hacer reaccionar aceite de palma con anhídrido maléico a una temperatura entre 170°C y 190°C en una atmosfera inerte, la cual puede ser nitrógeno	Se hace reaccionar aceite de girasol con anhídrido maléico a una temperatura de 200°C y 3 horas bajo una atmósfera de nitrógeno (Pág. 260, Col. 2, Párr. 2). Para la persona versada en la materia la presencia de la atmosfera de nitrógeno no permite la oxidación del aceite, por lo que el resultado esperado es el mismo si se hiciera a temperatura levemente menores.	La reacción entre el anhídrido maléico y el triglicérido insaturados ocurre entre 175 y 250°C, el triglicérido puede ser aceite de palma (Pág. 1, Párr. 12, Pág. 2, Párr. 18, Pág. 2, Párr. 26).
b. Hacer reaccionar el poliol obtenido con un surfactante y metil etil cetona durante 30 minutos para formar un prepolímero.	El poliol se hace reaccionar con MEK (metil etil cetona) y HTPB (hidrox terminal polibutadieno, el cual es un agente un surfactante, propelante) durante 30 minutos a 50°C (Pág. 261. Col. 2. Párr. 6). Para la persona versada en la materia se entiende que existe un paso previo de adición de glicerol para la obtención del poliol, según se menciona en el ejemplo 1 de la presente solicitud (Fl. 23 del radicado 11-1300078-00000-0000).	No se menciona
En donde el poliol tiene un peso molecular entre 374 y 3366 con un número de hidroxilo entre 50 y 450 mgKOH/g muestra	No menciona.	No menciona.
c. Enfriar el prepolímero obtenido y adicionar toluen diisocianato con agitación mecánica a una temperatura de	A 70 °C se adiciona el toluen diisocianato y se agita por tres horas (Pág. 262, Col. 1, Párr. 2).	No se menciona

1<https://www.google.com.co/patents/US20090209441?>

dq=US20090209441&hl=es&sa=X&ei=596SVdOVGsTDggTu94CwAQ&ved=0CBsQ6AEwAA

2 Artículo 1: Gündüz, et al. Water-borne and air-drying oil-based resins. Progress in organic coatings.

2004, Vol. 49, Págs. 259 a 269.

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2do Art 45

70°C durante tres horas.		
d. Enfriar hasta 50°C y adicionar metil etil cetoxima hasta bloquear los NCO libres.	Se enfría a 50°C y los grupos NCO libres del prepolímero se bloquearon con metil etil cetoxima MEKO por 2 horas (Pág. 262, Col. 1, Párr. 3).	No se menciona
e. Adicionar trietilamina en un reactor agitado	Se adiciona TEA trietilamina y se agita por 30 min a 50°C (Pág. 262, Col. 1, Párr. 4).	No se menciona
f. Adicionar agua, gota a gota, para formar una emulsión en una cantidad de 50% en peso.	Bajo agitación continua y gota a gota se adiciona agua hasta un 50% en peso (Pág. 262, Col. 1, Párr. 5).	No se menciona

Los documentos D3 y D1 se consideran el estado de la técnica más cercano a la invención definida en la reivindicación 1 porque divulgan en el caso de D3 métodos donde se hace reaccionar anhídrido maléico con triglicéridos insaturados de aceite de girasol, y en el caso de D1, el aceite de palma como triglicérido que puede reaccionar con anhídrido maléico.

La diferencia entre la invención definida en la reivindicación 1 y el proceso de D3 consiste en que este último no menciona la producción de poliuretanos a partir del aceite de palma, en donde el poliol tiene un peso molecular entre 374 y 3366 con un número de hidroxilo entre 50 y 450 mg KOH/g muestra.

La diferencia entre la invención definida en la reivindicación 1 y el proceso de D1 consiste en que este último no menciona la reacción de maleinización seguida de la adición de MEK, en donde el poliol tiene un peso molecular entre 374 y 3366 con un número de hidroxilo entre 50 y 450 mg KOH/g muestra.

No se evidencia un efecto técnico inesperado con el hecho de obtener un poliol a partir de aceite de palma o de otro aceite renovable a las condiciones propuestas para la obtención de un poliuretano, donde el poliol tiene un peso molecular entre 374 y 3366 con un número de hidroxilo entre 50 y 450 mg KOH/g de muestra, porque la solución de la presente solicitud ya está divulgada en el documento D3 que enseña la obtención de poliol a partir de aceite de girasol, en donde el proceso posee etapas que conllevan a obtener las mismas características del monoglicérido bloqueado, del poliol y del barniz de poliuretano, donde el poliuretano obtenido presenta buenas propiedades físicas y mecánicas como dureza, adherencia, resistencia al impacto y flexión (Resumen).

Por lo tanto, el Problema Técnico Objetivo que pretende resolver esta invención se puede formular así: ¿cómo modificar el proceso conocido en D3 para obtener un poliuretano con buenas propiedades físicas y mecánicas a partir de polioles provenientes una materia prima alternativa?

Sin embargo, el empleo de aceite de palma como triglicérido para maleinización para obtener un poliol, ya está divulgado en el documento D1 que se refiere a la obtención de polioles mediante la reacción de triglicéridos insaturados de origen vegetal y anhídrido maléico (Pág. 1, Párr. 10, Pág. 1, Párr. 12, Pág. 2, Párr. 26). La reacción entre el anhídrido maléico y triglicéridos de origen vegetal que contienen ácidos grasos insaturados, el triglicérido puede ser aceite de palma (Pág. 1, Párr. 10, Pág. 1, Párr. 12, Pág. 2, Párr. 26), donde, la reacción entre el anhídrido maléico y el triglicérido insaturados ocurre entre 175°C y 250°C, el triglicérido puede ser aceite de palma (Pág. 1, Párr. 12, Pág. 2, Párr. 18, Pág. 2, Párr. 26).

En consecuencia, la persona del oficio normalmente versada en la materia, incluiría aceite de palma o cualquier triglicérido instaurado de origen vegetal del documento D1

en el proceso divulgado en el documento D3 para llegar así al objeto de la reivindicación 1 de la solicitud. Por lo cual se considera obvia. Cabe decir que los documentos D1 y D3, no enseñan que el polioliol tiene un peso molecular entre 374 y 3366 con un número de hidroxilo entre 50 y 450 mg KOH/g muestra, sin embargo, una persona normalmente versada en la materia con el saber general de la técnica conoce que un polioliol basado en aceite de palma puede tener un número de hidroxilo de 385 mg KOH/g (...) y un peso molecular que varía entre 712 y 986 (...). En general, los polioliols de poliéster típicos utilizados en la fabricación de espuma de PU rígido tienen un peso molecular medio de aproximadamente 930 con un rango de valores de hidroxilo desde 350 hasta 390 mg KOH/g. Por lo tanto, este polioliol a base de aceite de palma podría ser utilizado como un componente de polioliol para la preparación de espuma de PU rígido (Pág. 221, Párr. 2. Characterization of Palm Oil-bases Polyol)³. Similarmente, es conocido que un polioliol de aceite de palma (PKO RBD) con un valor de hidroxilo de 350 a 370 mg KOH/g de muestra y peso molecular de 477 (...), donde las propiedades mecánicas de la espuma producida a partir del polioliol muestran buenos resultados en comparación con su homólogo convencional (Pág. 5541, Col. 2, último párrafo a Pág. 5542, Col. 1, primer párrafo)⁴. Adicionalmente, se conoce que espumas de poliuretano (PU) se pueden preparar usando un polioliol a base de aceite de palma (PO-p) (...), donde el movimiento de la cadena de poliuretano se vuelve más flexible a mayor contenido de PO-p en todo el polímero, lo que indica que las moléculas de monoglicéridos funcionan como segmentos blandos (...), lo cual, conduce al desarrollo de un nuevo tipo de espumas de poliuretano que utilizan el aceite de palma como materia prima (Resumen) (...) las espumas de poliuretano (PU) preparadas fueron de tipo semi-rígido (...) con una densidad aparente de 0,13 g/cm³ (...) La figura 5 muestra los cambios de la resistencia a la compresión (σ/p) y módulo de compresión (E/p), donde, cada parámetro para ambas series disminuye al aumentar el contenido de PO-p (Pág. 3815, Col. 2, Fig. 5, Párr. 3)⁵.

Por lo tanto, la persona versada en la materia enfrentada al problema técnico de disponer de una materia prima alternativa para obtener polioliols para producir un poliuretano con buenas propiedades físicas y mecánicas, y con una serie de conocimientos específicos de la invención, estaría motivada a realizar experimentación de rutina e incluir un polioliol de aceite de palma con un peso molecular entre 374 y 3366 con un número de hidroxilo entre 50 y 450 mg KOH/g en el proceso que se da a conocer en D1 y D3, para disponer de un polioliol adecuado para obtener un poliuretano deseado con buenas propiedades físicas y mecánicas, tal como se encuentra reclamado en la reivindicación 1 de la solicitud, motivo por el cual se considera obvia. Cabe decir, que la solución al anterior problema técnico objetivo se encuentra dentro de un diseño de procesos, lo cual se encuentra dentro de la práctica habitual de la persona versada en la materia que trabaje en la fabricación de poliuretanos.

Por su parte, la reivindicación 2 no menciona características inventivas adicionales tampoco se pueden considerar inventivas.

De igual manera, la reivindicación dependiente 3 no menciona características técnicas tangibles adicionales que puedan brindarle nivel inventivo al objeto de la reivindicación 2, puesto que estas se encuentran redactadas en términos de resultados.

3 Artículo 2: S Chuayjuljit, Et al. Preparation and Properties of Palm Oil-based Rigid Polyurethane Nanocomposites Foams. Journal of Reinforced Plastics and Composites. Vol. 29. No. 2. 27 de Noviembre de 2008. Págs. 218 a 224.

4 Artículo 3: K.H. Badri, Z. Othman, S.H. Ahmad. Rigid polyurethane foams from oil palm resources. [Journal of Materials Science](#). Agosto 2004, Volume 39. Págs. 5541-5542.

5 Artículo 4: Ryohei tanaka et al. Preparation and characterization of polyurethane foams using a palm oil-based polyol. Bioresource Technology, Elsevier Bv, GB. Vol. 99, No. 9. 22 de febrero de 2008. Págs. 3810 -3816.

6. Conclusión

Los requisitos de Patentabilidad de la presente solicitud están afectados así:

Ítem	Documento	Reivindicaciones afectadas	Requisito que afecta
D1	US 2009/0209441	1 a 3	Nivel Inventivo
D3	Artículo 1	1	Nivel inventivo

7. Respuesta a los argumentos del señor solicitante

Argumentos con respecto a la claridad de la solicitud

El señor solicitante argumenta que “...las propiedades medidas en esta reivindicación (densidad, Módulo de Young y Esfuerzo máximo) son ampliamente utilizadas en las caracterización de materiales y dentro de ellos los poliuretanos. Para el módulo de Young y esfuerzo máximo es común medirlos haciendo una prueba de compresión al material, tal y como se realizó en este caso para obtener valores reportados (...) Por lo tanto, tales expresiones deben mantenerse en el pliego reivindicatorio”.

Se reitera que las características como Densidad, Módulo de Young y Esfuerzo Máximo, corresponden a resultados a alcanzar dado que dichas características dependen de las características de los componentes, de las proporciones de dichos componentes, y del método de fabricación del poliuretano, tal como se enseña en la descripción así: Las rutas y modalidades descritas, permiten entonces obtener las espumas de poliuretano mediante la reacción de los polioles producidos con metilen difenil diisocianato (MDI). Para dicho propósito se mezcla el poliol obtenido con un poliol de cadena corta (dietilenglicol, 1,6 butanodiol), un catalizador (dibutyltin dilaurate, octoato de estaño, catalizadores de aminas terciarias, agua, un surfactante (a base de silicona u organosiloxanos)) y metilen difenil diisocianato (MDI). La reacción da lugar a la formación de espuma de poliuretano rígida (Pag. 10, Párrs. 4 y 5). Dependiendo del número de hidroxilo obtenido para el poliol pueden obtenerse espumas de poliuretano flexibles, semirrígidas y rígidas (Pág. 10, Párr. 5). Por lo tanto, dichas características no definen el producto, puesto que dichas características incluirían no solo la solución propuesta por el solicitante, sino todas las alternativas presentes o futuras que lleguen a ese resultado.

Argumentos con respecto a D1

El señor solicitante afirma que el “...el documento D1 se refiere a la obtención de polioles mediante la reacción de triglicéridos instaurados de origen vegetal y anhídrido maléico, pero en ninguna parte de D1 se hace mención o referencia específicamente al aceite de palma (...) no hay evidencia alguna que el sugiera a la persona con conocimientos medios en el campo técnico que el aceite de palma podrá ser útil en el proceso documento D1 (...)”

Se aclara que no tiene razón porque el documento D1 enseña que en la reacción entre el anhídrido maléico y triglicéridos de origen vegetal que contienen ácidos grasos insaturados, el triglicérido puede ser aceite de palma (Pág. 1, Párr. 10, Pág. 1, Párr. 12, Pág. 2, Párr. 26). Es así, que el documento D1 tiene suficiente antecedente con el problema técnico que trata la invención, dado que enseña la maleinización de ácidos grasos de aceites vegetales como por ejemplo aceite de palma, por lo cual, dichos argumentos no resultan persuasivos para desvirtuar el presente análisis de patentabilidad.

Argumentos con respecto al estudio de nivel inventivo

El señor solicitante reitera que “...La persona versada en la materia sabe con seguridad que no hay manera de predecir con certeza que el aceite de palma vaya a ser exitoso si es utilizado como materia prima en el método divulgado en el documento D1. Es así como la invención no resulta obvia en vista de las enseñanzas del arte previo citado”.

Es importante señalar que dado que la invención no muestra un efecto técnico que resulte sorprendente e inesperado en relación al estado de la técnica, la invención resulta obvia a la luz de las enseñanzas de los documentos D1 y D3, sin embargo, dada la respuesta de la solicitante donde se especifican las características del poliálcool base para la obtención del poliuretano, se trasladan otros documentos conocidos que hacen parte del conocimiento de la persona versada en la materia que demuestran que la invención no tiene altura inventiva.

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que debe dar respuesta dentro del término de sesenta (60) días contados a partir del día siguiente de la fecha de notificación de la presente comunicación. En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.

Se invita al solicitante se sirva indicar, si así lo considera, su renuncia al término faltante de sesenta (60) días para dar respuesta a este requerimiento y presentarla por escrito.

Finalmente, se le recuerda al solicitante que si como respuesta a este requerimiento llegara a modificar el capítulo reivindicatorio y éste contenga más de diez (10) reivindicaciones, no pagará la tasa de modificación voluntaria pero sí la correspondiente al pago por reivindicación adicional.

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e), del capítulo quinto del título primero de la Circular Única No. 10 de 2001.



JOSÉ LUIS SALAZAR LÓPEZ
Director de Nuevas Creaciones (c)

El anterior requerimiento fue notificado por fijación en lista, de fecha 2015-11-24

Elaboró: Yenny Marcela Campos Borda

Revisó: Olga Ximena Benavides Salazar

Yenny Campos

Search history

Search 1: TAC=(polyol and palm oil and hydroxyl and molecular weight) (Results 50)

Search 2: TAC=(polyol and palm oil and hydroxyl and molecular weight and polyurethane) (Results 23)

Search 3: TAC=(polyol and palm oil and hydroxyl and molecular weight and polyurethane) (Results 23)

Title: **POLYURETHANES** PREPARED FROM GLYCERIDE REACTION PRODUCTS

Abstract: Source: US3637539A ABSTRACT OF THE DISCLOSURE A new group of **polyurethanes** are described and claimed together with methods for their production, the said **polyurethanes** being the reaction products of a polyisocyanate with a **polyol** component, of which latter a substantial part is a reaction mixture of hydrocarbon fatty acid glyceride with dialkanolamine, in which at least about half of the fatty acid has been converted into alkanol-

Classifications:

International (IPC 8-9): B29C70/68 C08G18/36 C08G18/38 C23C30/00 (Advanced/Invention); B29C70/00 C08G18/00 C23C30/00 (Core/Invention)

International (IPC 1-7): B29G B29H9/10 C08C17/08 C08D13/08 C08F47/10 C08G18/14 C08G18/28 C08G18/36 C08G18/38 C08G22/04 C08G22/06 C08G22/08 C08G22/44 C08L75/04 C10G7/00 C22C29/00 C22F1/18

CPC: C08G2101/0025 C08G2101/005 C08G2101/0058 C08G18/36 C08G18/3825 C23C30/005

European: C08G18/36 C08G18/38F5B C23C30/00B M08G101/00F M08G101/00K3 M08G101/00K5

US: 260/2.5 260/2.5AM 521/129 521/167 528/74.5

Family:

Publication number	Publication date	Application number	Application date
AT297320 B	19720327	AT19680009842	19681009
AT297321 B	19720327	AT19680009946	19681011
BE722285 A	19690414		19681014
BE722287 A	19690414		19681014
CH439763 A	19670715	CH19630005730	19630507
CH553232 A	19740830	CH19680015267	19681011
CH553835 A	19740913	CH19680015266	19681011
CS158226 B2	19741015	CS19680007024	19681011
CS174764 B2	19770429	CS19680007023	19681011
DE1247671 B	19670817	DE1962B067199	19620511
DE1802500 A1	19690529	DE19681802500	19681011
DE1802503 A1	19690529	DE19681802503	19681011
DK131945 B	19750929	DK19680004816	19681007
DK131945 C	19760223	DK19680004816	19681007
DK133816 B	19760726	DK19680004817	19681007
DK133816 C	19761213	DK19680004817	19681007
ES359102 A1	19700701	ES19680359102	19681011
ES359104 A1	19700701	ES19680359104	19681011
FI49314 B	19750131	FI19680002906	19681014
FI49314 C	19750512	FI19680002906	19681014
FI49727 B	19750602	FI19680002907	19681014
FI49727 C	19750910	FI19680002907	19681014
FR1588352 A	19700410		19681014
FR1588353 A	19700410		19681014
GB1247671 A	19710929	GB19680008268	19680220
GB1248919 A	19711006	GB19680047716	19671012
IE32410 B	19730725	IE19680001201	19681008
IE32410 L	19690412	IE19680001201	19681008
IE32893 B	19740109	IE19680001200	19681008
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IL31633 A0	19690430	IL19690031633	19690216
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LU57048 A	19690625		19681009
LU57049 A	19690625		19681009
NL161471 B	19800215	NL19680014676	19681014
NL161471 C	19800215	NL19680014676	19681014
NL161472 B	19800215	NL19680014676	19681014
NL161472 C	19800215	NL19680014676	19681014
NL6814676 A	19690415	NL19680014676	19681014
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PL79351 P	19750630	PL19680129471	19681011
PL80673 P	19750830	PL19680129472	19681011
SE347278 B	19720731	SE19680013774	19681011
SE347596 B	19720807	SE19680013775	19681011
US3637539 A	19720125	US19680765027	19681004
US3637540 A	19720125	US19680765641	19681007
YU237668 A	19741031	YU19680002376	19681011
YU32764 B	19750630	YU19680002376	19681011

Priority:

DE1962B067199 19620511 GB19670046671 19671012 GB19680047715 19671012
GB19680008263 19680220 GB19680008268 19680220 GB19680008286 19680220

Probable Assignee: BETEILIGUNGS AND PATENTVERW GMBH

Assignee(s): (std): ANDERSEN H ; ANDERSEN H C ; ANDERSEN HANS CHRISTIAN ; ANDERSON H ; ANDERSON H C ; B STUREL ; ANDREA EMILIO E WOLFF ; ANDREA EMILIO EGGERSLURA WOLFF ; ALDO MARIA ANDREA EMILO EGGERS ; BETEILIGUNGS AND PATENTVERW GMBH ; EGGERS LURA ALDO MARIA ANDREA ; EGGERS LURA A ; WOLFF PER ; HENNING KAABER ; WOLFF PER ; KAABER HENNING ; KABER H ; WOLFF F ; KAABER ; KAABER H ; WOLFF P ; HC ANDERSEN ; WOLF P ; KAAER H ; WOLFF

Assignee(s): PER WOLFF ; PER AKE HALLBERG ; KAABER SVEND HENNING ; KAABER H DK ; ANDREA EMILIO E ; BETEILIGUNGS UND PATENTVERWALTUNGSGESELLSCHAFT MIT BESCHRAENKTER HAFTUNG ; HANS CHRISTIAN ANDERSEN KASTANIENBAUM ZWITSERLAND PER WOLFF EN HENNING KAABER BEIDEN FARUM DENEMARKEN ; H C ANDERSON ; HANS CHRISTIAN ANDERSEN ; HANS CHRISTIAN ANDERSEN KASTANIENBAUM ZWITSERLAND ; EGGERS LURA ALDO MARIA ANDREA EMILIO ; ALDO MARIA ANDREA EMILO EGGERS LURA ; BETEILIGUNGS UND PATENTVERWALTUNGSGESELLSCHAFT MIT

Inventor(s): (std): WOLFF PER ; WOLFF P ; SCHUHMACHER DR ING GUENTER ; LARSEN HANS OLE ; LARSEN H O ; KAHRMANN HELMUT ; KAABER HENNING ; HELMUT KAHRMANN ; EGGERS LURA ALDO MARIA ANDREA ; DR SCHUHMACHER GUENTER ING ; WOLFF F ; LARSEN J ; LARSEN H

Inventor(s): LARSEN H DK ; ALDO MARIA ANDREA EMILO EGGERS LURA ; HANS OLE LARSEN ; ING SCHUHMACHER GUENTER DR ; HENNING KAABER ; PER WOLFF

Agent(s): REINHOLD COHN AND PARTNERS

Title: THERMAL TRANSFER RECORDING MEDIUM

Abstract: Source: US4707406A A thermal transfer recording medium comprising (i) a support, (ii) a heat-fusible colorant layer and (iii) adhesion layer between said support and said colorant layer; said adhesion layer containing at least one resin selected from the group (A) consisting of a **polyurethane** resin, a phenoxy resin, a polyester resin and a polycarbonate resin, and at least one copolymer selected from the group (B) consisting of a vinyl acetate copolymer and an acrylate copolymer. According to the medium of this invention, adhesive force between the support and the colorant layer can be consolidated and thus good pattern printing can be obtained without film peel-off for a large number of times even when applied power may be increased.

Classifications:

International (IPC 8-9): B41M5/28 B41M5/30 B41M5/337 B41M5/382 B41M5/42

B41M5/44 (Advanced/Invention);

B41M5/40 B41M5/42 (Advanced/Non-invention);

B41M5/26 B41M5/28 B41M5/30 B41M5/40 (Core/Invention)

International (IPC 1-7): B41M5/18 B41M5/26 B41M5/40

CPC: Y10S428/913 Y10S428/914 B41M5/44 B41M5/423 Y10T428/31507 Y10T428/31551

Y10T428/31565 Y10T428/31587 Y10T428/31591 Y10T428/31605 Y10T428/31681

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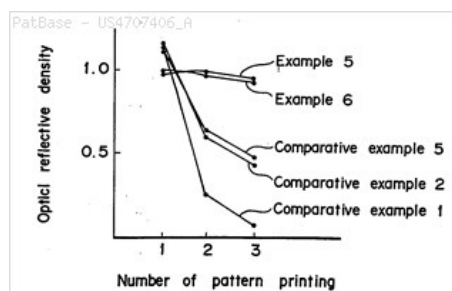
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European: B41M5/40C2 B41M5/44 L41M5/42B L41M5/44

US: 428/195 428/32.61 428/32.8 428/336 428/412 428/423.1 428/423.7 428/424.8

428/425.1 428/425.8 428/458 428/461 428/463 428/480 428/481 428/483 428/484

428/488.1 428/488.4 428/500 428/511 428/516 428/518 428/522 428/913 428/914



Family:

Publication number	Publication date	Application number	Application date
JP1635012 C3	19920120	JP19850002642	19850112
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JP1680073 C3	19920713	JP19850008447	19850122
JP2058118 B4	19901206	JP19850002642	19850112
JP2059799 B4	19901213	JP19850002643	19850112
JP3042594 B4	19910627	JP19850008447	19850122
JP61162390 A2	19860723	JP19850002642	19850112
JP61162391 A2	19860723	JP19850002643	19850112
JP61179787 A2	19860812	JP19850008447	19850122
US4707406 A	19871117	US19850815249	19851231

Priority:

JP19850002642 19850112 JP19850002643 19850112 JP19850008447 19850122

Probable Assignee: KONISHIROKU PHOTO IND

Assignee(s): (std): KONISHIROKU PHOTO IND

Assignee(s): KONISHIROKU PHOTO IND CO ; KONISHIROKU PHOTO IND CO LTD ; KONISHIROKU PHOTO INDUSTRY CO ; KONISHIROKU PHOTO INDUSTRY CO LTD ; KONICA CORP

Inventor(s): (std): ABE TAKAO ; INABA YOSHIHIRO ; KOSHIZUKA KUNIHIRO ; MAEHASHI TATSUICHI

Title: Trimethylolheptanes and use thereof

Abstract: Source: US4935488A Novel trimethylolheptanes having three highly reactive **hydroxy** groups are provided. They are useful as raw materials for the production of polyesters for use in or as raw materials or modifiers for paints, inks, adhesives, coating compositions and molding resins. Uses for the trimethylolheptanes are also provided.

Classifications:

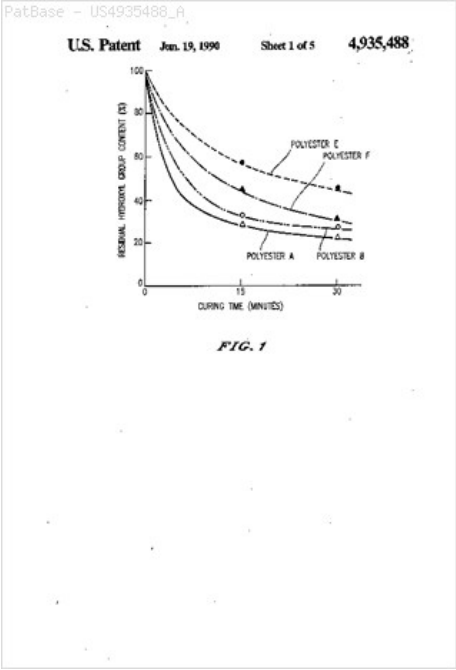
International (IPC 8-9): C07C27/00 C07C29/14 C07C29/141 C07C29/16 C07C31/22 C07C67/00 C07C69/34 C07C69/54 C08F290/00 C08F299/00 C08G18/32 C08G63/02 C08G63/12 C08G63/16 C08G63/20 C08G63/46 C08G63/48 C08K5/10 C09D167/00 C09D167/08 C09D175/00 C09D175/06 C09J167/00 (Advanced/Invention); C08G18/32 C08G63/12 C09D167/00 C09J167/00 (Advanced/Non-invention); C08G18/00 C08G63/00 C09D167/00 C09D167/08 C09D175/00 C09D175/06 C09J167/00 (Core/Invention); C08G18/00 C08G63/00 C09D167/00 C09J167/00 (Core/Non-invention)

International (IPC 1-7): C07C29/14 C07C29/141 C07C29/16 C07C31/22 C07C67/08 C07C69/34 C07C69/54 C08F120/20 C08F220/20 C08F299/00 C08G18/32 C08G63/02 C08G63/12 C08G63/20 C08G63/48 C08K5/10 C09D167/00 C09D175/00 C09D175/06 C09J167/00

CPC: C07C31/22 C08G63/16 C08G63/48 C09D167/00

European: 124B69/54 C07C31/22 C08G63/16 C08G63/48 C09D167/00

US: 525/437 525/440 525/440.03 525/445 525/447 525/451 528/272 528/295.5 528/296 528/302 528/304 528/308.6 528/392 528/396 560/190 560/201 560/204 568/853



Family:

Publication number	Publication date	Application number	Application date
CA1329810 A1	19940524	CA19890597255	19890420
DE68917352 D1	19940915	DE19896017352	19890419
EP0338540 A2	19891025	EP19890107060	19890419
EP0338540 A3	19910703	EP19890107060	19890419
EP0338540 B1	19940810	EP19890107060	19890419
JP1268655 A2	19891026	JP19880099115	19880420
JP1299241 A2	19891204	JP19880127678	19880524
JP2193945 A2	19900731	JP19890012667	19890120
JP2194018 A2	19900731	JP19890012666	19890120
JP2622151 B2	19970618	JP19880127678	19880524
JP2667896 B2	19971027	JP19890012666	19890120
JP2824060 B2	19981111	JP19880099115	19880420
US4935488 A	19900619	US19890340791	19890420

Priority:

JP19880099115 19880420 JP19880127678 19880524 JP19890012666 19890120
JP19890012667 19890120 CA19890597255 19890420

Probable Assignee: KURARAY CO

Assignee(s): (std): KURARAY CO

Assignee(s): KURARAY CO LTD ; KURARAY CO LTD KURASHIKI OKAYAMA JP ; MATSUMOTO YOICHI ; TOKITOH YASUO ; OMATSU TOSHIHIRO ; YANO MAKOTO ; YOSHIMURA NORIAKI ; HIRAI KOJI ; ISHIDA MASAO ; KUBO KEIJI

Inventor(s): (std): HIRAI KOJI ; ISHIDA MASAO ; KUBO KEIJI ; MATSUMOTO YOICHI ; OMATSU TOSHIHIRO ; TOKITO YASUO ; TOKITOH YASUO ; YANO MAKOTO ; YOSHIMURA NORIAKI

Inventor(s): YOSHIMURA NORIAKI KURASHIKI CITY OKAYAMA JP ; YANO MAKOTO KURASHIKI CITY OKAYAMA JP ; TOKITOH YASUO KURASHIKI CITY OKAYAMA JP ; OMATSU TOSHIHIRO KURASHIKI CITY OKAYAMA JP ; MATSUMOTO YOICHI KAMISU MACHI KASHIMA DISTRICT IBA ; MATSUMOTO YOICHI KAMISU MACHI KASHIMA DISTRICT... ; KUBO KEIJI KURASHIKI CITY OKAYAMA JP ; ISHIDA MASAO KURASHIKI CITY OKAYAMA JP ; HIRAI KOJI KURASHIKI CITY OKAYAMA JP

Agent(s): KIRBY EADES GALE BAKER

Designated states: BE CH DE FR GB IT LI NL

Title: **Polyol** blends for producing hydrocarbon-blown **polyurethane** and polyisocyanurate foams

Abstract: Source: US5922779A Disclosed are aromatic polyester **polyols**, polyester **polyol** resin blends, methods for preparing such compositions and **polyurethane** and polyisocyanurate foams made using the compositions, wherein the resin blends generally comprise: (a) an aromatic polyester **polyol** formed by a reaction between a phthalic acid based material; a hydroxylated material having a functionality of at least 2; and a hydrophobic material; (b) a nonionic surfactant; and (c) a C4-C7 hydrocarbon blowing agent.

Classifications:

International (IPC 8-9): C08G18/36 C08G18/40 C08G18/42 C08G18/66 C08G18/72 C08J9/14 (Advanced/Invention)

International (IPC 1-7): C08G18/42 C08J9/14

CPC: C08G18/4018 C08G18/4288 C08G2101/0025 C08G2101/005 C08J9/141 C08J2205/052 C08J2205/10 C08J2375/04 C08J9/142

European: C08G18/40A2 C08G18/42M C08J9/14B C08J9/14D M08G101/00F M08G101/00K3 M08J205/052 M08J205/10 M08J375/04

US: 252/182.24 521/114 521/131 521/172

Family:

Publication number	Publication date	Application number	Application date
AT215101 E	20020415	AT19980950968T	19981007
AU199896877 A1	19990503	AU19980096877	19981007
AU200042113 A5	20001114	AU20000042113D	20000407
CA2305276 AA	20000410	CA19982305276	19981007
CA2305276 C	20081118	CA19982305276	19981007
DE69804483 D1	20020502	DE19986004483	19981007
DE69804483 T2	20030102	DE19986004483T	19981007
EP1023351 A1	20000802	EP19980950968	19981007
EP1023351 B1	20020327	EP19980950968	19981007
EP1171500 A1	20020116	EP20000921849	20000407
ES2172928 T3	20021001	ES19980950968T	19981007
US5922779 A	19990713	US19970949239	19971010
US6359022 BA	20020319	US19990289043	19990409
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WO9919377 A1	19990422	WO1998US21077	19981007

Priority:

US19970949239 19971010 WO1998US21077 19981007 US19990289043 19990409

WO2000US09281 20000407

Probable Assignee: STEPAN CO

Assignee(s): (std): HICKEY F LEO ; ROONEY KEVIN L ; STEPAN CO ; STEPAN COMPANY

Assignee(s): HICKEY F ; STEPAN CO NORTHFIELD

Inventor(s): (std): F LEO HICKEY ; HICKEY F LEO ; HICKEY LEO ; ROONEY KEVIN L

Inventor(s): KEVIN L ROONEY ; HICKEY F

Agent(s): MBM INTELLECTUAL PROPERTY LAW LLP

Designated states: AE AG AL AM AT AU AZ BA BB BE BF BG BJ BR BY CA CF CG CH CI CM CN CR CU CY CZ DE DK DM DZ EE ES FI FR GA GB GD GE GH GM GN GR GW HR HU ID IE IL IN IS IT JP KE KG KP KR KZ LC LI LK LR LS LT LU LV MA MC MD MG MK ML MN MR MW MX NE NL NO NZ PL PT RO RU SD SE SG SI SK SL SN SZ TD TG TJ TM TR TT TZ UA UG US UZ VN YU ZA ZW

Title: TRANSESTERIFIED **POLYOL** HAVING SELECTABLE AND INCREASED FUNCTIONALITY AND URETHANE MATERIAL PRODUCTS FORMED USING THE **POLYOL**

Abstract: Source: US2002058774A The present invention includes a **polyol** produced according to the process comprising reacting a multifunctional alcohol with a first multifunctional component to form a reaction product and reacting the reaction product with a vegetable oil to form a **polyol**. The present invention also relates to the material comprising the reaction product of an A-side and a B-side, wherein the A-side comprises an isocyanate and the B-side comprises the product formed by the process comprising the steps of reacting a multifunctional alcohol with a first multifunctional component to form a precursor **polyol** and then reacting the precursor **polyol** with a vegetable oil to form a vegetable based **polyol** with selectable functionality.

Classifications:

International (IPC 8-9): B05D1/00 B05D1/02 B05D1/34 B05D3/02 B05D5/00 B05D7/00 B32B33/00 B32B37/00 B32B37/12 B32B37/14 B32B37/24 C08G18/00 C08G18/10 C08G18/28 C08G18/32 C08G18/36 C08G18/40 C08G18/42 C08G18/48 C08G18/64 C08G18/65 C08G18/66 C08G18/76 C08H5/00 C08H9/00 C08J9/00 C08J9/14 C08J9/34 C08L67/08 C08L75/00 C08L75/08 C09K3/00 D05C15/04 D06N7/00 (Advanced/Invention);

B32B3/02 C08G101/00 (Advanced/Non-invention);

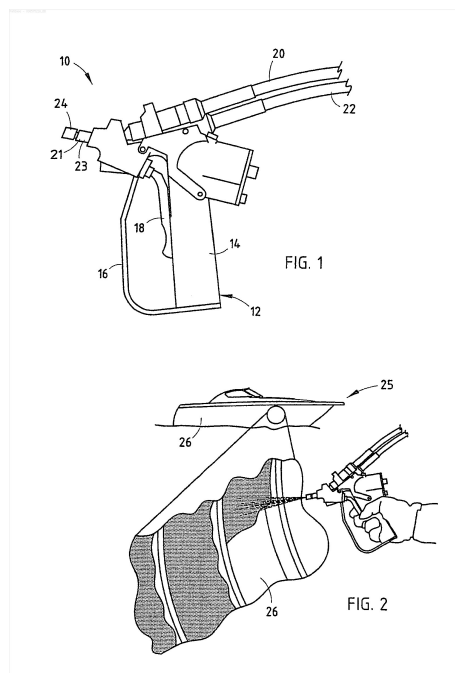
B32B33/00 C08G18/00 C08J9/00 D05C15/00 D06N7/00 (Core/Invention)

International (IPC 1-7): A46D1/00 B05D1/02 B05D1/34 B05D3/02 B32B27/00 B32B3/02 B32B3/26 B32B31/00 B32B31/10 B32B33/00 C08B37/00 C08G18/00 C08G18/32 C08G18/36 C08G18/40 C08G18/60 C08G18/64 C08G18/65 C08G18/76 C08H5/00 C08J9/00 C08J9/34 C08K3/00 C08L67/08 C08L75/00 C08L75/08 D03D27/00 D04H11/00 D05C15/04 D05C17/00 G08H5/00

CPC: C08J9/0023 D06N7/0071 D06N2205/20 D06N7/0063 D06N2203/068 D06N2205/04 D06N7/0086 D06N2203/042 C08J9/14 C08G18/36 C08G18/6696 C08G2101/0016 C08J2375/04 C08G18/3206 C08G18/664 C08G18/7671 C08G2101/0033 C08G18/6607 Y10T428/23979 Y10T428/23986 Y10T428/23993 Y10T428/31551 C08G18/4288 C08G18/10 C08G18/4018 C08G2101/0008 C08G2101/0025 C08G2101/0083 Y10T428/24995

European: C08G18/10 C08G18/32A2 C08G18/36 C08G18/40A2 C08G18/42M C08G18/66C2 C08G18/66M2A C08G18/66P6 C08G18/76D2B C08J9/00K4 C08J9/14 D06N7/00B6 M08G101/00B M08G101/00D M08G101/00F M08G101/00H M08G101/00P M08J375/04

US: 156/309.6 156/309.600S 156/322 156/322S 156/72 156/72P 252/182.24 252/182.240S 252/182.28 427/243 427/244 427/244P 427/372.2 427/372.200P 427/384 427/384S 427/385.5 427/389.9 427/394 427/402 427/402S 427/421.1 427/426 427/426S 427/427.2 427/427.3 427/427.4 428/304.4 428/304.400S 428/423.1 428/423.100P 428/85 428/85S 428/95 428/95P 428/96 428/96S 428/97 521/109.1 521/110 521/117 521/137 521/151 521/155 521/170 521/172 521/173 521/174 521/51 521/84.1 524/589 525/137 525/151 525/155 525/51 525/841 527/301 527/301P 528/44 528/44P 528/44S 528/55 528/65 528/74.5 528/74.500P 528/75 528/85 536/119 536/119S 536/123.1 536/123.100S 536/53 536/53S 554/169 554/24 554/3 554/30 554/30S



Family:

Publication number	Publication date	Application number	Application date
AT286929 E	20050115	AT19990946975T	19990917
AU199959268 A1	20000403	AU19990059268	19990917
AU199959268 A5	20000403	AU19990059268	19990917
AU766760 B2	20031023	AU19990059268	19990917
BRPI9913784 A	20010529	BR1999P113784	19990917
BRPI9913784 B1	20100713	BR1999P113784	19990917
CA2344378 AA	20000323	CA19992344378	19990917
CA2344378 C	20120904	CA19992344378	19990917
CN1245428 C	20060315	CN19998012274	19990917
CN1323326 A	20011121	CN19998012274	19990917
DE69923210 D1	20050217	DE19996023210	19990917
DE69923210 T2	20060105	DE19996023210T	19990917
DE69923210 T3	20080724	DE19996023210T	19990917
DK1127086 T3	20050523	DK19990946975T	19990917
DK1127086 T4	20080513	DK19990946975T	19990917
EP1127086 A1	20010829	EP19990946975	19990917
EP1127086 A4	20010919	EP19990946975	19990917
EP1127086 B1	20050112	EP19990946975	19990917
EP1127086 B2	20080109	EP19990946975	19990917
ES2235516 T3	20050701	ES19990946975T	19990917
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GT200000029 A	20010907	GT20000000029	20000316
JP2002524627 T2	20020806	JP20000570219T	19990917
MXPA01002680 A1	20020408	MX2001PA02680	20010314
PT1127086 T	20050429	PT19990946975T	19990917
TWI257399 B	20060701	TW20000104795	20000515
US2002058774 AA	20020516	US20010944212	20010831
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US2002119321 AA	20020829	US20010004733	20011204
US2002121328 AA	20020905	US20010974301	20011010
US2003105178 AA	20030605	US20020253252	20020924
US2003191274 AA	20031009	US20010974303	20011010
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US2004209971 AA	20041021	US20040843943	20040512
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US2005131092 AA	20050616	US20050042972	20050125
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US2005182228 AA	20050818	US20050108368	20050418
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US2009223620 AA	20090910	US20090470630	20090522
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US6180686 BA	20010130	US19980154340	19980917
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US6881763 BB	20050419	US20030639109	20030812
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US6979477 BB	20051227	US20010004733	20011204
US7063877 BB	20060620	US20010974302	20011010
US7084230 BB	20060801	US20040843943	20040512
US7537665 BB	20090526	US20050181419	20050714
US7595094 BB	20090929	US20050042980	20050125
US8062710 BB	20111122	US20090569457	20090929
US8333905 BA	20121218	US20070932943	20071031
US8449946 BB	20130528	US20110301305	20111121
US8575226 BB	20131105	US20050042972	20050125
WO0015684 A1	20000323	WO1999US21511	19990917

Priority:

US19980154340	19980917	US19990646356	19990917	WO1999US21511	19990917
US20000230463P	20000906	US20010099743	20011010	US20010974302	20011010
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US20000239161P	20001010	US20000251068P	20001204	US20000646356	20000914
US20070933049	20071031	US20050181419	20050714	US20090470630	20090522
US20090569457	20090929	US20050042980	20050125	US20040843943	20040512
US20050042972	20050125	US20110301305	20111121	US20010004733	20011204
US20030634026	20030804	US20030639303	20030812	US20050108368	20050418
US20030639109	20030812	US20020253252	20020924	US20070932943	20071031

Probable Assignee: RHINO LININGS CORP

Assignee(s): (std): KREIFELS LES P ; KURTH RICHARD A ; KURTH THOMAS M ; RHINO LININGS CORP ; SOUTH DAKOTA SOYBEAN PROCESSORS LLC ; TANDEM POLYMERS INC ; TURNER ROBERT B ; URETHANE SOY SYSTEMS CO ; URETHANE SOY SYSTEMS CO I ; URETHANE SOY SYSTEMS COMPANY INC ; VAN THOMME TODD A

Assignee(s): URETHANE SOY SYSTEMS CO INC DOVER ; COMERICA BANK ; URETHANE SOY SYSTEMS CO INC ; URETHANE SOY SYSTEMS COMPANY ; URETHANE SOY SYSTEMS CORP

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Designated states: AL AM AT AU AZ BA BB BE BF BG BJ BR BY CA CF CG CH CI CM CN CU CY CZ DE DK EE ES FI FR GA GB GD GE GH GM GN GR GW HR HU ID IE IL IN IS IT JP KE KG KP KR KZ LC LI LK LR LS LT LU LV MC MD MG MK ML MN MR MW MX NE NL NO NZ PL PT RO RU SD SE SG SI SK SL SN SZ TD TG TJ TM TR TT TZ UA UG US UZ VN YU ZW

Title: Process for the production of oleochemical **polyols**

Abstract: Source: US2002099230A The present invention is related to an improved process for obtaining oleochemical **polyols** from oils, principally of a vegetable origin. The **polyols** obtained consist of a mixture of ethers, esters, primary and secondary alcohols and have the characteristic of being self-compatible with the new blowing agents: hydrochlorofluorocarbons, HCFC's, hydrofluorocarbons, HFC's and hydrocarbons, HC's of a low **molecular weight** and low boiling point. The process of this invention is characterized because it uses Lewis type acids in such a way that they do not form precipitates and therefore it is not necessary to remove precipitates from the **polyol**. The process of the present invention makes it possible to obtain **polyols** with high functionality and controlled reactivity. These characteristics render the product suitable for use as a raw material in the production process of rigid foams, such as **polyurethane** for spraying, refrigeration and imitation wood, coatings, among others.

Classifications:

International (IPC 8-9): C08G18/36 C08G18/42 C08G18/48 C08G65/12 C08G65/26 (Advanced/Invention);
C08G18/00 C08G65/00 (Core/Invention)
International (IPC 1-7): C0731/12 C07C31/18 C07C51/16 C08F283/00
CPC: C08G18/36 C08G18/4288 C08G18/4891 C08G65/12 C08G65/2609 C08G65/2624 C08G65/2675 C08G2101/0025 C08G2101/005
European: C08G18/36 C08G18/42M C08G18/48T C08G65/12 C08G65/26C1L C08G65/26F1L C08G65/26P3F M08G101/00F M08G101/00K3
US: 521/130 521/137 525/530 549/525 554/124 554/132 554/149 554/170 554/213 554/227

Family:

Publication number	Publication date	Application number	Application date
MXPA00011394 A1	20030312	MX2000PA11394	20001121
US2002099230 AA	20020725	US20010989464	20011121
US6548609 BB	20030415	US20010989464	20011121

Priority:

MX2000PA11394 20001121 MX2000PA01394 20001121

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Inventor(s): RAMIREZ DE ARELLANO ABURTO NICOLAS

Title: **POLYURETHANE** DISPERSIONS BASED ON FATTY ACID DIALKANOLAMIDES

Abstract: Source: US2003191273A The invention relates to aqueous **polyurethane** dispersions based on fatty acid dialkanolamides, to a process for preparing them and to use as coating compositions.

Classifications:

International (IPC 8-9): C08G18/00 C08G18/08 C08G18/12 C08G18/38 C08G18/66 C08G18/68 C08G18/75 C09D175/04 C09D175/08 C09D175/12 C09D175/14 (Advanced/Invention);
C08G18/00 C09D175/12 C09D175/14 (Core/Invention);
C08G (Subclass/Invention);
C09D (Subclass/Non-invention)

International (IPC 1-7): C08G18/00 C08G18/08 C08G18/32 C08G18/38 C08G18/60 C08G18/75 C08J3/03 C09D175/04 C09D175/08 C09D5/02 C09D5/12

CPC: C08G18/0823 C08G18/12 C08G18/3825 C08G18/6696 C08G18/683 C09D175/12 C09D175/14

European: C08G18/08B6C C08G18/12 C08G18/38F5B C08G18/66P6 C08G18/68B C09D175/12 C09D175/14

US: 524/591 524/839 524/840 525/123 525/131 528/44 528/44P 528/49 528/71 528/75 528/85

Family:

Publication number	Publication date	Application number	Application date
AT322525 E	20060415	AT20030006281T	20030321
CN1275995 C	20060920	CN20031024376	20030404
CN1451672 A	20031029	CN20031024376	20030404
DE10215053 A1	20031023	DE20021015053	20020405
DE50302857 D1	20060518	DE20035002857	20030321
DK1350824 T3	20060717	DK20030006281T	20030321
EP1350824 A1	20031008	EP20030006281	20030321
EP1350824 B1	20060405	EP20030006281	20030321
ES2261808 T3	20061116	ES20030006281T	20030321
HK1057053 A1	20070504	HK20030109397	20031224
US2003191273 AA	20031009	US20030403222	20030331
US6710120 BB	20040323	US20030403222	20030331

Priority:
DE20021015053 20020405 DE20035002857 20030321

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Inventor(s): WEIKARD ; JAN WEIKARD ; R GERTZMANN C IRLLER J WICKARD ; ROLF GERTZMANN ; ROLF ROSCHU ; IRLE ; CHRISTOPH IRLE ; ERHARD LUHMANN ; GERTZMANN

Designated states: AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LI LU MC NL PT RO SE SI SK TR

Title: POLYESTER **POLYOLS** FOR **POLYURETHANE** ADHESIVES

Abstract: Source: US2006205909A A polyester **polyol** prepared from a composition including a phthalic acid based material containing more than 10 percent by weight of ortho-phthalic or derivatives thereof, an aliphatic dicarboxylic acid (e.g., dodecanedioic acid), and a **polyol** (e.g., a glycol). A **polyurethane** adhesive, such as a **polyurethane** reactive hot-melt adhesive, is made using the polyester **polyol**, which exhibits improved initial bonding strength, shortened setting time, and ability to bond to low surface energy substrates such as ABS. The methods to prepare the polyester **polyol** and the **polyurethane** adhesive, and the method to use them are also disclosed.

Classifications:

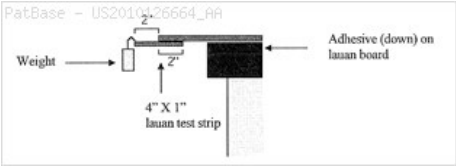
International (IPC 8-9): B32B37/12 C08G18/00 C08G18/12 C08G18/42 C09J175/06 (Advanced/Invention)

International (IPC 1-7): C08G18/42

CPC: C08G18/12 C08G18/4202 C08G18/4216 C08G2170/20

European: C08G18/12 C08G18/42A C08G18/42B2D5 M08G170/20

US: 156/331.7 156/331.700P 528/44 528/44P 528/52 528/52S 528/66 528/66S



Family:

Publication number	Publication date	Application number	Application date
US2006205909 AA	20060914	US20040546496	20040312
US2010126664 AA	20100527	US20100642566	20100205
WO04083274 A1	20040930	WO2004US07807	20040312

Priority:

US20030454222P 20030313	US20040546496 20040312	WO2004US07807 20040312
US20100642566 20100205	US20060546496 20060405	

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Assignee(s): STEPAN COMPANY

Inventor(s): (std): O BRIEN MICHAEL E

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Agent(s): MCANDREWS HELD AND MALLOY LTD

Designated states: AE AG AL AM AT AU AZ BA BB BE BF BG BJ BR BW BY BZ CA CF CG CH CI CM CN CO CR CU CY CZ DE DK DM DZ EC EE EG ES FI FR GA GB GD GE GH GM GN GQ GR GW HR HU ID IE IL IN IS IT JP KE KG KP KR KZ LC LK LR LS LT LU LV MA MC MD MG MK ML MN MR MW MX MZ NA NE NI NL NO NZ OM PG PH PL PT RO RU SC SD SE SG SI SK SL SN SY SZ TD TG TJ TM TN TR TT TZ UA UG US UZ VC VN YU ZA ZM ZW

Title: **POLYOLS** AND **POLYURETHANES**, POLYURETHANEFORMS USING THE SAME

Abstract: Source: US2009023823A The present invention relates to a preparing method of **polyols** and **polyurethane**, polyurethaneforms using the same by depolymerizing the polyester, polyamide and **polyurethane** with the polymeric fatty acid monopoly **hydroxyl** alcoholide, and additionally react with the polybasic acid, **polyol** and amine to prepare acid value of 0.5~1 DKOH/g, **hydroxyl** value of 10~500 DKOH/g, and amine value of 1~50 DKOH/g in **polyol**, and **polyurethane** and polyurethaneforms using the same. This is to transform the double bond of the unsaturated fatty acid from the component of the oils and fats in conjugate double bond to induce the Diels-Alder reaction, and with the improvement of the reactivity to form stability combination in chemical structure to prevent the separate leaching appearance of fatty and fatty oil from the final product, and having the fine compatibility with the polyether-**polyol** as well as transparent and storage stability. Furthermore, it has 100 percent of solid with very low viscosity at the room temperature for easy handling while having a great reactivity with the isocyanate that this preparing **polyol** having excellent chemical and mechanical properties. And, in particular, by recycling the waste edible oil and waste synthetic resin that can be employed as industrially useful material for environment-friendly and economical advantage.

Classifications:
International (IPC 8-9): C08G18/36 C08J11/04 C08J11/18 C08J11/24 (Advanced/Invention);
C08G18/36 C08J11/18 (Advanced/Non-invention);
C08G18/00 C08J11/00 (Core/Invention)
CPC: Y02W30/706 C08J11/22 C08G18/4018 C08G18/4288 C08G18/4833 C08G18/606 C08G18/6492 C08G2101/0025 C08J2367/02 C08J2375/04 C08J2377/00
European: C08G18/40A2 C08G18/42M C08G18/48F C08G18/60D C08G18/64V C08J11/22 M08G101/00F M08J367/02 M08J375/04 M08J377/00
US: 521/40 521/40.5 521/48.5 521/48.500P 521/49 521/49.5 521/49.8 528/272 528/295.5 528/308.2 528/332 528/335 528/480 528/486 528/495 528/74.5

Family:

Publication number	Publication date	Application number	Application date
CN101090935 A	20071219	CN200580042409	20051010
KR101168766 B1	20120726	KR20040081160	20041011
KR20060032121 A	20060414	KR20040081160	20041011
US2009023823 AA	20090122	US20050577050	20051010
US8030364 BB	20111004	US20050577050	20051010
WO06080743 A1	20060803	WO2005KR03366	20051010

Priority:
KR20040081160 20041011 WO2005KR03366 20051010

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Inventor(s): KIM HOE SENG

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Designated states: AE AG AL AM AT AU AZ BA BB BE BF BG BJ BR BW BY BZ CA CF CG CH CI CM CN CO CR CU CY CZ DE DK DM DZ EC EE EG ES FI FR GA GB GD GE GH GM GN GQ GR GW HR HU ID IE IL IN IS IT JP KE KG KM KP KZ LC LK LR LS LT LU LV LY MA MC MD MG MK ML MN MR MW MX MZ NA NE NG NI NL NO NZ OM PG PH PL PT RO RU SC SD SE SG SI SK SL SM SN SY SZ TD TG TJ TM TN TR TT TZ UA UG US UZ VC VN YU ZA ZM ZW

Title: **POLYURETHANE** FOAMS MADE WITH VEGETABLE OIL HYDROXYLATE, POLYMER **POLYOL** AND ALIPHATIC POLYHYDROXY ALCOHOL

Abstract: Source: US2006235100A The present invention provides **polyurethane** foams made from a polyisocyanate and a **polyol** component containing a polymer **polyol** (PMPPO), a vegetable oil hydroxylate and an aliphatic polyhydroxy alcohol, and optionally a non-vegetable oil-based **polyol**. The vegetable oil hydroxylates are environmentally-friendly, bio-based **polyols**. The inclusion of low amounts of a polymer **polyol** unexpectedly results in a foam having significantly improved tear strength. The combination of polymer **polyol** and aliphatic polyhydroxy alcohol provides improved foam processing while maintaining or improving tear strength of the foam.

Classifications:

International (IPC 8-9): C08G101/00 C08G18/00 C08G18/10 C08G18/28 C08G18/32 C08G18/36 C08G18/40 C08G18/44 C08G18/48 C08G18/76 C08J9/00 C08J9/228 (Advanced/Invention);
C08G101/00 C08G18/00 C08G18/28 C08G18/36 C08J9/00 (Advanced/Non-invention);
C08G18/00 C08J9/00 (Core/Invention);
C08G (Subclass/Invention)

International (IPC 1-7): C08G18/00 C08G18/65

CPC: C08G18/36 C08G18/409 C08G2101/00

European: C08G18/36 C08G18/40D M08G101/00

US: 521/172

Family:

Publication number	Publication date	Application number	Application date
AT430769 E	20090515	AT20060006995T	20060331
BRPI0601267 A	20061205	BR2006PI01267	20060407
CA2541924 AA	20061013	CA20062541924	20060405
CA2541924 C	20140211	CA20062541924	20060405
CN1858082 A	20061108	CN200610074692	20060412
CN1858082 B	20110622	CN200610074692	20060412
DE602006006612 D1	20090618	DE200660006612T	20060331
EP1712578 A1	20061018	EP20060006995	20060331
EP1712578 B1	20090506	EP20060006995	20060331
HK1093998 A1	20120504	HK20070100279	20070109
HK1093998 A3	20070316	HK20070100279	20070109
IN00631DE2006 A	20070706	IN2006DE00631	20060310
IN255306 B	20130215	IN2006DE00631	20060310
JP2006291208 A2	20061026	JP20060109821	20060412
JP4917825 B2	20120418	JP20060109821	20060412
KR20060108512 A	20061018	KR20060033055	20060412
PT1712578 T	20090625	PT20060006995T	20060331
RU2006111985 A	20071027	RU20060111985	20060412
RU2419637 C2	20110527	RU20060111985	20060412
US2006235100 AA	20061019	US20050105138	20050413

Priority:

US20050105138 20050413 CA20062541924 20060405

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Designated states: AL AT BA BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK NL PL PT RO SE SI SK TR YU

Preparation and Properties of Palm Oil-Based Rigid Polyurethane Nanocomposite Foams

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ABSTRACT: In this study, palm oil-based polyurethane (PU)/montmorillonite (MMT) nanocomposite foams were produced via an *in situ* polymerization method. The palm oil-based polyol synthesized by transesterification reaction of palm oil and pentaerythritol was reacted with commercial polymeric diphenylmethane diisocyanate in the presence of water (blowing agent), *N,N*-dimethylcyclohexylamine (catalyst), polydimethylsiloxane (surfactant) and MMT to produce rigid PU nanocomposite foams. The obtained foams containing different MMT contents (1, 3, and 5 wt%) were characterized for their structure, morphology, density, hardness, compressive strength and thermal stability. X-ray diffraction patterns revealed that the nanocomposites formed were exfoliated. Scanning electron micrographs showed that the cells of the obtained PU foams were closed cells. The nanocomposite foams showed a higher number of cells with a smaller cell size as the amount of MMT increased. The density and the compressive strength of the foams increased with the increasing amount of MMT and were in the range of 38.5–46.6 kg/m³ and 116.7–171.6 kPa, respectively. Moreover, addition of MMT also improved the thermal stability of the foams.

KEY WORDS: palm oil, polyol, polyurethane foam, montmorillonite, nanocomposite.

INTRODUCTION

RIGID POLYURETHANE (PU) foams are highly cross-linked closed-cell thermoset materials of low density [1]. They are widely used in construction and refrigerators for thermal insulating purposes due to their excellent thermal properties. Products in a density ranging from 30 to 200 kg/m³ can withstand temperatures down to –196°C [2]. PU foams are prepared by the polymerization reaction of polyols with diisocyanates and a blowing agent. To control and modify both the reaction and properties of the PU foam, a wide variety of additives such as catalysts, surfactants, fillers, cross-linking agents, chain extenders, colorants, and flame retardants may be added [3]. In recent years, it has been found that addition of nanoclay into the polymer foam composition results in foams having improved properties. Nanoclay can act as a nucleating agent in the foam process and can also act as a gas barrier [4]. Kresta et al. found that nanoclay improved the thermal insulation properties of rigid PU foam [4]. Javni et al. studied the effect of nanosilica filler on PU foam properties and they found that the hardness and compressive strength of flexible foams with nanosilica were increased whereas the compressive strength of rigid foams was decreased with the increasing concentration of nanosilica [5]. Cao et al.

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have reported that the presence of 5 wt% organoclay in rigid PU foams resulted in an increase in cell density, a reduction of cell size and an increase in reduced compressive strength [6]. In another study, Widya and Macosko have shown that by adding only 1 wt% nanoclay, rigid PU foams exhibited reduced cell size and no mechanical strength improvements were observed [7]. Recently, Mondal and Khakhar found that the mean cell size decreased and the compressive modulus and the storage modulus increased with the addition of clay [8].

Currently, most commercial polyols used for PU manufacture are derived from petroleum which is a non-renewable resource. To date, many researchers are searching for alternative resources as raw materials for polyols. Vegetable oils are inexpensive renewable resources. Castor oil, which consists of hydroxyl groups, was used as the polyol component in rigid PU foam production [9]. However, other vegetable oils lack functional groups suitable to react with isocyanate to form urethane bonds. Several researchers have investigated the possibilities of converting vegetable oils (e.g., palm oil, rape seed oil, and soy bean oil) into polyols for producing PU foams [10–13]. Each year, Thailand produces a large amount of palm oil not only for domestic consumption, but also for export. Due to the abundant supply of this renewable resource, the potential use of palm oil as an alternative raw material for preparing polyurethane foam is possible. However, palm oil, which is a triglyceride, has no hydroxyl groups to react with isocyanate to produce PU. In this study, treatment of palm oil with pentaerythritol produced a highly (OH) functionalized product. The obtained polyol was then used to prepare PU nanocomposite foams by *in situ* polymerization using montmorillonite (MMT) as nanoclay. The molecular weight and the hydroxyl value of the palm oil-based polyol were determined. The structure and morphology of the foams were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The effect of nanoclay on the cell structure and properties of the PU nanocomposite foams was also studied.

EXPERIMENTAL

Materials

Palm oil with an acid value of 0.055 and an iodine value of 56.11 was obtained from Morakot Industries Co., Ltd. (Bangkok, Thailand). Pentaerythritol and polymeric diphenylmethane diisocyanate (PMDI) (with isocyanate content of 29.3%) were supplied by Siam Chemical Industry Co., Ltd. (Samutprakarn, Thailand). *N,N*-dimethylcyclohexylamine (DMCHA) used as a catalyst was provided by South City Co., Ltd. (Bangkok, Thailand). The surfactant (PDMS) used in this work is a polydimethylsiloxane-ether copolymer (Dabco DC-193 from Air Products) and was donated by IRPC Co., Ltd. (Rayong, Thailand). Sodium montmorillonite (Na^+ -MMT) with cationic exchange capacity (CEC) of 71 meq/100 g was supplied by the Metallurgy and Materials Science Research Institute, Chulalongkorn University. All materials were used as received without further purification.

Preparation and Characterization of Palm Oil-based Polyol

Palm oil (200 g) in a 500 mL four-necked round-bottom flask, equipped with a stirrer, a thermometer, a condenser, a water separator, and N_2 gas inlet, was heated up to 150°C with stirring at a speed of 500 rpm under nitrogen atmosphere. Pentaerythritol (89 g) was

added and the mixture was stirred and heated to 200°C followed by the addition of calcium oxide (0.15 g). The temperature was then raised to 245°C and the mixture was maintained at this temperature until a sample (1 part) was soluble in ethanol (3 parts). The obtained product was allowed to cool to room temperature under nitrogen atmosphere and its chemical structure was analyzed using an FTIR spectrophotometer (Spectrum I 1760X). The hydroxyl and acid values were determined based on ASTM D4274-05 Method C and ASTM D1639, respectively. The viscosity was determined at 30°C using a Brookfield viscometer (Model RVT). The molecular weight and the molecular weight distribution were also characterized by gel permeation chromatographer (GPC) (Waters 600) using tetrahydrofuran (THF) as a solvent and standard polystyrene as a reference.

Preparation of Palm Oil-based Rigid PU Nanocomposite Foams

Rigid PU nanocomposite foams were prepared from palm oil-based polyol, MMT, distilled water, DMCHA, PDMS and PMDI. To investigate the effect of the nanoclay on the properties and morphology of the PU foam, the amount of MMT was varied from 1 to 5 wt% based on the total weight of polyurethane. The amount of polyol, PMDI, distilled water, DMCHA, and PDMS were fixed. The foam formulation used in this study is given in Table 1. The required amount of MMT was first dispersed in polyol by a high shear mixer at 1000 rpm for 2 min. Distilled water, DMCHA, and PDMS were later well mixed with the obtained dispersion for 1 min by a high speed mixer, and then mixed for another 30 s after the PMDI was added. At the creamy stage (the mixture turning creamy), the mixture was poured into an open mold and allowed to rise freely. The cream time (the time from mixing to initiation of foaming) and rise time (the time from mixing to full expansion of foaming) were recorded. After that, the foam was removed from the mold and allowed to post-cure for 2 days at room temperature before cutting into test specimens.

Characterization and Property Measurements of Palm Oil-based Rigid PU

NANOCOMPOSITE FOAMS

The chemical structures of the obtained palm oil-based rigid PU nanocomposite foams were characterized by the Spectrum I 1760X FTIR spectrophotometer. The clay dispersion in PU nanocomposite foams was determined by X-ray diffraction (XRD) using a Bruker D8 diffractometer (40 kV, 40 mA) equipped with $\text{CuK}\alpha$ radiation ($\lambda = 0.1542 \text{ nm}$) at room temperature. The XRD pattern was obtained for a 2θ range of 1–10° at a scanning rate of 1°/min. A scanning electron microscope (SEM) (Jeol JSM-5900 LV) was used to examine the cellular morphology of the foam samples in perpendicular to foam rising direction. The accelerated voltage was 15 kV.

Table 1. Formulation for palm oil-based polyurethane nanocomposite foams.

Sample (g)	PMDI (g)	Polyol (g)	Distilled water (g)	DMCHA (g)	PDMS (g)	MMT (g)
Neat PU foam	60	40	1.2	0.3	3	–
PU/1MMT foam	60	40	1.2	0.3	3	–
PU/3MMT foam	60	40	1.2	0.3	3	–
PU/5MMT foam	60	40	1.2	0.3	3	–

For density measurement, the PU foams were cut into specimens with dimensions of about $50 \times 50 \times 25$ mm (width $\times$ length $\times$ thickness). The exact dimensions were measured using a vernier caliper. The specimens were accurately weighed to determine their densities using the equation, density = mass/volume. Hardness of the foams was determined based on ASTM D2240-2000 using Shore C Durometer (GS-701N Teclock). The density and hardness of the foams were ascertained using the average value from five specimens.

The compressive strength of the foams was determined using an Instron Universal Testing Machine (Lloyd L 500) with a load cell of 1.5 kN. The test was performed according to ASTM D1621-20. The size of the specimen was $50 \times 50 \times 25$ mm (width $\times$ length $\times$ thickness), and the cross-head speed was 12.5 mm/min. The compressive stress at 10% deformation of its original thickness was calculated. The compressive strength of the foams was obtained using the average value from five specimens.

Thermogravimetric analysis (TGA) of the foams was performed using a thermogravimetric analyzer (Mettler Toledo TGA/SDTA 851^o) at a temperature range from 50 to 800°C with a heating rate of 20°C/min under nitrogen atmosphere.

RESULTS AND DISCUSSION

Characterization of Palm Oil-based Polyol

The polyol obtained from transesterification reaction of palm oil with pentaerythritol was a yellowish viscous liquid and can completely dissolve in ethanol. Its FTIR spectrum exhibits a peak corresponding to OH-stretching at wave number of 3374 cm^{-1} . This indicates the presence of a compound having hydroxyl groups. The FTIR spectrum of this polyol also shows peaks of primary and secondary hydroxyl groups at wave numbers of 1050 and 1110 cm^{-1} , respectively.

The obtained palm oil-based polyol had a viscosity of 300 poise which was much higher than that of the regular palm oil (60 poise at 30°C). This high viscosity is due to hydrogen bonding associated with the hydroxyl groups. This polyol had an acid and a hydroxyl value of 1 and 385 mg KOH/g, respectively. Analysis of the polyol by GPC indicated that it consists of compounds in which the number-average molecular weight varied between 712 and 986 with a polydispersity index of 1.2. Generally, typical polyester polyols used in rigid PU foam manufacture have an average molecular weight of about 930 with a hydroxyl value range from 350 to 390 mg KOH/g [1]. Thus, this palm oil-based polyol could be used as a polyol component for preparing rigid PU foam.

Preparation, Characterization, and Property Measurements of Palm Oil-based Rigid PU Nanocomposite Foams

The palm oil-based polyol was used to prepare rigid PU nanocomposite foams according to the formulations given in Table 1. Table 2 shows the cream time and rise time for the foaming of rigid PU foam. Usually, the cream time and rise time for the typical rigid PU foam are 24 and 90 s, respectively [3]. The data presented in Table 2 shows that both the cream time and rise time of the prepared foams are longer. This phenomenon could be attributed to the secondary hydroxyl groups which have lower reactivity existing in the palm oil-based polyol. Results also show that the cream times of the foams containing MMT (45–46 s) remain unaltered in comparison to that of the foam without MMT (46 s). However, the nanocomposite foams show a small increase in the rise time

Table 2. Cream time and rise time of palm oil-based polyurethane nanocomposite foams.

Sample (s)	Cream time (s)	Rise time
Neat PU foam	46	114
PU/1MMT foam	44	115
PU/3MMT foam	46	118
PU/5MMT foam	45	120

with higher MMT content. This may be due to the increase in viscosity at higher MMT loadings that made the reaction slower. Earlier, Widya and Macosko also found that high clay loading caused viscosity increase [7].

The nanocomposite foams produced are rigid and light-weight. They are light yellow due to aromatic isocyanate content. It is also observed that the yellowness of the foams tend to be higher with increasing amount of MMT. This could be due to the increase in the unreacted isocyanate content with higher amount of MMT.

The features of the FTIR spectra for the nanocomposite foams are nearly unchanged compared to that of the neat PU foam. This indicates that the chemical structure of the PU foams did not change by the addition of nanoclay in the polymer matrix. These FTIR spectra exhibit the characteristic peaks of urethane linkages at wavenumbers of 3380 cm^{-1} (-NH stretching), 1720 cm^{-1} (-CO stretching), 1510 cm^{-1} (-NH bending), and 1380 cm^{-1} (-OCONH asymmetric stretching). They also show a characteristic peak of unreacted isocyanate groups at 2270 cm^{-1} . The intensity of this peak increases as the amount of MMT increases showing that the foam with higher MMT content had more amounts of unreacted isocyanate groups. This could be explained that higher levels of MMT loadings caused an increase in the viscosity of the system leading to a decrease in isocyanate group reactivity due to a decrease in molecular mobility.

The clay dispersion in the PU nanocomposite foams was studied by means of X-ray diffraction. The MMT has a characteristic diffraction peak (d -001 plane) at $2\theta = 5.99^\circ$, corresponding to a gallery spacing of 1.47 nm calculated from the Bragg equation ($\lambda = 2d\sin\theta$, $\lambda = 0.1542\text{ nm}$). The XRD patterns of the PU nanocomposite foams are much closed to that of the neat PU foam and show no significant peak in the 2θ range of $1\text{--}10^\circ$. The result implies that the clay layers in the nanocomposite foams could be mostly exfoliated in the PU matrix. This is in good agreement with recent work by Mondal and Khakhar [8], which shows that the unmodified clay forms exfoliated nanocomposites. The XRD patterns also show that higher amount of MMT in the PU foam might result in less efficiently exfoliation of clay.

Scanning electron micrographs of the PU foams at cross-sections perpendicular to the foam rising direction are presented in Figure 1, showing polygon closed-cell structures with many windows. The neat PU foam has fewer cells and a larger cell size than those of the PU nanocomposite foams. Meanwhile, the nanocomposite foams show a higher number of cells with a smaller cell size as the amount of MMT increased. The neat PU foam has an average cell size of $307\text{ }\mu\text{m}$ whereas the PU/1 MMT, PU/3 MMT and PU/5 MMT nanocomposite foams have average cell size of 300, 286, and $277\text{ }\mu\text{m}$, respectively. In other words, the PU foams containing 1, 3, and 5 wt% nanoclay have a higher cell density and smaller cell size than those of the neat PU foam. Thus, it can be concluded that the nanoclay has an effect on reducing the cell size. This may be explained that the nanoclay increased the viscosity of the system leading to restraining the expansion of the cells.

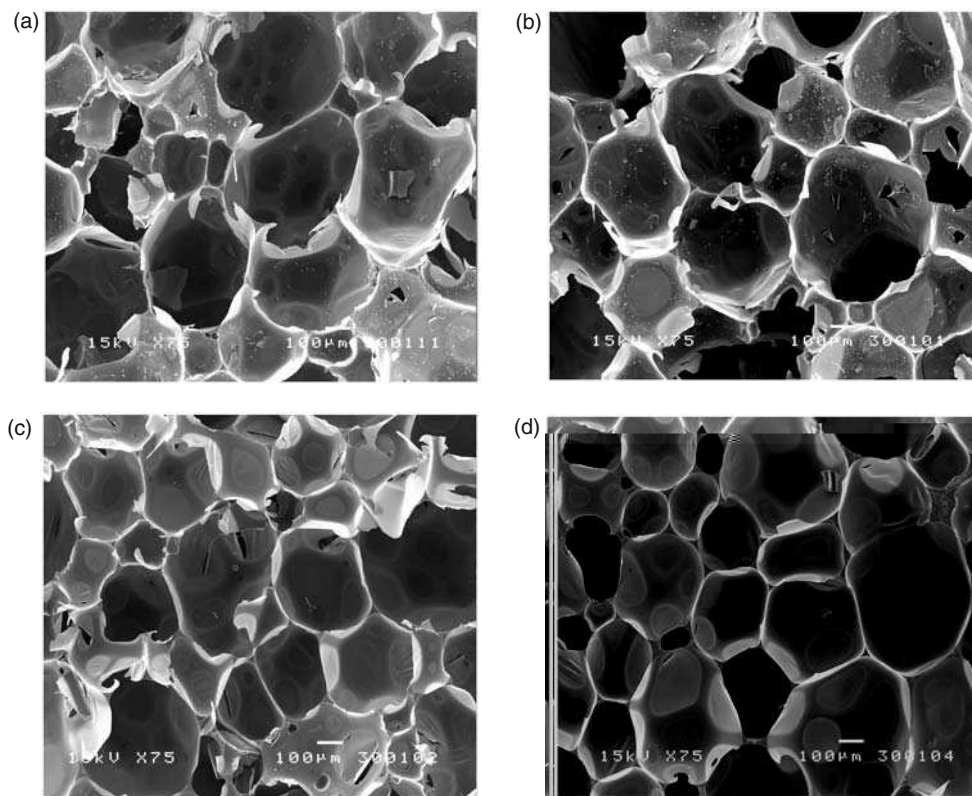


Figure 1. SEM micrographs of (a) neat PU foam, (b) PU/1 MMT foam, (c) PU/3 MMT foam and (d) PU/5 MMT foam.

The physical properties of the PU nanocomposite foams in comparison with the neat PU foam are presented in Table 3. The data in Table 3 shows that the addition of clay has an effect on the density and compressive strength of the PU foams but not on hardness. The hardness of the foams is nearly constant whereas the densities and compressive strengths of the nanocomposite foams are higher than those of the neat PU foam. The density of the nanocomposite foam increased as the amount of MMT increased and is in the range of 40.0–46.6 kg/m³. Similarly, the nanocomposite foam exhibits a higher compressive strength with higher clay loading. It is generally known that the mechanical properties of PU rigid foam are largely dependent on the foam density [1]. Therefore, the increase in the compressive strength with the increasing amount of MMT may be due to the increase in foam density. In addition, the SEM pictures in Figure 1 show that the cell structures of the foams are more uniform and compact with higher amount of MMT. Higher MMT loadings caused an increase in the viscosity of the matrix which would slow down the rupture of the cell walls [14] resulting in higher density and compressive strength. The dispersed nanoclay may also help improve the compressive strength which is probably owing to the formation of a clay barrier layer around the cell.

The thermal stability of all the PU foams was investigated by TGA and the results are displayed in Figure 2. The TGA curves for all samples reveal two degradation processes. The first stage of the degradation is associated with the first 30% of weight loss and the second stage with the weight loss ranging from 52 to 56%. The onset degradation

Table 3. Physical properties of palm oil-based polyurethane nanocomposite foams.

Sample	Density (kg/cm ³)	Compressive strength (kPa)	Hardness (Shore C)
Neat PU foam	38.5	117	37
PU/1MMT foam	40.0	121	38
PU/3MMT foam	44.4	145	37
PU/5MMT foam	46.6	172	38

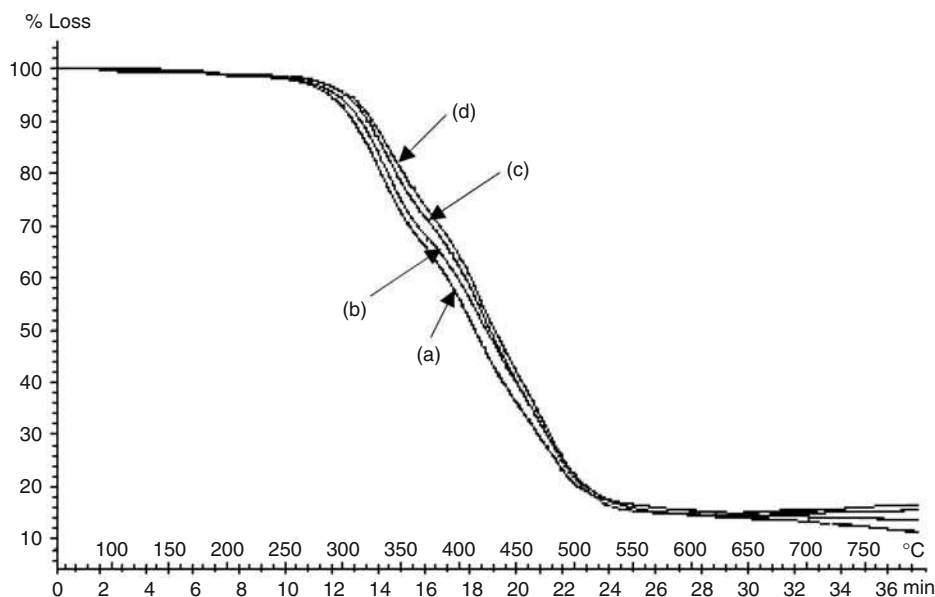


Figure 2. TGA thermograms of (a) neat PU foam, (b) PU/1 MMT foam, (c) PU/3 MMT foam and (d) PU/5 MMT foam.

temperature of the neat PU foam is at 290.9°C which is lower than that of the nanocomposite foams (300°C). In addition, TGA thermograms of the nanocomposite foams were shifted toward high temperatures as compared to the neat PU foam and as the amount of MMT increased. This indicates that MMT improved the thermal stability of PU foam by preventing the heat to expand quickly and limit further degradation.

CONCLUSIONS

Palm oil-based polyurethane/montmorillonite nanocomposite foams were synthesized successfully via an *in situ* polymerization method. The polyol prepared from palm oil could be used as one of the raw materials for preparing the PU foams. X-ray patterns showed that the layered silicates were mostly exfoliated in the nanocomposites. SEM micrographs disclosed that all foams exhibited polygon closed-cell structure. The compressive strength of the foam was remarkably improved with the incorporation of 5 wt% of MMT. Thermal stability of palm oil-based PU/MMT nanocomposite foams was also higher than that of the neat PU foam.

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REFERENCES

1. Oertel, G. (1994). *Polyurethane Handbook*, Hanser Publications, Munich.
2. Demharter, A. (1966). Polyurethane Rigid Foam, a Proven Thermal Insulating Material for Applications between $+130^{\circ}\text{C}$ and -196°C , *Cryogenic*, **38**(1): 113–117.
3. Woods, G. (1990). *The ICI Polyurethanes Book*, Wiley, New York.
4. Kresta, J. E., Nu, J. and Crooker, R. M. (2003). Polyurethane Foam Containing Nanoclay, U.S. Patent 6,518,324.
5. Javni, I., Zhang, W., Karajkov, V., Petrovic, Z. S. and Divjakovic, V. (2002). Effect of Nano- and Micro-Silica Fillers on Polyurethane Foam Properties, *Journal of Cellular Plastics*, **38**(3): 229–239.
6. Cao, X., James Lee, L., Widya, T. and Macosko, C. (2005). Polyurethane/Clay Nanocomposites Foams: Processing, Structure and Properties, *Polymer*, **46**(3): 775–783.
7. Widya, T. and Macosko, C. (2005). Nanoclay-Modified Rigid Polyurethane Foam, *Journal of Macromolecular Science, Part B: Physics*, **44**(6): 897–908.
8. Mondal, P. and Khakhar, D. V. (2007). Rigid Polyurethane-Clay Nanocomposite Foams: Preparation and Properties, *Journal of Applied Polymer Science*, **103**(5): 2802–2809.
9. Baser, S. A. and Khakhar, D. V. (1993). Castor Oil-Glycerol Blends as Polyols for Rigid Polyurethane Foams, *Cellular Polymers*, **12**(5): 390–401.
10. Chian, K.S. and Gan, L.H. (1998). Development of a Rigid Polyurethane Foam from Plam Oil, *Journal of Applied Polymer Science*, **68**(3): 509–515.
11. Hu, Y. H., Gao, Y., Wang, D. N., Hu, C. P., Zu, S. and Vavoverloop, L. (2002). Rigid Polyurethane Foam Prepared from a Rape Seed Oil Based Polyol, *Journal of Applied Polymer Science*, **84**(3): 591–597.
12. Guo, A., Javni, I. and Petrovic, Z. (2000). Rigid Polyurethane Foams Based on Soybean oil, *Journal of Applied Polymer Science*, **77**(2): 467–473.
13. John, J., Bhattacharya, M. and Turner, R. B. (2002). Characterization of Polyurethane Foams from Soybean oil, *Journal of Applied Polymer Science*, **86**(12): 3097–3107.
14. Singh, A. P. and Bhattacharya, M. (2004). Viscoelastic Changes and Cell Opening of Reacting Polyurethane Foams from Soy Oil, *Polymer Engineering and Science*, **44**(10): 1977–1986.

Rigid polyurethane foams from oil palm resources

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Presently, most polyols used in polyurethane (PU) industry are petrochemical-based where crude oil and coal are used as starting raw materials. However, these materials are expensive, [1] the rate of depletion is high, and they require high technology processing systems. This necessitates a look at utilizing plants that can serve as an alternative feed stocks for monomers in polymer industry. Palmeri oil, vernonia oil, castor oil, and recently carandol oil (extracted from the cashew nut shell), have been synthesized to replace the petrochemical-based polyols [2–4]. Malaysia, a country, which is known globally as the major producer of palm oil, has also participated in researches involving the utilization of palm oil in the oleochemical industry, namely the production of polyurethane polyols. Many works have been published [5–9] regarding this, basically focused on making full use of the oil from the palm tree.

Approximately 22% of the waste from the palm oil industry consists of empty fruit bunch fibers (EFB). These resources, along with a vast quantity of agricultural residues, can be utilized in natural fiber-based composites. The EFB can function as a reinforcing agent or as filler. It is advantageous as compared to the inorganic fillers due to its production cost and higher percentage of filler loading [8, 9]. Moreover, it offers low density, high deformability, no abrasion, and most important, low production cost. In addition, it is obtained from renewable resources and is environmental-friendly. Because the properties of the agro-based fiber result from the chemistry of the cell wall components, modifying the basic chemistry of the cell wall to the polymers can change the basic properties of the fiber. Dimensional stability can be highly improved by bulk-ing the fiber cell wall either with simple bonded chemicals or by impregnation with water-soluble polymers. In most cases the polymer does not enter the cell wall and is located in the cell lumen, so by using this technology the mechanical properties can be greatly enhanced. Coupling agents improve the bonding strength between the fiber and resin. It is the main focus of this study to incorporate organic fillers into the PU to form PU composites in identifying the enhancement properties of filler in refined, bleached, and deodorized, palm kernel oil (RBD PKO) based PU composite. It is also the aim of this study to produce PU foam for insulation purposes. Over the last few years considerable attention has been devoted to these studies: synthesis of the PU polyol from RBD PKO and the production of EFB fiber-filled polyurethane (PU) composites [6–8].

The synthesis was carried out according to the modified procedure of Pourjavadi *et al.* in 1998. The diethanolamine and the potassium acetate were mixed homogeneously in a ratio of 90:10. This reagent and the RBD PKO were mixed to a 20:80 stoichiometric ratio to get the highest functionality value possible. The reaction was carried out in a laboratory scale. The mixture was continuously stirred in a 2-L glass reactor and was reacted at 175–185 °C for 30 min. The samples collected were then analyzed. The EFB fiber was sieved to grade the particles into different sizes. The filler sizes used in this study were of 45–53, 106–150, 300–500 microns. The sieved fibers were then dried in a vacuum oven to a constant weight at 105 °C for approximately 20 hrs [10]. The silane-based coupling agent was mixed with ethanol to form a 10 wt% silanol solution containing silane concentration of 1, 3 and 5% [10]. The surface treatment of the EFB fiber was carried out based on the method suggested by the manufacturer (Dow Corning Sdn Bhd 1995). Mixture of 140 g of crude MDI and 100 g of the resin (100 part by weight (pbw) RBD PKO-based polyol, 2 pbw Tegostab B8408, 0.3 pbw TMHDA, 0.15 pbw PMDETA and 4.5 pbw water) was agitated vigorously using a standard propeller with a speed of 5000 rpm for 10 s at 25 °C. The mixture was poured into a waxed mold, covered, and screwed tightly. The foam was demolded after 10 min. The EFB fiber-filled composites were prepared by using a blend of RBD PKO polyol, surfactant, catalysts, water, and the treated and/or untreated EFB (0, 1.5, 2.5, 3.5, 4.5, 5.5, and 6.5 w/v% of the whole system). Water addition was varied to match the free-rise density to be in the range of 37–39 kg/m³. Molded foams were characterized for their apparent densities, compressive strength, dimensional stability, and water absorption, following standard method BS4370: Part 1:1988 (Rigid PU foam produced by the press injection method). The insulation value (k-factor or λ -value) of the PU foam and PU composites was determined using the Thermal Conductivity Analyzer model Anacon at a testing temperature of 10 °C and specimen thickness of 20–30 mm. Method BS4370: Part 2: 1993 was followed. A scanning electron microscope (SEM) model Philips, by gold coating $\times 200$ magnification was used to observe the specimens' surfaces.

The derivatized RBD PKO-based polyol is a golden yellow liquid with a cloud point of 13 °C. It has very low moisture content of 0.09% and low viscosity of 374 cps and specific gravity of 0.992 at room temperature. Both FTIR and GC-MS identified the resulting compound as 2-hydroxy-undecanoamide. From the hydroxyl value

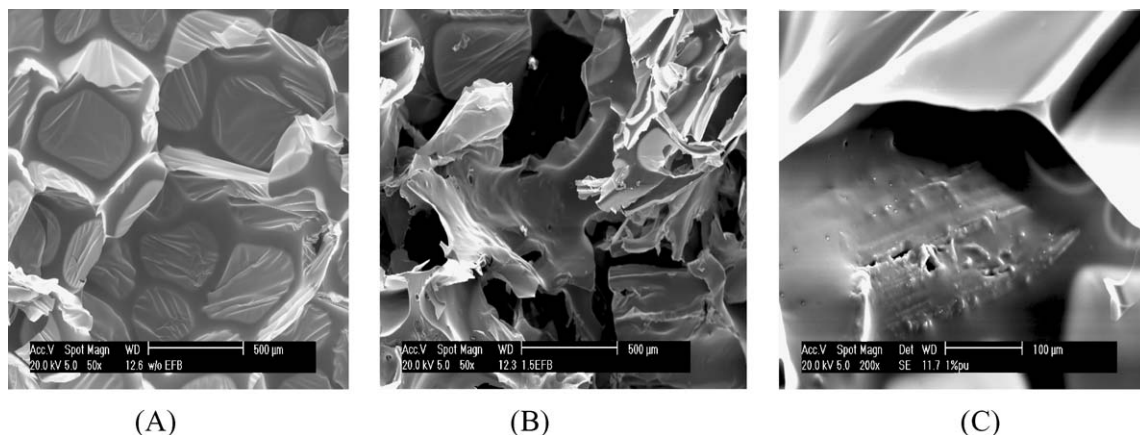


Figure 1 SEM micrographs of (A) the unfilled PU foam, (B) untreated EFB-filled PU foam, and (C) treated EFB-filled PU foam (X200).

obtained and the estimated molecular weight from the GC-MS of 350–370 mg KOH/g sample and 477 respectively, the functionality of the polyesteramide was calculated [11] as 3.0, suitable for rigid foam application. The mechanical properties of the foam produced from the polyol showed good results as compared to its conventional counterpart. For a PU system, the cellular structure played a major role in the determination of good mechanical properties, whereas the untreated EFB-filled PU resulted in ruptured cell walls. This impairment was overcome by the usage of silane as a coupling agent by means of surface modification of the EFB fiber as filler. Maximum stress at 10% deflection of the untreated EFB-filled PU (industrial standard of more than 180 kPa) for 45–53, 106–150 and 300–500 μm was identified at 5.5, 4.5 and 2.5% of fiber loading, respectively. The compressive strength increased to a maximum of 4.5% EFB fiber loading for all concentrations of silane treated PU composites. This increment is almost twice the amount of EFB fiber of the control PU composite, with the untreated EFB fiber (2.5% fiber loading). However, with the addition of 1% silane, the overall strength deteriorated with a maximum value of about 180 kPa at 4.5% fiber loading. Less improvement in strength was observed with the addition of 3% silane to the fiber. The strength dropped below 180 kPa once it reached its maximum value, at about 200 kPa. The optimum values for both the fiber loading and the compressive strength were achieved at 5% silane. The results indicate that EFB fiber has played a role as filler when untreated, and can also be used as a reinforcing agent once treated with silane. This can be observed from the relationship between the compressive strength and the compression modulus. The thermal insulation value, k -factor for the unfilled PU, untreated EFB-filled PU, and the treated EFB-filled PU with powder form EFB, are 0.0244, 0.0253, and 0.0229 W/m·K respectively. Inclusion of untreated EFB ruptured the cellular structure due to poor bonding of EFB/matrix, leading to a higher rate of diffusion and increased the k -factor. The tearing shown by the SEM micrograph in Fig. 1B gives a good indication of the occurrence of fiber bundle pull-out, as compared to a uniform cellular structure of the unfilled foam (Fig. 1A). This may explain the poor compressive strength properties of the composites and the low percentage of EFB

fiber loading. Fig. 1C of the treated EFB-filled PU gives a good indication of the improvement of interfacial bonding between the constituent phases. The EFB fiber is well bonded to the matrix. This is the possible explanation in describing the improvement in the dimensional stability and the compressive strength of the composites.

Appropriate addition of natural EFB fiber improves the stiffness of the composites but degrades the strength property. This trade off in properties has been encountered with the application of silane coupling agent, which preserves the continuity between the dispersed phase and the matrix. Stress concentration, agglomeration of fibers and dispersion factors can be resolved by employing silane. In terms of application, this composite is most suitable in structures where stiffness and dimensional stability is of prime importance, but is only a secondary choice in areas where structural strength is more vital than component rigidity. Moisture content can lead to poor processability and porous products. Treatment of natural fiber with chemicals can reduce the moisture gain.

References

1. W. I. TAN and S. AHMAD, in Proceedings of the 2001 PIPOC International Palm Oil Congress, organized by Ministry of Primary Industries (Malaysia, 2001) p. 99.
2. A. POURJAVADI, N. REZAI and M. J. ZOHURIAAN-M, *J. Appl. Polym. Sci.* **68** (1998) 173.
3. P. NAYAK, D. K. MISHRA, D. PARIDA, K. C. SAHOO, M. NANDA, S. LENKA and P. L. NAYAK, *ibid.* **63**(5) (1997) 671.
4. A. K. SAHA, S. DAS, D. BHATTA and B.C. MITRA, *ibid.* **71** (1999) 1505.
5. H. D. ROZMAN, B. K. KON, A. ABUSAMAH, R. N. KUMAR and Z. A. MOHD ISHAK, *ibid.* **69** (1998) 1993.
6. K. H. BADRI, S. H. AHMAD and S. ZAKARIA, *ibid.* **81** (2001) 384.
7. *Idem.*, *J. Mater. Sci. Lett.* **19** (2000) 1355.
8. *Idem.*, *Nuclear Sci. J. Malaysia* **18**(2) (2000) 57.
9. H. D. ROZMAN, G. S. TAY, R. N. KUMAR, A. ABUSAMAH, H. ISMAIL and Z. A. MOHD ISHAK, *Eur. Polym. J.* **37**(6) (2001) 1283.
10. Z. A. MOHD ISHAK, A. AMINULLAH, H. ISMAIL and H. D. ROZMAN, *J. Appl. Polym. Sci.* **68** (1999) 2189.
11. G. WOOD, "ICI Handbook" (The ICI PU and John Wiley & Sons Publication, New York, 1991).

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Preparation and characterization of polyurethane foams using a palm oil-based polyol

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Abstract

Polyurethane (PU) foams were prepared using a palm oil-based polyol (PO-p). At the first stage, palm oil was converted to monoglycerides as a new type of polyol by glycerolysis. A yield of the product reached 70% at reaction temperature of 90 °C by using an alkali catalyst and a solvent. At the second stage, PU foams were prepared from mixtures of the polyol and polyethylene glycol (PEG) or diethylene glycol (DEG) and an isocyanate compound. Characterization of the foams was carried out by thermal and mechanical analyses. The analyses showed that the chain motion of polyurethane becomes more flexible at the higher PO-p content in the whole polymer, which indicates that the monoglyceride molecules work as soft segments. The study here may lead to a development of a new type of polyurethane foams using palm oil as a raw material.

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Keywords: Palm oil; Glycerolysis; Monoglyceride; Polyurethane foam; Thermal analysis

1. Introduction

Palm oil (PO) is one of the most widely used plant oils in the world. It is produced from oil palm (*Elaeis guineensis*), which is grown in mass plantation in tropical countries such as Malaysia, Indonesia and Nigeria. The oil consists of triglycerides (Tri-G) and diglycerides (Di-G) and McNeill and Berger (1993) reported that 95% of the oil is Tri-G and 5% Di-G and carbons of the carboxyls are ranging 10–20 with or without double bonds. Palm oil is mainly used for food applications, but it is also used in some other industries such as soap, detergent and cosmetic production. In recent years, quite a number of research and development works have been carried out for utilizing palm oil in wide range of application, including bio-diesel fuel (Kalam and Masjuki, 2002; Mohamad and Ali, 2002).

Production of bio-based plastics and composites is thought to be one of the most important issues in the research and development for the protection of global environment (Wang et al., 2002; Yang et al., 2004). Research studies on bio-based polyurethanes have great potential in contributing to such development. In general, polyurethanes have been applied in various products such as thermal insulation and medical implants. The polymer is synthesized by a reaction of an isocyanate compound such as diphenylmethane diisocyanate (MDI) and a polyhydroxyl-containing polymer, i.e., polyol, such as polyethylene glycol (PEG). The preparation of various types of polyurethane products has been extensively studied in recent years, especially containing biomass-originated raw materials (Asano et al., 2001; Hatakeyama, 2002; Hatakeyama et al., 1998; Hatakeyama and Hatakeyama, 2004; Kurimoto et al., 2000; Kurimoto et al., 2001). Moreover, it has become clear from previous studies that the biomass-based PUs have biodegradability (Hatakeyama et al., 1995).

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However, polyols for the polyurethane production are mostly derived from petrochemicals in general. Preparation of the polyurethanes from palm oil may expand the application of the oil in various areas as environment-friendly materials, because of its abundance and renewability. Moreover, it may lead to the replacement of petrochemical products by this naturally occurring plant oil.

There are several research studies of using palm oil for PU preparation (Chian and Gan, 1998; Tuan Noor Maznee et al., 2001). PO consists of mainly triglycerides (Tri-Gs), thus it is necessary to introduce hydroxyl groups to a molecule of Tri-G for urethane reaction. Siwayanan et al. (1999) have reported the preparation of polyols from PO by epoxidation for PU production. By their method, Tri-G molecules were converted to polyols by the reaction with epoxides, followed by the reaction with polyhydric alcohols.

Conversion of triglycerides to monoglycerides is an alternative method for introducing hydroxyls for palm oil, which becomes a 'palm oil-based polyols (PO-p)'. Monoglyceride (Mono-G) is a fatty acid ester of glycerol, and three main processes are widely known for its preparation: (1) glycerolysis of fats and oils with glycerol, (2) enzymatic synthesis by using lipase catalysts and (3) direct esterification of fatty acids or their alkyl esters with glycerol (Noureddini and Medikonduru, 1997). McNeill and Berger have reported a study of the enzymatic synthesis for the preparation of Mono-Gs from palm oil (McNeill and Berger, 1993). However, the glycerolysis has not been applied for palm oil to produce Mono-Gs so far.

In this paper, the first part describes the preparation of Mono-Gs from palm oil as a polyol by glycerolysis. Using this polyol (PO-p), polyurethane foams were prepared and their properties were examined in the second part of this paper.

2. Experimental procedures

The following two distinct processes are described in this section: (1) glycerolysis of palm oil for polyol preparation, and (2) preparation of polyurethane foams using the palm oil-based polyol.

2.1. Glycerolysis of palm oil for polyol preparation

2.1.1. Materials

Palm oil (PO) was kindly provided from MALPOM Industries BHD, Malaysia, as a crude grade (=CPO, crude palm oil). Glycerol, sodium hydroxide (NaOH) and *t*-butyl alcohol (*t*-BuOH) were purchased from Wako Pure Chemical Industries, LTD, Japan. Tetradecane (TD), which was used as an internal standard for the quantification, was also purchased from the Wako. PO and the chemicals were used without further purification.

It has been reported by McNeill and Berger (1993) that the carboxyl groups of palm oil consist of 45.6 wt% of $\text{CH}_3(\text{CH}_2)_{14}\text{COO}-$ (C16:0, palmitic), 36.4 wt%

$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COO}-$ (C18:1, oleic) and 10.3% $\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COO}-$ (C18:2, linoleic). Using their precise data for the carboxyls, molecular weights of the PO triglycerides and diglycerides are calculated to be 846.6 and 595.1, respectively, assuming that Tri-G and Di-G have the same carboxyl contents. Moreover, a carboxyl group is expressed as C *x*:*y* in this paper, which *x* is the number of C and *y* the number of double bonds.

2.1.2. Methods

Approximately 20 g of glycerol was placed in a 300 mL three-necked round-bottom flask, equipped with a water-cooling condenser and a thermometer. Accurately weighed PO was added to the flask at the weight ranging 10 ~ 40 g, together with 20 mL of *t*-BuOH as a solvent. Tetradecane (TD) was also accurately weighed to 0.4 g and added to the mixture as an internal standard. 0.2 g of NaOH was then dissolved into the mixture, which works as a catalyst of the glycerolysis.

Placing the flask in a mantle heater, the mixture was heated to approximately 90 °C and was kept for 2 h with continuous stirring. After the reaction completed, the flask was immediately cooled down to the room temperature (*ca.* 20 °C). Ten percent hydrochloride (HCl) (1.8 g) solution was then added to neutralize the alkali catalyst. A homogeneous mixture obtained was dark orange, which was originated from the color of β -carotene naturally contained in PO.

Transesterification of triglyceride (Tri-G) by the glycerolysis undergoes in the presence of an alkali catalyst at an elevated temperature. At this stage, the products must be monoglyceride (Mono-G) and diglyceride (Di-G). Then the Di-G does react with glycerol, resulting in the production of two Mono-Gs. Therefore, one Tri-G can be theoretically converted to 3 Mono-Gs by the glycerolysis.

Quantitative analyses of the Mono-G products were carried out by capillary gas chromatography (GC), according to AOCS (The American Oil Chemists' Society) Official Method Cd 11b-91. A prepared mixture without purification was reacted with bis-trimethylsilyl-trifluoro-acetamide (BSTFA) and trimethylchlorosilane (TMCS) for the conversion of its components to trimethylsilyl (TMS) derivatives. GC analyses of the TMS-derivatized samples were carried out by using a HP6890 GC (Agilent Technologies LTD) equipped with a flame indicator detector (FID) and a capillary column of HP-5 (crosslinked 5% PH ME siloxane).

Prior to the reacted samples, calibration curves were created for two major Mono-G products, i.e., C16:0 and C18:1 Mono-Gs, as C16:0 and C18:1 carboxyls are dominant in the composition of palm oil Tri-Gs. Standard samples of the Mono-Gs were purchased from Sigma Chemical Co. Standard solutions were prepared by dissolving a Mono-G and an internal standard of tetradecane (TD) with various weight ratios in pyridine. The Mono-G in a standard solution was TMS-derivatized as same as the reaction mixture and was analyzed by the GC. Ratios of

the peak area between the Mono-G and TD were calculated and plotted against the weight ratios of the two. Linear relationships were obtained for both C16:0 and C18:1 Mono-Gs, which were used for quantitative analysis of the Mono-Gs in the reacted mixtures.

From the quantitative analysis, the best PO/glycerol ratio was determined for the preparation of a palm oil-based polyol (PO-p), which showed the highest yield of the Mono-Gs. Then the mixture was subjected to the purification process for the removal of *t*-BuOH and unreacted glycerol. At first, the alcohol was removed by the evaporation under vacuum. Then twice a volume of *n*-hexane was added to the remained mixture in a glass container with a screw cap. The container was shaken vigorously to dissolve Mono-G products into the *n*-hexane. After leaving the mixture for overnight, the separation occurred, resulting in an *n*-hexane layer at the top and an unreacted glycerol layer at the bottom. The hexane layer was analyzed by GC and the removal rate of the unreacted glycerol was determined in comparison of the peak areas of glycerol, TD and the Mono-Gs before and after the purification process.

2.2. Preparation of polyurethane foams using the palm oil-based polyol

2.2.1. Materials

A palm oil-based polyol (PO-p) used in this section was prepared by the glycerolysis and the purification process as described in the previous section. Polyethylene glycol (PEG) having molecular weight of 200, diethylene glycol (DEG) and poly (phenylene methane) polyisocyanate (MDI polymer) was commercially obtained.

2.2.2. Methods

A polyurethane (PU) foam was prepared by mixing the PO-p with either PEG or DEG at the beginning. Then 0.1% of dibutyltin dilaurate (DBTDL), a catalyst, was added to the mixture, together with water (1%) and a surfactant (0.2%), forming a 'pre-mixture'. The content of PO-p in each pre-mixture varied between 20 and 80 wt%. Then MDI was added and the reaction was allowed to proceed at room temperature with vigorous stirring. Molecular ratio of isocyanate to hydroxyl groups (NCO/OH ratio) was kept at 1.2 for all samples.

Thermal analyses of thermogravimetry (TG) and differential scanning calorimetry (DSC) were carried out for the PU foams. A Seiko TG/DTA 220-SSC6200 and a Seiko DSC 6200 were used for TG and DSC measurements, respectively. For the TG analysis, an accurately weighed sample (approx. 7 mg) was heated from 25 to 600 °C at the rate of 20 °C/min with N₂ gas purging. The DSC measurement was carried out for a sample (accurately weight, approx. 5 mg) at heating rate of 10 °C/min between –120 and 120 °C under N₂ atmosphere.

Mechanical strengths and moduli of PU foams were determined using a Shimadzu Autograph AG-10TB,

according to JIS K7220. A foam sample was cut in a cube of 1 cm × 1 cm × 1 cm. Compressive strength and modulus of each sample were recorded for three replicates from each PU foam sample. Prior to the measurement, an accurate size and a weight were measured for the sample for calculating its density.

3. Results and discussion

3.1. Preparation of palm oil-based polyol by glycerolysis

Quantitative analysis was carried out for detecting C16:0 and C18:1 carboxyl groups converted to Mono-Gs after the reaction of glycerolysis. As mentioned previously, fatty acids of C16:0 and C18:1 carboxyls account for 45.6 and 36.4 wt%, respectively, making total 82% of the whole fatty acids from PO. When glycerolysis occurs, it seems that carboxyl groups at the C1 and C3 positions of Tri-Gs are more likely to be exchanged by OH groups, compared with the C2 position. It has been reported by Deffense that more than 80% of Tri-G has C16:0 and/or C18:1 at the C1 and/or C3 positions (Deffense, 1985). From this aspect, the quantitative analyses of Mono-G with C16:0 and C18:1 carboxyls were considered to represent the total efficiency of conversion from PO to Mono-G by the glycerolysis.

A mixture obtained by the reaction consists of glycerides (mainly Mono-Gs), unreacted glycerol and PO and *t*-BuOH, together with a trace amount of NaCl and water after the neutralization of the catalyst. GC analysis of the mixture was carried out for determining the reaction products. Assuming that there was no effect on the internal standard of TD during the glycerolysis, the amounts of C16:0 and C18:1 monoglyceride products were calculated by using the calibration curves of the standards and the amount of TD added. Results of three reaction mixtures containing different amounts of PO are given in Table 1.

The production percentage shown in the table is simply calculated by dividing total amount of C16:0 and C18:1 Mono-Gs by an initial amount of PO. Theoretically, one molecule of Tri-G reacts with two molecules of glycerol, i.e., 0.5 of (PO/glycerol) ratio, which results in the production of three Mono-Gs. However, Sample 3 in Table 1 had only reacted approximately 1%, whereas the yield was more than 70% when the glycerol added are far much in excess as Sample 1. These results show that the glycerolysis reaction does occur at reaction conditions applied in this study with the reaction efficiency dependent on the PO/glycerol ratio. On the other hand, nearly 90% of glycerol molecules are left unreacted for producing Mono-Gs at the higher yield. This suggests that an optimum condition of glycerolysis should be examined for the Mono-G production with high efficiency.

By more precise calculation, the conversion rates of the monoglycerides have been determined as molecular masses of fatty acids before and after the glycerolysis, which are

Table 1
Percentage and conversion rate of monoglycerides (Mono-Gs) produced at various PO-glycerol ratios

No.	PO used (g)	PO/glycerol molar ratio	Amount of mono-G produced (g)		Production (%)	Conversion rate (%)	
			C16:0	C18:1		C16:0	C18:1
1	10.2	0.05	3.49	3.89	72.4	60.9	86.5
2	20.0	0.1	1.06	0.945	10.0	9.35	10.7
3	40.0	0.2	0.372	0.122	1.24	1.64	0.690

also given in Table 1. The calculation was carried out as follows:

Conversion rate (%)

$$= \frac{W_{\text{Mono-G}}}{M_{\text{Mono-G}}} \times \left(\frac{W_{\text{PO}}(\text{g}) \times 0.95}{846.6} \times 3 + \frac{W_{\text{PO}}(\text{g}) \times 0.05}{595.1} \times 2 \right) \times \text{mol\% of the carboxyl in PO} \times 100 \quad (1)$$

where $W_{\text{Mono-G}}$ is the monoglyceride produced, $M_{\text{Mono-G}}$ is molecular weight of the Mono-G, W_{PO} palm oil added at the beginning. Moreover, mol% of the carboxyl in PO is 48.4 and 35.1 for C16:0 and for C18:1, respectively.

The result shows a significant difference between C16:0 Mono-G and C18:1 Mono-G, especially at a higher yield. It may arise from the difference in the position of carboxyl groups at triglyceride (Tri-G) molecules. According to Defense, 82–90% of Tri-Gs has C16:0 carboxyl group at the C1 and/or C3 and only 14–17% of them has the carboxyl at the C2 position (Defense, 1985). On the other hand, only 38–41% of Tri-Gs has C18:1 carboxyl group at the C1 and/or C3, but 59–65% at the C2. The analyses carried out in this study have determined only Mono-Gs with a carboxyl group at the C1 (or C3) position. Therefore, the higher yield of 1-Mono-G with C18:1 may be produced efficiently by the reaction between the C2-position C18:1 carboxyl groups and glycerol molecules. On the other hand, the C1-position C16:0 carboxyl groups may be slightly less reactive compared to the C18:1 or, possibly, more 2-Mono-G with C16:0 may be produced. It is necessary to have further studies to investigate the details of the glycerolysis reaction.

A monoglyceride mixture prepared at the same condition as Sample 1 in Table 1 was analyzed by GC before and after the purification. The analysis data clearly shows that the peak of glycerol becomes much smaller after the purification when compared with the peaks of tetradecane (=TD, internal standard) and the Mono-Gs. Extraction of Mono-Gs into *n*-hexane was according to the method by Corma et al. for the separation of fatty products from glycerol (Corma et al., 1998). However, the unreacted glycerol seemed to be partially solubilized in the hexane layer, so that the peak of glycerol was still detected after the purification process. Assuming that there was no loss of TD, C16:0 Mono-G and C18:1 Mono-G, unreacted glycerol in the purified product mixture was analyzed from the comparison of the peak areas between glycerol and these substances. Ratios of the peak areas were calculated from the calibration curves as given in Table 2, which Ratio 1

Table 2
Removal rate of unreacted glycerol from monoglyceride products

	Ratio of peak areas		Removal rate (%)
	Before (ratio 1)	After (ratio 2)	
Glycerol/TD	84.0	8.38	90.0
Glycerol/C16:0 Mono-G	9.66	1.02	89.4
Glycerol/C18:1 1 Mono-G	8.29	0.846	89.8

TD: tetradecane; Mono-G: monoglyceride.

Removal rate (%) = (1 – Ratio2/Ratio1) × 100.

expresses the ratio of the peak area of glycerol to that of a standard substance before the purification and Ratio 2 expresses the same peak area ratio after the purification. The removal rate of the glycerol was estimated from the Ratio 1 and 2.

It shows that almost 90% of unreacted glycerol has been removed by the purification procedure. There is no difference among the three standard substances, TD and Mono-Gs, which may indicate that there is no loss in the extraction of Mono-Gs and TD during the purification process. Although the removal of unreacted glycerol was not 100%, the purification of Mono-Gs by using *n*-hexane seemed to be quite effective for the production of Mono-Gs studied here. In addition, a larger scale preparation was carried out to produce the Mono-Gs from 200 g of PO and 400 g of glycerol. The removal rate of unreacted glycerol was 83–85%, calculated from the Mono-G standards. This result may indicate that the purification process employed in this study is applicable to a large scale production of Mono-Gs by palm oil glycerolysis.

3.2. Preparation and characterization of palm oil-based polyurethane foams

Polyurethane (PU) foams prepared in this study were semi-rigid type and the foams became more dark and yellowish with increasing PO-p content in the pre-mixture, probably because of the original orange colour of palm oil. Apparent densities of the PEG-contained foams were scattered between 0.05 and 0.13 g/cm³, whereas the DEG-contained foams had almost the same values of 0.06–0.07 g/cm³. It has been reported that good foam samples have the densities of ca. 0.04–0.05 g/cm³ (Hirose et al., 1994). From this viewpoint, it happened that the DEG-contained foams prepared in this study had better shapes than the foams containing PEG.

Thermal decomposition behaviour of PU foams was studied by thermogravimetry (TG). Fig. 1 shows TG curves of PEG- or DEG-contained PU foams. Each curve expresses the change in the percentage of weight residue, $(m_T/m_{20}) \times 100$, where m_T is the sample weight at temperature T and m_{20} at 20 °C (starting temperature). The curves show a multi-step decrease in this temperature range, especially with high PO-p contents. The starting temperature of the thermal decomposition (T_{di}) was determined as the temperature at which samples show a 1% weight loss. Thermal decomposition temperature (T_d) was determined as the temperature of the cross point of extrapolated baseline and tangent line in a TG curve.

T_{di} , T_d and weight residue at 500 °C were plotted against the PO-p content in the pre-mixture for the PU foams as shown in Fig. 2. For all foams, T_d decreased with increasing PO-p content, whereas T_{di} kept almost constant at ca.

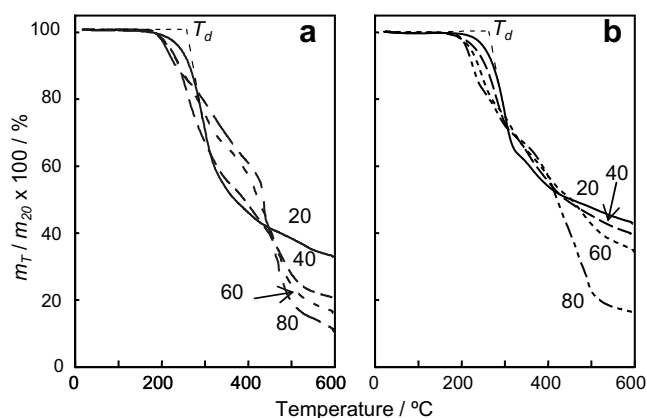


Fig. 1. TG curves of the PEG- or DEG-contained foams having various PO-p contents as indicated on each curve (%): (a) PEG; (b) DEG.

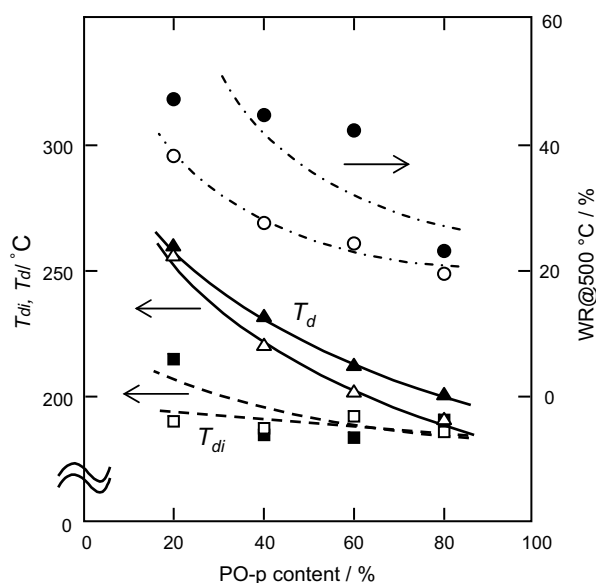


Fig. 2. Starting (T_{di}) and thermal decomposition (T_d) temperatures and weight residues (WR@500 °C) of PU foams having various PO-p content; PEG series: open symbols; DEG series: closed symbols.

200 °C for both PEG and DEG series. From a separate study, thermal degradation of PO-p itself started at very early stage of the TG analysis, i.e., below 100 °C. Kurimoto et al. showed that the degradation of PEG starts at around 200–250 °C (Kurimoto et al., 2001). Moreover, it has been studied that urethane bonds dissociate to form hydroxyl and isocyanate groups at around 250 °C (Hirose et al., 1994). According to these observations, it is considered that the dissociation of urethane bonding starts at T_{di} for all PU foams studied here, irrespective of the PO-p content. The decrease of T_d along the PO-p content, on the other hand, may be due to the introduction of thermally unstable PO-p molecules into PU structure. Therefore, T_d seems to be the decomposition temperature of the polyol molecules, either PO-p or the ethylene glycols.

For weight residue (WR) at 500 °C, the percentage decreased with increasing PO-p content for both PEG and DEG series. As same as the T_d decrease, this indicates that PU structure has become thermally unstable by introducing PO-p segments into ethylene glycol segments of PEG or DEG.

It can also be observed from Fig. 2 that T_d and WR of the DEG series seem to be higher than those of the PEG series, irrespective of PO-p content. Both DEG and PEG have two OH groups in one molecule. Molecular weight of DEG is 106 and that of PEG used in this study is 194, as commercially labelled 200. It means that 100 g of DEG has approximately 2 mols of OH groups, whereas 1 mol for PEG. When the PO-p content is expressed in wt%, total OH content must be higher for a DEG-contained sample than a PEG-contained sample at the same PO-p content. As been mentioned in Section 2.1.2, the molecular ratio of isocyanate groups to hydroxyl groups (NCO/OH) was kept constant at 1.2 for all samples studied here. Therefore, the urethane linkage between OH groups and NCO groups are more in the DEG series and less in the PEG series. Moreover, NCO groups are quite reactive, which may create additional bondings to the urethane linkage. It is also likely to happen in the DEG samples rather than the PEG samples. This may lead to the different behaviour between the both series for the thermal decomposition as shown in Fig. 2.

DSC analysis was carried out to study phase transition of PU foams. Fig. 3 shows stacked DSC curves of PU's containing PEG or DEG. As shown in the figure, two inflectional points were observed by the gap in the baseline due to glass transition (T_{g1} and T_{g2}) for each sample. T_g 's of both series were plotted against the PO-p contents as Fig. 4. The glass transition occurs as a step increase in the heat capacity (C_p) of the sample during heating, which is due to an enhancement of molecular motion in the polymer (Hatakeyama and Quinn, 1994). From each DSC curve, heat capacity difference (ΔC_p) was determined at each transition temperature, ranging 0.02 to 0.07 J/g K for T_{g1} 's and 0.11 to 0.39 for T_{g2} 's. As the ΔC_p at T_{g2} were much larger than the ΔC_p at T_{g1} , it is reasonable to consider that T_{g2} corresponds to relatively large enhancement

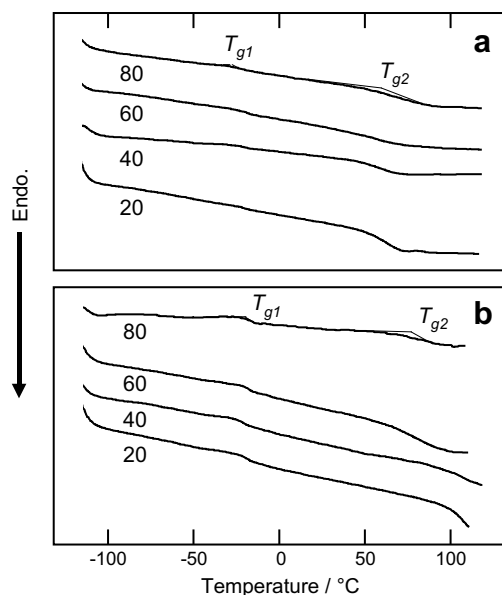


Fig. 3. DSC curves of the PEG- or DEG-containing foams having various PO-p contents as indicated on each curve (%): (a) PEG; (b) DEG.

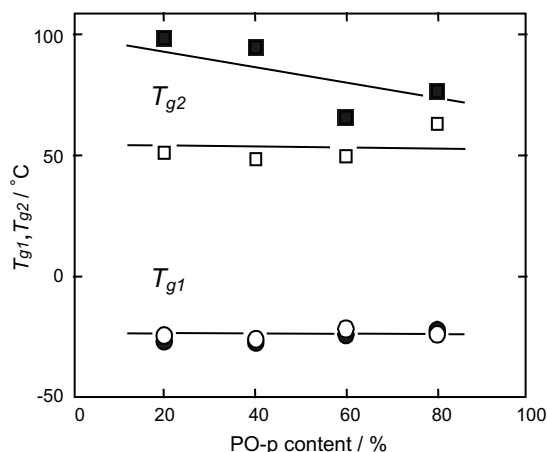


Fig. 4. Relationship between glass transition temperatures (T_{g1} and T_{g2}) and PO-p content; PEG series: open symbols; DEG series: closed symbols.

in molecular motion, whereas T_{g1} is due to rather small movement.

Glass transition at T_{g1} may be attributed to long alkyl carboxyls from the PO-p molecules. The carboxyl groups are assumed to be sticking out from the backbone formed with oxyethylene, glycerol and urethane bonds. Therefore the relaxation of the carboxyls may be independent from the backbone, which leads to constant T_{g1} for all samples.

Enhancement of molecular motion at T_{g2} , on the other hand, may be due to the backbone of PU. As PEG is originally the longer oxyethylene molecule when compared with DEG, the backbone containing PEG is more flexible than that with DEG molecules. This may result in the lower T_{g2} for the PEG series as shown in Fig. 4. However, the dependence of T_{g2} on PO-p content is not clear for both DEG and PEG series. For the DEG series, T_{g2} seems to be decreasing along the PO-p content, whereas it looks almost constant

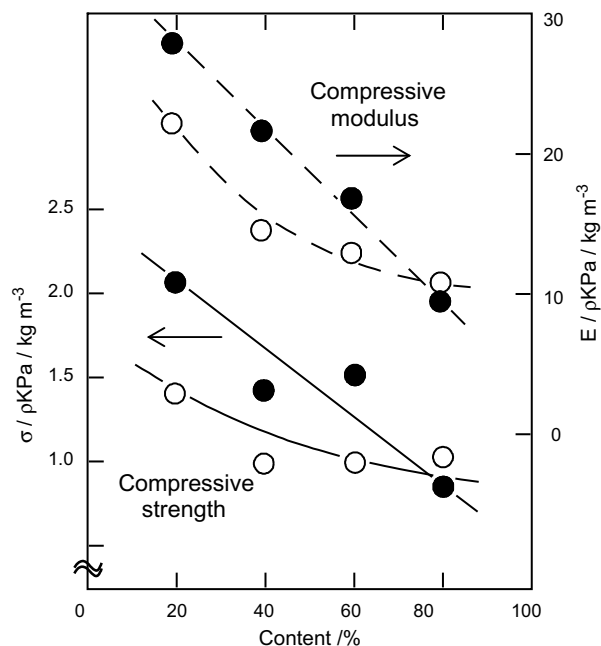


Fig. 5. Changes of compressive strength (σ/ρ) and compressive modulus (E/ρ) along PO-p content; PEG series: open symbols; DEG series: closed symbols.

for the PEG-containing PU. The difference may be related to some complicated alignment and interaction of oxyethylene and PO-p molecules, so that it is necessary to conduct further investigation on the effect of the polyol structure and T_{g2} .

Mechanical properties of the PU foams prepared in this study were also determined as shown in Fig. 5 for compressive strengths (δ) and moduli (E). Each strength or modulus was divided by the sample density (ρ), because these properties are very much dependent on the density and densities of the foam samples were so scattered, especially for the PEG series, as been mentioned previously.

The figure expresses changes of δ/ρ and E/ρ with the PO-p content in the mixtures with DEG or PEG. It is clearly shown that each parameter for both series decreases with increasing the PO-p content. It may be in good agreement with the results of DSC analysis, which suggests that the PO-p molecules work as soft segments in the PU foam. When a pressure is applied, the sample containing more soft segments may be easier to be compressed. Therefore, it reflects in the mechanical properties of the PU foams prepared in this study.

Difference between the DEG series and the PEG series may be the same reason as the phenomena observed at the thermal analyses. The main chain motion in the whole PU is more restricted for the foam containing DEG than that with PEG. So the effect of the PO-p content is the greater for the DEG series.

4. Conclusions

In this study, monoglycerides are derived from palm oil by glycerolysis at the yield of 70%, using an alkali catalyst

and a solvent. After the glycerolysis, 90% of unreacted glycerol is removed by the purification process using *n*-hexane.

Polyurethane foams are prepared using the palm oil-based polyol (PO-p), mixed with polyethlen glycol (PEG) or diethylene glycole (DEG). Chain motion of polyurethane becomes more flexible at the higher PO-p content in the polymer. Monoglyceride molecules, main components of the PO-p, work as soft segments in the whole PU because of the presence of long alkyl chains.

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References

- Asano, Y., Hatakeyama, H., Hirose, S., Hatakeyama, T., 2001. Preparation and physical properties of saccharide-based flexible polyurethane foams. In: Kennedy, J.F., Phillips, G.O., Williams, P.A., Hatakeyama, H. (Eds.), *Recent advances in environmentally compatible polymers*. Woodhead Publishing Ltd., Cambridge, UK, pp. 241–246.
- Chian, K.S., Gan, L.H., 1998. Development of a rigid polyurethane foam from palm oil. *J. Appl. Polym. Sci.* 65, 509–515.
- Corma, A., Iborra, S., Miquel, S., Primo, J., 1998. Catalysts for the production of fine chemicals – Production of food emulsifier, monoglycerides, by glycerolysis of fats with solid base catalysts. *J. Catal.* 173, 315–321.
- Deffense, E., 1985. Fractionation of palm oil. *J. Am. Oil Chem. Soc. (JAOCS)*. 62, 376–385.
- Hatakeyama, H., 2002. Thermal analysis of environmentally compatible polymers containing plant components in the main chain. *J. Therm. Anal. Calor.* 70, 755–795.
- Hatakeyama, T., Hatakeyama, H., 2004. *Thermal Properties of Green Polymers and Biocomposites*. Kluwer Academic Publishers, Dordrecht, the Netherlands.
- Hatakeyama, T., Quinn, F.X., 1994. *Thermal Analysis: Fundamentals and Applications to Polymer Science*. John Wiley & Sons, Chichester, UK.
- Hatakeyama, H., Hirose, S., Hatakeyama, T., Nakamura, K., Kobashigawa, K., Morohoshi, N., 1995. Biodegradable polyurethanes from plant components. *J. Macromol. Sci.: Pure Appl. Chem.* A32, 743–750.
- Hatakeyama, T., Tokashiki, T., Hatakeyama, H., 1998. Thermal properties of polyurethanes derived from molasses before and after biodegradation. *Macromol. Symp.* 130, 139–150.
- Hirose, S., Kobashigawa, K., Hatakeyama, H., 1994. Preparation and physical properties of polyurethanes derived from molasses. *Sen-i Gakkaishi*. 50, 538–542.
- Kalam, M.A., Masjuki, H.H., 2002. Biodiesel from palm oil – an analysis of its properties and potential. *Biomass Bioenergy* 23, 471–479.
- Kurimoto, Y., Takeda, M., Koizumi, A., Yamauchi, S., Doi, S., Tamura, Y., 2000. Mechanical properties of polyurethane films prepared from liquefied wood with polymeric MDI. *Bioresource Technol.* 74, 151–157.
- Kurimoto, Y., Takeda, M., Doi, S., Tamura, Y., Ono, H., 2001. Network structures and thermal properties of polyurethane films prepared from liquefied wood. *Bioresource Technol.* 77, 33–40.
- McNeill, G.P., Berger, R.G., 1993. Enzymatic glycerolysis of palm oil fractions and a palm oil based model mixture: Relationship between fatty acid composition and monoglyceride yield. *Food Biotechnol.* 7, 75–87.
- Mohamad, I.A.I-W., Ali, O.A.I-S., 2002. Experimental evaluation of the transesterification of waste palm oil into Biodiesel. *Bioresource Technology*. 85, 253–256.
- Noureddini, H., Medikonduru, V., 1997. Glycerolysis of fats and methyl esters. *J. Am. Oil Chem. Soc. (JAOCS)*. 74, 419–425.
- Siwayanan, P., Ooi, T.L., Shaari, N.Z.K., Ahmad, S., Wiese, D., Chua, M.C., 1999. Recent development in palm-based polyols. In: *Proceedings of the 1999 PORIM International Palm Oil Congress (Oleochemicals)*. Palm Oil Research Institute Malaysia, Kuala Lumpur, pp. 59–64.
- Tuan Noor Maznee, T.I., Norin, Z.K.S., Ooi, T.L., Salmiah, A., Gan, L.H., 2001. Effect of additives on palm-based polyurethane foams. *J. Oil Palm Res.* 13, 7–15.
- Wang, Q., Narita, J., Xie, W., Ohsumi, Y., Kusano, K., Shirai, Y., Ogawa, H.I., 2002. Effects of anaerobic/aerobic incubation and storage temperature on preservation and deodorization of kitchen garbage. *Bioresource Technology*. 84, 213–220.
- Yang, H.-S., Kim, D.-J., Lee, Y.-K., Kim, H.-J., Jeon, J.-Y., Kang, C.-W., 2004. Possibility of using waste tire composites reinforced with rice straw as construction materials. *Bioresource Technol.* 95, 61–65.

Water-borne and air-drying oil-based resins

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Abstract

New water-borne polyurethane resins were produced using maleinized monoglyceride (MMG), hydroxyl-terminated polybutadiene (HTPB), toluene di-isocyanate, and ethylene diamine (EDA). Maleinization was performed in order to insert hydrophilic groups in the fatty acid residues, which were then inserted to the backbone of polyurethane. The MMG was mixed with HTPB in different proportions, and the mixture was used as the polyol part of water-borne polyurethane resin. It was then reacted with toluene di-isocyanate, and the isocyanate end groups were blocked with methyl ethyl ketoxime (MEKO). The ratio of MMG to total polyol was changed between 40 and 70 mol%, while the [NCO]/[OH] ratio was kept at 1.5 in all samples. The carboxylic acid groups of MMG were then neutralized with triethyl amine. The formation of ionic groups imparts water dispersibility. Chain extension was performed by adding EDA and baking at 125 °C. Hardness, adhesion, impact resistance, bending, and abrasion resistance tests were applied to the specimens. The samples exhibited good physical and mechanical properties.

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Keywords: Water-borne; Water dispersed; Polyurethane; Maleinization; Monoglyceride; Air-drying

1. Introduction

Polyurethanes exhibit excellent abrasion resistance, toughness, chemical and corrosion resistance and a wide range of mechanical strengths, thus they have found extensive applications in the high performance coatings for the automotive, appliance, and wood industries [1]. In the 1980s, the automakers started to shift from solvent-based to water-based paints to reduce the amount of volatile combustibles. The increasing trend towards water-dispersed paints accelerated the research on the development of new type of polymeric resins for use in paint industry [2,3]. The research on water-borne paints goes down to early fifties, and the work was mostly concentrated on the use of maleinized oils [4].

Most polyurethane paints available in the market are usually made by using polyester polyols to impart sufficient rigidity to the resin. However, polyether polyols are also used as partial substitute to make resins with improved flexibility. Polyethers increase also the dispersion of the resin in water because they have higher number of hydrophilic groups on

the backbone. The use of polyethylene and polybutylene glycol at appropriate ratios may help to balance the hydrophilic and hydrophobic properties at the desired level. Water-borne alkyds drew continuous attention as the availability of raw materials and the superior properties of the product are concerned. The alkyd resins may also be made water dispersible by mixing a normally synthesized resin with a specially synthesized alkyd which contains high acidic groups. The high acidic groups can be achieved by using a chemical with high functionality such as trimellitic anhydride. The styrenated alkyd may be made water-borne by using hydrophilic monomers such as acrylic acid or methacrylic acid [4]. The research on oil containing water-borne resins is still an active subject in paint industry and new patents were introduced using different raw materials and techniques [5–8]. In recent years, water-dispersed epoxy resins also have gained importance [9]. Although water-dispersed paints display excellent performance in many areas of applications they lack abrasion resistance, chemical resistance and general durability [10]. The research work on water-borne resins and paints cover a wide range from synthesis to characterization [11–15].

Water dispersion of polyurethanes is usually achieved by having carboxyl acid residues on the backbone and quaternizing these groups by tertiary amines. The organic salts thus formed become dispersible in water. The most preferred

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monomer to incorporate hydrophilic group is dimethylol propionic acid though tartaric acid can also be used with some precaution; that is, heavy branching must be prevented during synthesis when tartaric acid is used [14,15]. Polyurethanes contain a soft and a hard segment on the backbone with polyesters (or polyethers) comprising the soft segment, and the urethane group the hard segmental part. Air-drying polyurethane resins can be synthesized by substituting the polyester with monomers containing double bonds on the backbone such as monoglycerides [15]. However, the use of pure monoglyceride results in a thick mixture which is apt to easy gelation. Therefore, it needs to be diluted by using a polyol. The polyol can be of polyester or polyether origin.

The aim of this work was to synthesize water dispersible polyurethane resin containing (i) fatty acid residues to provide air drying and (ii) maleinized fatty acid residues to achieve water dispersion. In other words, the traditionally used dimethylol propionic acid has been substituted by maleinized fatty acids. To improve air drying hydroxyl-terminated polybutadiene (HTPB) was partly used on the backbone. The research work concentrated on synthesizing a maleinized monoglyceride (MMG) derivative from sunflower oil. The monoglyceride derivative contained both fatty acid residues and hydrophilic groups. Two different MMG derivatives were synthesized and the resins made from them were characterized for their properties.

2. Experimental

2.1. Raw materials

The raw materials used were sunflower oil, sodium hydroxide (Merck), sulfuric acid (99.5% pure; Merck), methyl ethyl ketone (99.5% pure; Delta Kimya), toluene sulfonic acid, glycerine (99.5% pure; Birpa Ltd. Ş.), maleic anhydride (Volkan Boya), HTPB (MW = 2700 g/mol; SAGE), toluene diisocyanate (TDI) an isomeric commercial grade mixture (işbir A.Ş.), methyl ethyl ketoxime (MEKO; Volkan Boya), triethylamine (TEA; ÇBS A.Ş.), ethylene diamine (EDA; Merck), and nitrogen gas (99.999% pure; Habaş).

HTPB was dehydrated by passing nitrogen gas through it for 30 h. MEK and MEKO were dehydrated over molecular sieves. MMG, after its production, was dehydrated under vacuum at 50 °C, for about 2 h, and then magnesium sulfate salt was used to remove any remaining water. Other materials were used as-received.

2.2. Synthesis of MMG derivatives

MMG derivative was produced by two different methods. They are denoted here as Method I and Method II. A number of trials were made to synthesize MMG by direct maleinization of monoglyceride. However, gelation took place in all of these trials because of the reaction of anhydride groups

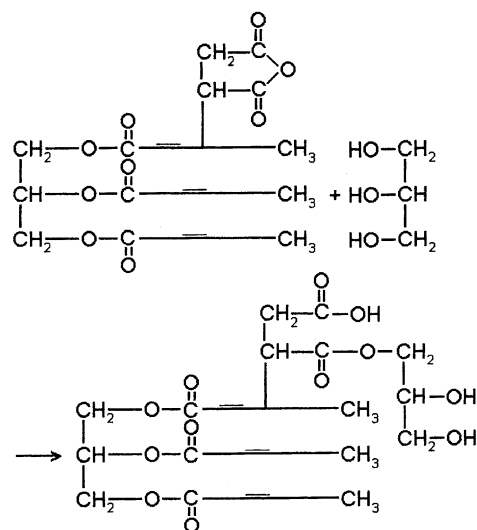
of maleic anhydride and hydroxyl groups of glycerin. In another trial, the oil was maleinized and then reacted with glycerin, but the material gelled in this case too. Therefore, two different methods described below were used to synthesize MMG derivative. The experiments were carried in a 5-necked glass reactor of about 1 l in volume. It is equipped with a stirrer, condenser, thermometer, nitrogen and feed inlet.

2.2.1. Method I

The following steps were performed:

1. The sunflower oil was reacted with maleic anhydride at 200 °C under nitrogen atmosphere for 3 h.
2. The maleinized oil was cooled to 100 °C, and glycerine was added to the reactor. The reaction continued until the acid number came down to a value of 90. As seen in equation the maleinized oil was hydrolyzed with glycerin to yield monoglyceride. It now has two hydroxyl groups to react with a di-isocyanate to make polyurethane, has one carboxylic group that can be used for water dispersion, and two fatty acid residues having double bonds for air drying.

However, this MMG derivative, named MMG-I, resulted in brownish color when used in making polyurethane resin. Therefore, another MMG derivative was synthesized by following another method:



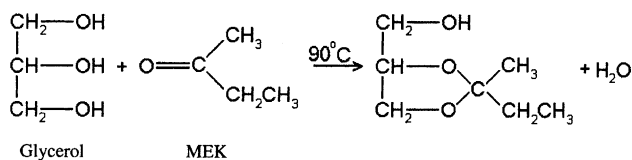
2.2.2. Method II

In this method we needed to use fatty acids in the synthesis of MMG. Therefore, fatty acids were first obtained from the alcoholysis of sunflower oil. The oil was mixed with 1:1 ethanol–water solution, and stoichiometric amount of sodium hydroxide (3 mol per mole of oil) was added. The hydrolysis reaction was carried at 80 °C under reflux until a homogeneous mixture was obtained. The mixture was poured into a saturated solution of sodium chloride in order to precipitate the soap. Then soap was dissolved in water and

reacted with stoichiometric quantity of sulfuric acid. This separates fatty acid phase from water phase. The saturated fatty acids, stearic acid (6 wt.%) and palmitic acid (11 wt.%) with melting points of 69.6 and 63.1 °C, respectively, precipitate at room temperature, and they were filtered out to increase the unsaturation in the final product. The liquid fatty acid phase was washed with water for several times and put under vacuum to remove water.

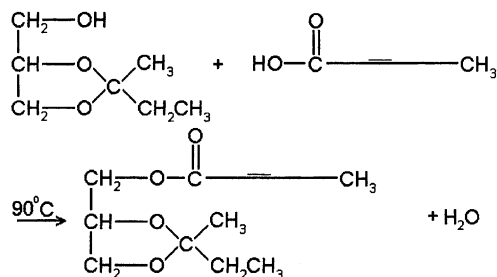
In order to synthesize MMG the following steps were performed:

1. Glycerol was reacted with MEK at 90 °C, using toluene sulfonic acid as a catalyst. Thus two of the hydroxyl groups of glycerine were blocked with MEK:



The reaction water was removed by azeotropic distillation with toluene during reaction.

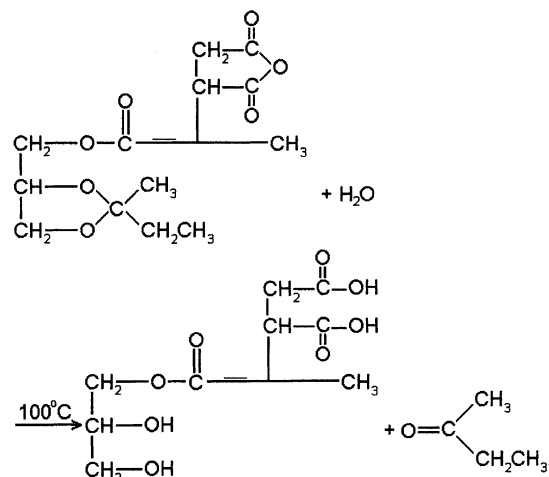
2. The resultant material was reacted with fatty acid mixture using the same catalyst. The fatty acid mixture contains about 35% by weight oleic acid, 62.6% linoleic, and 2.4% linolenic acid. Thus totally unsaturated fatty acid residues are introduced into the structure:



The resulting water was again removed by azeotropic distillation with toluene.

3. The material was washed with water for several times to remove the catalyst. Then, toluene was removed under vacuum.

4. The synthesized chemical was maleinized by reacting it with 30 mol% of maleic anhydride at 200 °C and under nitrogen atmosphere.
5. The maleinized product was hydrolyzed by reacting it with water in the presence of several drops of sulfuric acid, and thus a new maleinized monoglyceride derivative, named MMG-II, was obtained.
6. The MMG derivative was washed with water for several times and then put under vacuum for about 3 h to remove water and MEK produced as a by product:



As the two MMGs are compared, both have two hydroxyl groups, MMG-I has one carboxyl group while MMG-II has two. MMG-I has an additional two more fatty acid residues. The molecular weight of MMG-I is 1053 g/mol, and that of MMG-II is 455 g/mol.

2.3. Water-dispersed polyurethane varnish production

In all experiments, the [NCO]/[OH] ratio was kept at 1.5 in order to assure NCO termination of the prepolymer. The experiments were repeated by changing the ratio of MMG to HTPB. Several formulations of the feed are given in Table 1. The following procedure was carried out in making water-dispersed polyurethane:

1. HTPB and MMG were dissolved in MEK by stirring the mixture for 30 min at 50 °C. This was done in

Table 1
Basic formulations of the resin

Method	Sample	Ratio ^a (%)	MMG (mol)	HTPB (mol)	TDI (mol)	MEKO (mol)	TEA (mol)	EDA (mol)
I	A1	40	0.8	1.2	3.0	2.0	0.8	1.0
I	A2	50	1.0	1.0	3.0	2.0	1.0	1.0
I	A3	60	1.2	0.8	3.0	2.0	1.2	1.0
I	A4	70	1.4	0.6	3.0	2.0	1.4	1.0
II	B1	50	1.0	1.0	3.0	2.0	0.6	1.0
II	B2	55	1.1	0.9	3.0	2.0	0.66	1.0
II	B3	60	1.2	0.8	3.0	2.0	0.72	1.0
II	B4	65	1.3	0.7	3.0	2.0	0.78	1.0
II	B5	70	1.4	0.6	3.0	2.0	0.84	1.0

^a MMG/(MMG + HTPB).

order to have a homogeneous distribution of hydrophilic molecules in the polymer backbone.

2. TDI was added to the mixture and the reaction continued for 3 h with stirring at 70 °C. The reaction time was determined by using di-butylamine back titration method.
3. After the completion of the reaction, the prepolymer was cooled to 50 °C, and the free NCO groups of the prepolymer were blocked with MEKO for approximately 2 h. This step is not necessary. However, it is done to improve the shelf-life of the resin.
4. TEA was added to the solution to neutralize the carboxylic groups, and the mixture was stirred for 30 min, while maintaining the temperature at 50 °C.
5. Water was added to the solution at an amount to make 50% of the total mass from a stop-cock burette by one drop per two or three seconds under continuous stirring.

3. Results and discussion

3.1. Chain extension by baking

Ethylene diamine was used for the chain extension of blocked isocyanate groups. It was added at stoichiometric amounts to all samples prepared. It was added 2–3 h before the application step because it causes gelation at room temperature in 4 days after its addition.

3.2. Preparation of test panels

A standard of 30 μm wet film thickness was applied to test panels. This was done by using film casting knife (Braive-Instruments) on the panels. After casting, the test panels were put in an oven, where the temperature was increased to 125 °C, and maintained at this temperature for 3 h. The varnishes which were produced using MMG produced through Method II required a temperature of 175 °C to form a non-tacky film. The films dried in 1 day at room temperature without using any drier.

3.3. NMR spectroscopy

A Bruker-Spectrospin Avance (DPX 400) Ultra-Shield Nuclear Magnetic Resonance instrument was used to characterize the MMG. The characterization by using ^1H NMR spectroscopy was done only for MMG-II because the process used is a novel one. The characterization was done by comparing the spectroscopy of a mixture of maleic anhydride and monoglyceride in Fig. 1 with that of MMG in Fig. 2.

The results showed that the double bonds of MMG disappeared after the reaction. In Fig. 1, the peak at 6.2 ppm denotes the double bonds of maleic anhydride, and it disappeared after the reaction of maleic anhydride with monoglyceride as shown in Fig. 2. The other peaks appear in both figures because they have similar structure. The peak

at 5.2 ppm denotes the hydrogen atom bonded to the secondary carbon atom in the monoglyceride molecule. This peak covers also carbon–carbon double bond of the fatty acid residue. The peak at 4.1 ppm denotes the carboxylic and ester groups. The peak at 2.6 ppm corresponds to $-\text{CH}_2-$ groups adjacent to double bond in the fatty acid residue, and the one at 2.25 ppm denotes the $-\text{CH}_2-$ groups adjacent to the ester bond and the groups that are not bonded to the carbon atoms in the double bonds. The peak at 2.0 ppm corresponds to the $-\text{CH}_2-$ from maleic anhydride, and the one at 1.3 ppm denotes the $-\text{CH}_2-$ groups adjacent to methyl groups in the fatty acids and methyl ethyl ketone. The peak at 0.9 ppm denotes the $-\text{CH}_3$ group in the fatty acid and methyl ethyl ketone.

3.4. IR spectra

Hitachi (Model: 270-30) Infrared Spectrophotometer was used to characterize the samples. The IR spectrum of MMG-I and of MMG-II are shown in Figs. 3 and 4, respectively.

The peak at 3500 cm^{-1} corresponds to OH stretching, the small shoulder at 3000 cm^{-1} corresponds to unsaturated CH stretching, and the peak at 2900 cm^{-1} corresponds to CH_2 stretching. The peak at 1720 cm^{-1} corresponds to C=O stretching of ester, and the shoulder at 1700 cm^{-1} to C=O stretching of carboxylic group from maleic anhydride. The peak at 1460 cm^{-1} is due to $-\text{CH}_3$ bending and the broadening in the peak is due to *cis* C=C group. The peak due to $-\text{CH}_3$ bending exists at 1380 cm^{-1} , the peak at 1170 cm^{-1} corresponds to C–O–C stretching of ester, and the peak at 720 cm^{-1} is due to multiple CH_2 split from $(\text{CH}_2)_n$.

Both figures look similar, however, it can be noticed that in Fig. 3 the peaks at 3000 cm^{-1} has higher intensity and it is merged into the adjacent peak. This difference is due to the higher concentration of fatty acid residues with unsaturated bonds. The higher intensity of the peak below 1800 cm^{-1} shows the higher concentration of carboxylic groups from maleic anhydride. The higher intensity at 920 cm^{-1} is due to the higher dimer content because of the higher carboxylic acid groups.

Figs. 5 and 6 show the IR spectrum of the polyurethane produced by using MMG-I and MMG-II, respectively. The urethane bond was characterized by the presence of NH group at $3300\text{--}3500\text{ cm}^{-1}$. The peak at 2900 cm^{-1} is due to the CH stretching, and the peak at 1720 cm^{-1} corresponds to C=O stretching from ester groups. The other peaks are from the raw materials used. The absence of peaks in the range $2000\text{--}2300\text{ cm}^{-1}$ shows that all isocyanate groups were involved in the reaction, and that there are no significant isocyanate groups in the resin.

3.5. Color of the dry films

The varnish produced by using MMG-II, gave slightly yellow transparent films. On the other hand, the varnish produced from MMG-I gave brown and semitransparent films.

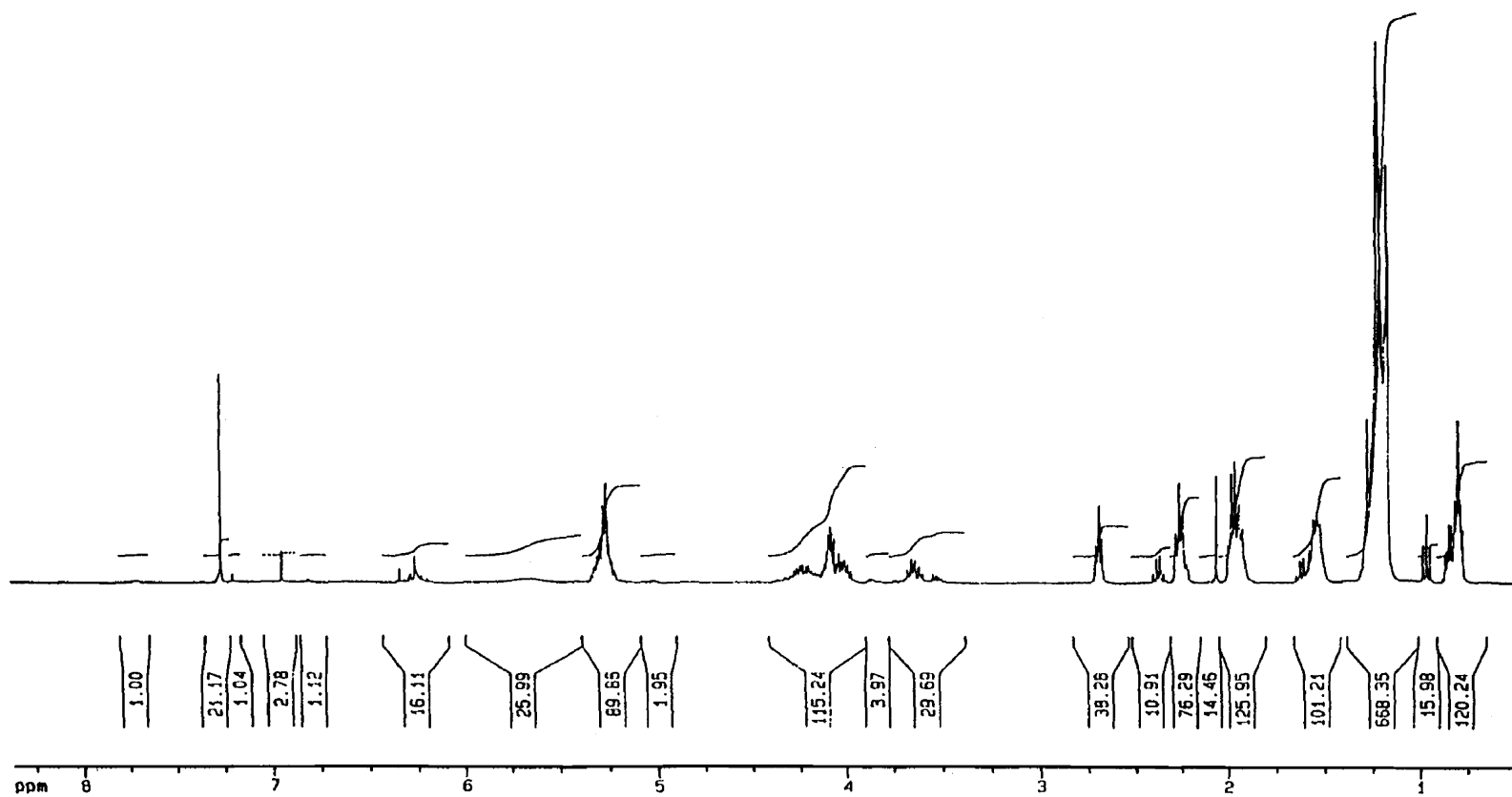


Fig. 1. NMR of monoglyceride and maleic anhydride mixture.

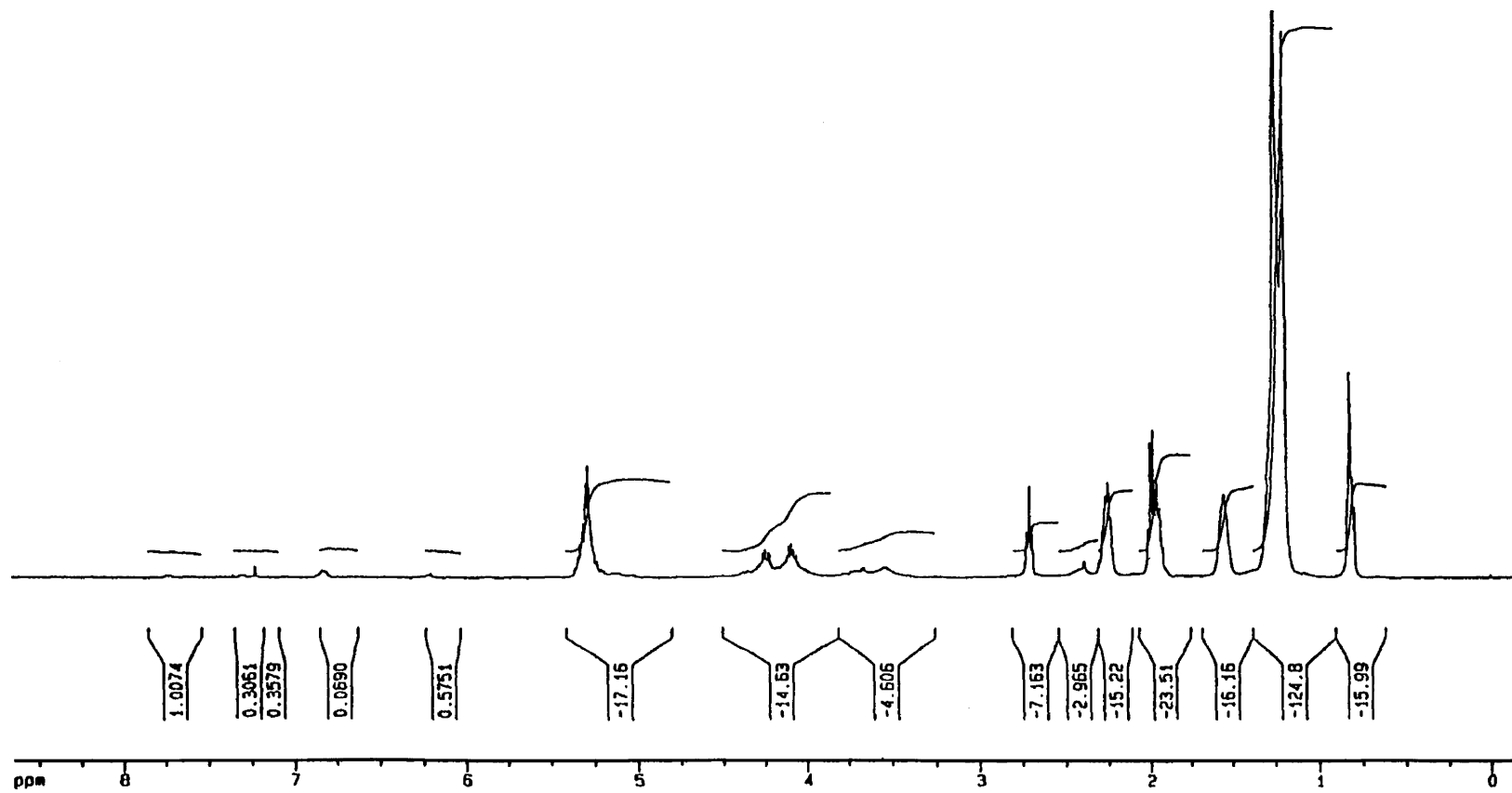


Fig. 2. NMR of MMG.

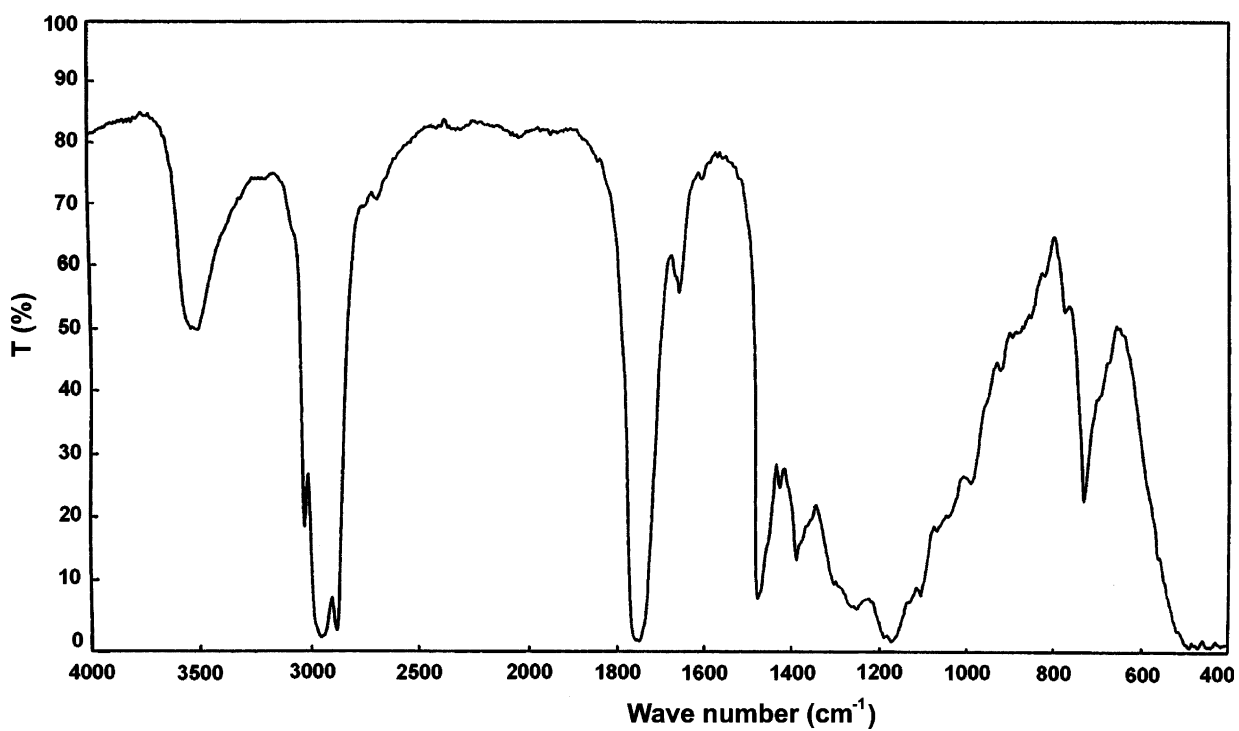


Fig. 3. IR of MMG produced by Method I.

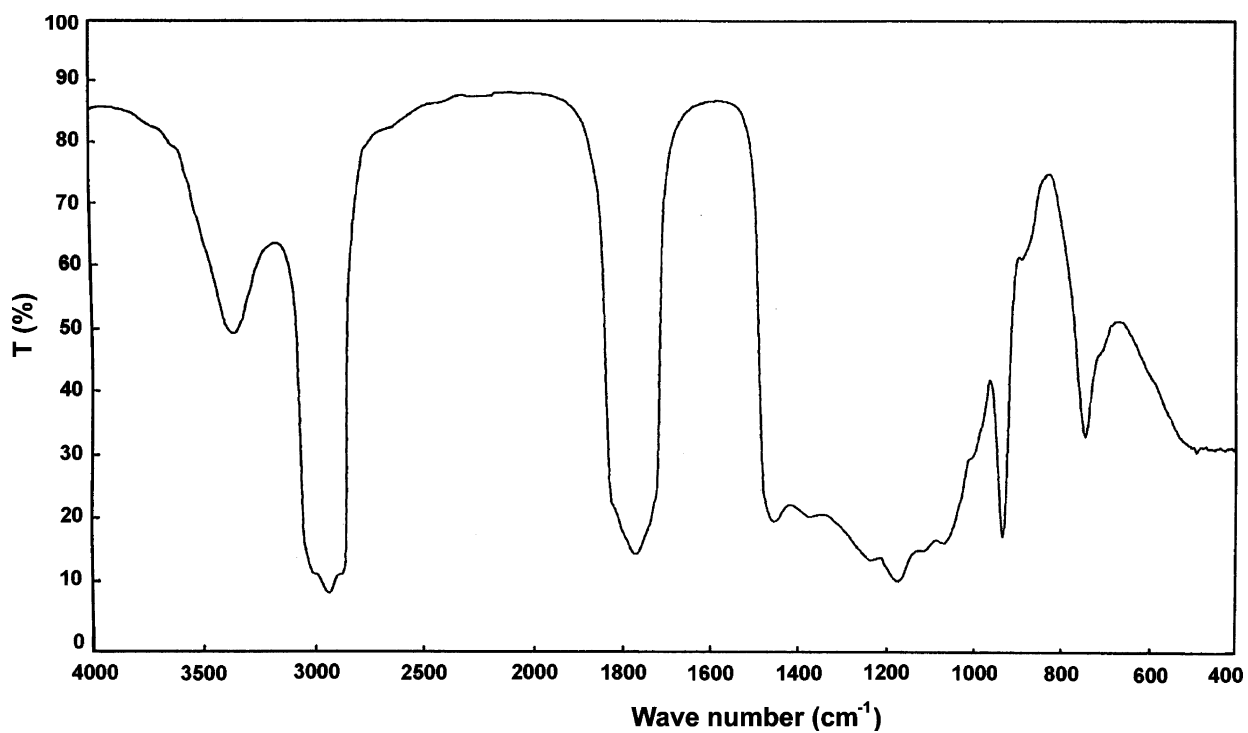


Fig. 4. IR of MMG produced by Method II.

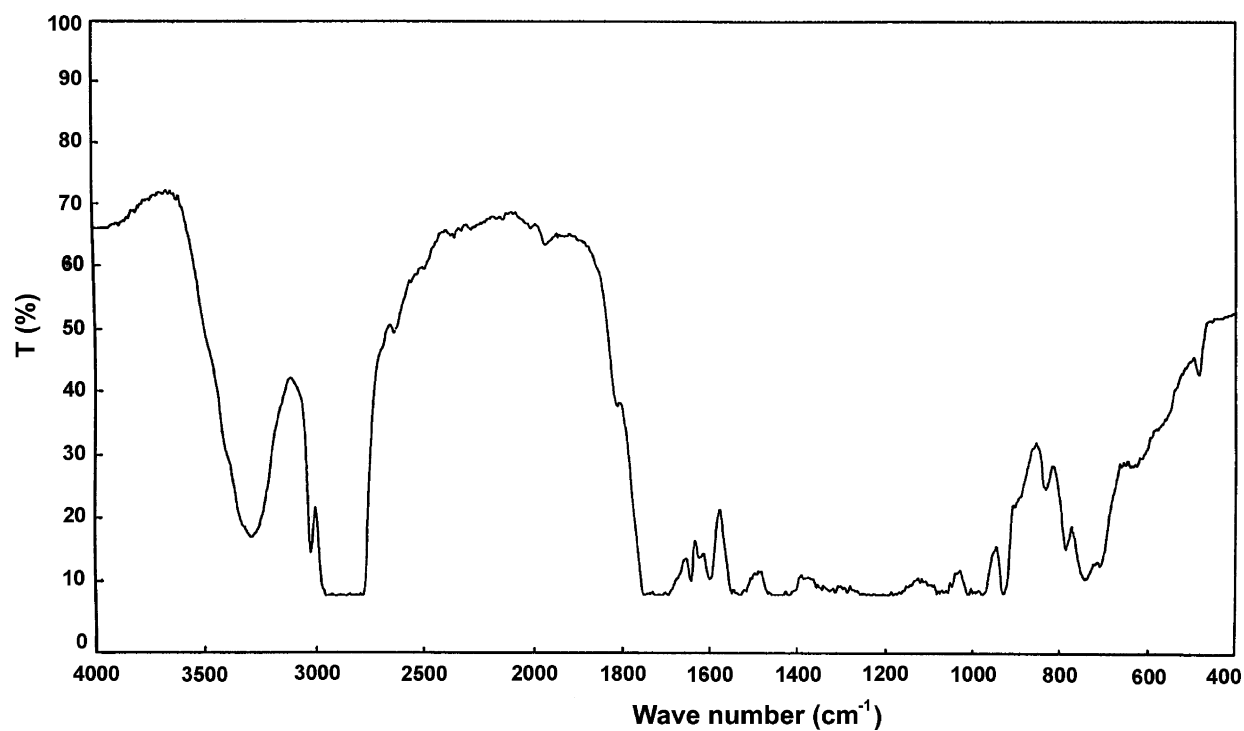


Fig. 5. IR spectrum of dry film of Sample A2.

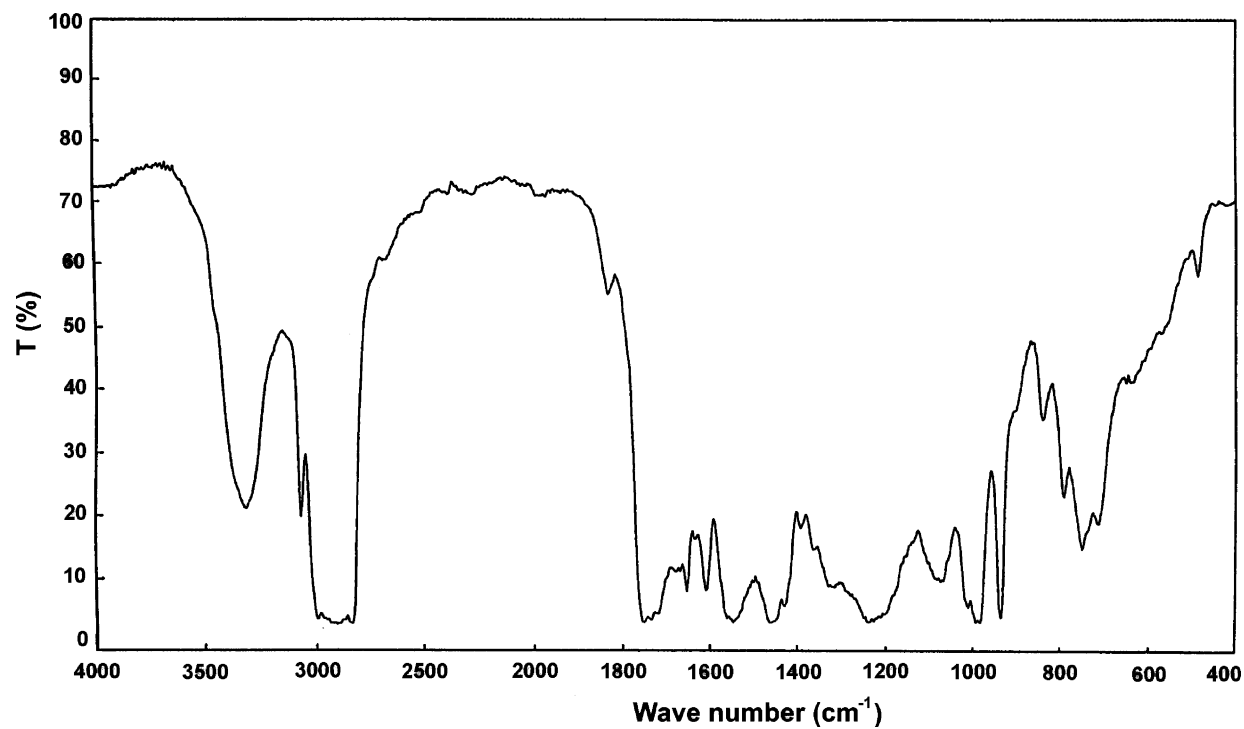


Fig. 6. IR spectrum of dry film of Sample B1.

Table 2
Gloss values for the samples

Method	Sample	Gloss value (%)		
		20°	60°	85°
I	A1	64.5	75.6	35.3
I	A2	21.0	53.2	48.0
I	A3	57.8	87.0	73.5
I	A4	25.5	55.0	49.2
II	B1	97.1	96.7	96.0
II	B2	86.8	90.3	95.0
II	B3	98.8	93.0	92.1
II	B4	78.3	89.0	87.3
II	B5	91.7	98.0	98.2

This difference is apparently due to higher ratio of fatty acid residues in the MMG produced by Method I.

3.6. Gloss test

A Rhopoint-Novoglass glossmeter was used to test the light reflection properties of the specimens. The gloss of dry films was measured at 20°, 60°, and 85°. The results were listed in Table 2. These results show that varnishes produced by using MMG-II had excellent gloss.

3.7. Hardness test

A Braive-Instrument Persoz Pendulum (No. 3034) was used. The principle of this test is based on the fact that the increase of hardness decreases the effect of friction, which increases the number of oscillations of the pendulum swinging on the test panel.

The dependence of hardness on the amount of MMG in the polymer can be seen in Figs. 7 and 8 for the varnishes produced by using MMG-I and MMG-II, respectively. In Fig. 7, the hardness decreases as the amount of MMG increases at all ratios used, while in Fig. 8 it first increases then decreases after 55% of MMG content. The decrease

of the amount of MMG results in a relative increase in the amount of HTPB. The double bond content of monoglyceride is about 1 per 9 carbon atoms and that of HTPB is about 1 per 4 carbon atoms. Therefore, HTPB gives denser cross-linking which results in higher hardness. It is also noticed that the varnish produced by using MMG-II has about twice higher hardness than that produced by using MMG-I. This is because MMG-I contains three fatty acid residues per molecule that makes the resin softer on drying whereas MMG-II contains only one fatty acid residue per molecule.

The decrease of hardness below 55% MMG in Fig. 8 can be due to the fact that hardness decreases with the increased branching. Branching in the polymer is due to the pendant fatty acid residues which come from MMG. The increase in the quantity of fatty acids increases side branches. There are two different cross-linkings which influence hardness: (i) the cross-linking due to double bonds of HTPB on the backbone and (ii) the cross-linking due to double bonds of fatty acid residues which are short branchings. As MMG decreases HTPB increases, so the double bonds on the backbone increase and the double bonds on the side branches decreases, or vice versa. The optimum ratio that balances both sources of hardness is 55% MMG in MMG-II containing varnish.

3.8. Mandrel bending test

A conical mandrel bending tester (Braive-Instruments No. 1510) was used. After coating the panels with the paint at a uniform thickness, they were fastened and bent over, and cracks were observed along the increasing radius of the conical mandrel. All samples passed bending test successfully without any cracks in the bent film. This is mainly due to the flexibility of the film which is a characteristic feature of polyurethanes.

3.9. Impact resistance test

A Gardner Impact tester (Model: 5510) was used for this test. A standard weight of (1+0.9 kg) was dropped on a film

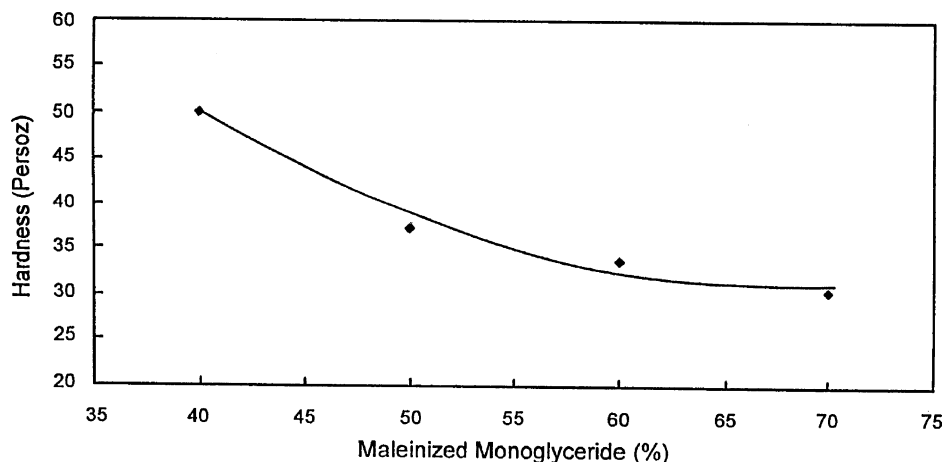


Fig. 7. Change of hardness with the percent of MMG-I in "MMG + HTPB".

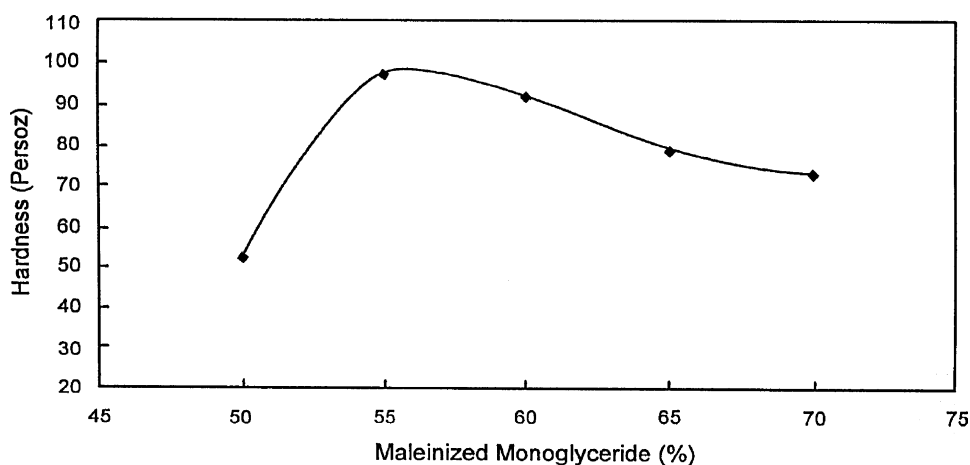


Fig. 8. Change of hardness with the percent of MMG-II in "MMG + HTPB".

coated on a metal plate from different heights. The impact value at which the film cracks is considered as the impact value for that sample. All tested samples showed resistance to impact up to 20 J which is the upper limit used without cracking.

3.10. Adhesion test

A crosshatch cutter was used to cut the film to produce a lattice pattern. After making a cross cut, the coating film was brushed with a soft tissue to remove any detached flakes of coating. Then, the pattern was checked according to ASTM D 3359 B. The maximum number of adhesion is "5" and the minimum is "0". Adhesion was tested on both a metal and a glass surface.

The adhesion test values for the samples are shown in Table 3. These results show that varnishes produced through Method I gives better adhesion than those produced through Method II. This is because MMG produced by Method I contains higher ratio of fatty acid residues, which improves adhesion. Also, it is obvious that Samples B1–B5 have better adhesion on metal plates than on glass plates.

Table 3
Adhesion test

Method	Sample	Adhesion number	
		Metal plate	Glass plate
I	A1	5 B	5 B
I	A2	5 B	5 B
I	A3	5 B	5 B
I	A4	5 B	5 B
II	B1	4 B	3 B
II	B2	5 B	0 B
II	B3	1 B	2 B
II	B4	1 B	1 B
II	B5	4 B	1 B

3.11. Abrasion resistance test

This test determines the resistance of coating film toward a falling abrasive. The abrasive is allowed to fall from a specified height through a guide tube onto a coated panel until the substrate becomes visible. The amount of abrasive per unit film thickness is reported as the abrasion resistance of the coating film. Silica sand was used as abrasive. All samples tested showed very good abrasion resistance and no significant loss in film thickness was observed.

4. Conclusions

1. The MMG-I containing varnish had darker color and lower gloss than the one that contains MMG-II.
2. In general, hardness showed a decreasing trend as the MMG ratio in the polyol increased.
3. The MMG-II-based varnish had higher hardness values than MMG-I-based varnish.
4. The optimum hardness in MMG-II-based varnish was achieved at 55% MMG ratio. This ratio may correspond to the optimum balance between the double bonds of HTPB and fatty acid residues.
5. The samples in which MMG-I was used showed much better adhesion compared to those in which MMG-II was used.
6. All samples tested for impact resistance showed resistance above 20 J.
7. All the tested samples passed conical mandrel bending test without any cracks.
8. No detectable loss in film thickness was observed after the abrasion resistance test.

References

- [1] P. Swaraj, Surface Coatings: Science and Technology, 2nd ed., Wiley, West Sussex, England, 1997, pp. 672–713.

- [2] H. Xiao, H.X. Xiao, B. Suthar, K.C. Frisch, Anionic blocked isocyanate-containing urethane prepolymer for coating applications, *J. Coat. Technol.* 67 (849) (1995) 19–26.
- [3] K.D. Weiss, Paint and coatings: a mature industry in transition, *Prog. Polym. Sci.* 22 (1997) 203–245.
- [4] P.K.T. Oldring, G. Hayward, *A Manual for Resins for Surface Coatings*, SITA Technology, 1987.
- [5] T. Kuwajima, K. Kida, S. Ishikura, US Patent 4,518,724 (1985).
- [6] P.G. Kooymans, J.J.M.H. Wintraecken, W.T. Raudenbusch, J.M.E. Seelen-Kruijssen, G.C.M. Schreurs, US Patent 4,401,774 (1983).
- [7] D.E. Knox, US Patent 5,093,463; 5,096,960; 5,137,965 (1992).
- [8] F.J. Slama, US Patent 5,883,180 (1999).
- [9] J.D. Elmore, D.S. Kincaid, P.C. Komar, J.E. Nielsen, *J. Coat. Technol.* 74 (931) (2002) 63–72.
- [10] C.L. Rodriguez, J. Weathers, Formulating water-based systems with propylene-oxide-based glycol ethers, *J. Coat. Technol.* 72 (905) (2000) 67–72.
- [11] C. Wang, G. Lin, J.H. Pae, F.N. Jones, Novel synthesis of carboxy-functional soybean acrylic-alkyd resins for water-reducible coatings, *J. Coat. Technol.* 72 (912) (2000) 55–61.
- [12] D.E. Fiori, D.A. Ley, R.J. Quinn, Effect of particle size distribution on the performance of two-component water-reducible acrylic polyurethane coatings using tertiary polyisocyanate crosslinkers, *J. Coat. Technol.* 72 (902) (2000) 63–69.
- [13] B. Zhong, C. Shaw, M. Rahim, J. Massingill, Novel coatings from soybean oil phosphate ester polyols, *J. Coat. Technol.* 73 (915) (2001) 53–57.
- [14] G. Gündüz, M. Gafaroğullari, Highly branched and tartaric acid-based water-borne resins, *J. Appl. Polym. Sci.* 80 (2001) 604–612.
- [15] G. Gündüz, Y. Idlibi, G. Akovali, *J. Coat. Technol.* 74 (931) (2002) 59–62.