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ACT: 519 PRESENTACION	

DIRECCIÓN DE NUEVAS CREACIONES

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

Asunto: Radicación: 14-23087- -3
 Trámite: 2
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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° 14-023087-00000-0000	4/Febrero/2014
Reivindicaciones:	Rad. N° 14-023087-00000-0000	4/Febrero/2014
Dibujos:	Rad. N° 14-023087-00000-0000	4/Febrero/2014

2. Análisis de la Prioridad

Se acepta la reivindicación de Prioridad porque esta solicitud fue presentada dentro del plazo establecido (Art. 9 D 486) y su contenido técnico corresponde con el de la prioridad reivindicada.

3. 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 estudiarán las reivindicaciones 1 a 7.

Título de la solicitud: "Proceso de obtención de poliuretanos a partir de aceite de palma y poliuretanos obtenidos" (Ver. Pág. 4 del Rad. N° 14-023087-00000-0000).

El problema técnico planteado en la solicitud consiste en la necesidad de suministrar espumas de poliuretano a partir de materias primas renovables 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 018/036.

4. De la Solicitud de Patente

Reivindicaciones (Art 30 D 486, Art 22 PCT)

Las reivindicaciones 6 y 7 no son claras porque las expresiones "*densidad*", "*módulo de Young*" y "*esfuerzo máximo*" son resultados a alcanzar, lo que no está permitido, no define al producto y/o método porque la invención no queda definida por el resultado a alcanzar, puesto que la reivindicación incluiría no sólo la solución propuesta por el solicitante, sino todas las alternativas presentes o futuras que lleguen a ese resultado. Se sugiere reemplazarla por las características esenciales estructurales que contribuyen a la obtención de ese efecto. En este caso llama la atención que con un mismo procedimiento se obtengan como resultado dos espumas de características diferentes tal como lo reclama la solicitante en las reivindicaciones 6 y 7.

Descripción (Art 28 D 486)

Si bien la descripción de la solicitud presenta métodos en la producción de espumas de poliuretanos a partir de aceite de palma que permiten comparar dichos métodos con el estado de la técnica, los resultados reportados presentan discrepancia con lo solicitado en el capítulo reivindicatorio, ya que para la presente solicitud divisional en la tabla resumen de composiciones y procedimientos se encuentra que (ruta 6) se obtienen polioles intermedios y poliuretanos diferentes a los caracterizados por densidad, módulo de Young y esfuerzo máximo (rutas combinadas 2 y 4), por lo que la presente solicitud carece de sustento para que una persona capacitada en la materia técnica correspondiente pueda ejecutar los métodos reclamados esperando una espuma rígida tal como la reclama la solicitante (Ver ruta 6, experimentos 1 y 2 de la Pág. 26, rutas combinadas 2 y 4, experimentos 19 y 25 a 27, Págs. 42, 44 y 45 del rad. N°. 14-023087-00000-0000)

Adicionalmente se solicita indicar la metodología empleada en la determinación del esfuerzo máximo con la que la solicitante diferencia si el producto obtenido es rígido o no ya que para la persona versada en la materia dicha rigidez se puede definir mediante la determinación del esfuerzo de compresión, siendo poco conocido el término esfuerzo máximo como propiedad de rigidez en el campo técnico de las espumas.

5. Determinación del Estado de la Técnica

El estado de la técnica se determinó con base en la fecha de presentación de la solicitud nacional, es decir, el 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.

Item	Documento	Título	Fecha de Publicación
D1	Art 1 ¹	"Preparation and characterization of polyurethane foams using a palm oil-based polyol"	14/Agosto/2007
D2	US 4067911	"Halogenated polyether-polyols and polyurethane foams manufactured from the latter"	10/Enero/1978

El documento D1 divulga un método para la obtención de polioles a partir de aceite de palma, terbutanol, glicerol e hidróxido de sodio, y el poliuretano asociado (Pág. 3811. Col. 2, Párr. 2 y Párr. 3, Pág. 3812, Col. 1, Párr. 3 y Párr. 4).).

El documento D2² divulga polioles y poliuretanos que emplean terbutanol y tolilen diisocianato (Col. 3, líneas 63 a 68 y Col. 5, líneas 44 a 50).

6. Examen de Patentabilidad (Art 14 D486)

Nivel inventivo (Art 18 D486)

La reivindicación 1 consiste en "*Proceso para la obtención de poliuretanos a partir de aceite de palma CARACTERIZADO PORQUE consta de los siguientes pasos*" (Ver Pág. 46 del Rad. N° 14-023087-00000-0000).

Comparación de las características técnicas **esenciales**, con las del Estado de la Técnica:

Características esenciales	D1	D2
Proceso para la obtención de poliuretanos a partir de aceite de palma caracterizado porque consta de los siguientes pasos	Proceso para la obtención de poliuretanos a partir de aceite de palma (Abstract).	Proceso para la obtención de polioles y poliuretanos (Col. 2, líneas 38 a 43).
a) Mezclar aceite de palma con glicerol, terbutanol como solvente e hidróxido de sodio como catalizador, en presencia de calor	Se mezclan aceite de palma, terbutanol, glicerol e hidróxido de sodio, se llevan a 90°C durante dos horas (Pág. 3811. Col. 2, Párr. 2 y Párr. 3).	No se menciona
b) Enfriar la mezcla del paso a)	Se enfria a temperatura ambiente la mezcla anterior (Pág. 3811. Col. 2, Párr. 3).	No se menciona
c) Neutralizar el producto de la reacción del paso a) con ácido clorhídrico al 10%	Se neutraliza el producto de la reacción del paso a) con ácido clorhídrico al 10% (Pág. 3811. Col. 2, Párr. 3).	No se menciona
d) Eliminar la glicerina y el solvente residual de la mezcla del paso c)	Se remueve el terbutanol y el glicerol por evaporación al vacío (Pág. 3812, Col. 1, Párr. 2).	No se menciona
e) Someter el producto del paso b) a evaporación para eliminar el solvente		No se menciona

¹ Tanaka, et al. Bioresource technology. 2008. Vol. 99. Págs. 3810 a 3818.

² <http://www.google.com/patents/US4067911>

f) Separar la fase orgánica obtenida del paso c) mediante la adición de n.hexano, permitiendo descartar la glicerina del poliol finalmente obtenido	Para remover el glicerol se mezcla con n-hexano y se permite separación de fases, para que por decantación se separe la fase acuosa que contiene el glicerol que no reaccionó (Pág. 3812, Col. 1, Párr. 2).	No se menciona
g) Tomar el poliol obtenido y mezclarlo en una proporción 50:50 con dietilenglicol con agitación	Se mezcla el poliol con relaciones desde el 20 al 80% con respecto a la mezcla total que contiene dietilenglicol (Pág. 3812, Col. 1, Párr. 3 y Párr. 4).	No se menciona
h) Adicionar 0,04g de surfactante, DBTL y agua en agitación permanente	Se adiciona un 0,1% de DBTL, un 0,2% de surfactante y un 1% de agua (Pág. 3812, Col. 1, Párr. 3 y Párr. 4).	No se menciona
i) Adicionar TDI manteniendo la agitación	No se menciona	Se adiciona tolieden diisocianato (TDI) para la polimerización (Col. 3, líneas 63 a 68).
j) Obtener el poliuretano	Se obtiene un poliuretano semi-rígido (Pág. 3813, Col. 2, Párr. 3).	No se menciona

Los documentos D1 y D2 se consideran el estado de la técnica más cercano a la invención definida en la reivindicación 1 porque divulgan en el caso de D1 un método para la obtención de polioles a partir de aceite de palma, terbutanol, glicerol e hidróxido de sodio, y el poliuretano asociado, y en el caso de D2, la obtención de poliuretanos por la reacción de polioles, terbutanol y tolieden diisocianato.

La diferencia entre la invención, definida en la reivindicación 1 y D1 consiste en que D1 no menciona la producción de poliuretanos empleando TDI, mientras la diferencia entre la invención, definida en la reivindicación 1 y el método del documento D2 consiste en que en D2 no se menciona la obtención de polioles a partir de aceite de palma, terbutanol, glicerol e hidróxido de sodio, ni la adición de DBTL y surfactante en la producción del poliuretano.

No se evidencia algún efecto técnico que logre la diferencia al incluir el TDI como fuente de isocianato porque la solución de la presente solicitud genera un producto con las mismas características del poliuretano obtenido en el documento D1.

Por lo tanto, el Problema Técnico Objetivo que pretende resolver esta invención se puede formular así “¿cómo obtener un método para producir un poliuretano que emplea un poliol e isocianato a partir de una fuente de isocianato alternativa a la revelada en el documento D1?”.

Sin embargo, el empleo de TDI para obtener un poliuretano, ya está divulgado en el documento D2 que se refiere a la obtención de espumas mediante alcoholisis para la generación de polioles y su polimerización con isocianatos (Col. 3, líneas 63 a 68).

En consecuencia, una persona normalmente versada en la materia incluiría la fuente de isocianatos como el TDI de D2 en el procedimiento para la obtención de poliuretano de la anterioridad D1, esperando con certeza lograr el método, como la de la reivindicación 1 de la solicitud, lo cual es considerado obvio y, por lo tanto, sin altura inventiva.

Asimismo, el documento D1 divulga las características de las reivindicaciones dependientes así:

Reivindicación 2: la reacción de glicerólisis se lleva a cabo a 90°C durante dos horas (Pág. 3811. Col. 2, Párr. 2 y Párr. 3).

Reivindicación 3: se deja enfriar la mezcla después de la reacción de glicerólisis hasta temperatura ambiente (Pág. 3811. Col. 2, Párr. 3).

Reivindicación 5: la obtención de un poliuretano (Pág. 3813, Col. 2, Párr. 3).

Asimismo, el documento D2 divulga las características de las reivindicaciones dependientes así:

Reivindicación 4: la evaporación por vacío del terbutanol residual (Col. 5, líneas 30 a 38), en donde para la persona versada en la materia una evaporación del terbutanol entre 85 a 95°C y durante 2 a 3 horas no presenta un efecto significativo que pueda producir un polirol diferente al mencionado en el documento D1

Puesto que las reivindicaciones dependientes 1 a 5 no mencionan características adicionales que hagan inventiva la solicitud, se considera que tales reivindicaciones tampoco tienen nivel inventivo.

Adicionalmente se reitera que, las reivindicaciones 6 y 7 no mencionan características técnicas y/o características tangibles adicionales que puedan brindarle nivel inventivo al objeto de la reivindicación 1, puesto que se encuentran redactadas en términos de resultados a alcanzar y/o efectos, debido a que la densidad, módulo de Young y esfuerzo máximo dependen del procedimiento y composición empleada para la obtención en este caso en este caso de una espuma de poliuretano, tal como se aprecia en la tabla resumen de composiciones y procedimientos (ruta 6, experimentos 1 y 2 de la pág. 26, rutas combinadas 2 y 4, experimentos 19 y 25 a 27, págs. 42, 44 y 45 del rad. N°. 14-023087-00000-0000), en donde se observa adicionalmente que para el procedimiento reclamado en la presente solicitud no se realiza la caracterización de la densidad, módulo de Young y esfuerzo máximo del poliuretano obtenido, caracterización que si se presenta en los poliuretanos obtenidos por otros procedimientos, por lo que es claro que se están obteniendo inicialmente polioles y después poliuretanos diferentes por el procedimiento reclamado en la presente solicitud con respecto a lo solicitado en las reivindicaciones 6 y 7.

7. Conclusión

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

Item	Documento	Reivindicaciones afectadas	Requisito que afecta
D1	Art 1	1 a 7	Nivel inventivo
D2	US 4067911	1 a 7	Nivel inventivo

8. Respuesta a los argumentos de la solicitante

En referencia al argumento de la solicitante, según el cual el análisis de nivel inventivo se encuentra realizado de forma equivocada al escoger dos documentos y no uno para desarrollar el método problema solución, no se establecieron todas la diferencias entre el documento D1 y la invención y que por lo tanto el problema técnico a solucionar es el de “¿cómo modificar o adaptar el procedimiento revelado en D1 para obtener espumas de poliuretano rígidas con menos reactivos a partir de polioles provenientes de aceite de palma?”, esta Oficina indica que el documento D1 es el antecedente más cercano a la invención y que con dicho documento es que se define el problema técnico a solucionar cuando se compara con la presente solicitud y en donde se encuentra que la diferencia entre la presente solicitud y el documento D1 es el agente entrecruzante empleado en la formación del poliuretano, por lo que es de esperarse que el dicho

agente entrecruzante es el que presenta una alternativa al efecto técnico en la obtención de poliuretanos ya que el procedimiento de D1 genera espumas semi-rígidas, y no la relación 50:50 entre el dietilenglicol y el poliol, la cual se encuentra contenida entre la relación 20 a 80% de la mezcla dietilenglicol - poliol según lo establece D1, encontrándose así que el documento D2 es el antecedente que soluciona dicho problema técnico tal como se establece en el numeral sexto de la presente decisión, mas sin embargo si se tuviera en cuenta el problema técnico indicado por la solicitante, el documento D2 también proporciona la solución alternativa a dicho problema ya que los reactivos empleados para la obtención de polioles mencionados en D1 es la misma a la presentada en la solicitud, con diferencia únicamente en el TDI y en donde D2 proporciona la alternativa de cambiar ese único reactivo diferente en el procedimiento final de entrecruzamiento para la obtención de los poliuretanos según se indica en D1.

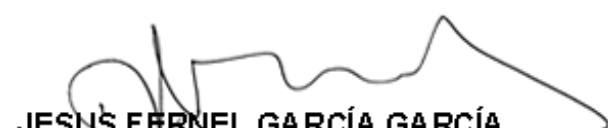
Por otra parte, si bien es cierto que *“un técnico que conozca del arte sabe que cambiar en el proceso de polimerización para la obtención del producto deseado”* según lo indica la solicitante, en el capítulo reivindicatorio se encuentra solo un método por lo que se esperaría obtener espumas con propiedades de módulo de Young, densidad y esfuerzo máximo dentro de un solo intervalo de magnitud y no dos como lo menciona la solicitante, ya que en ningún momento el método reclamado presenta dos diferentes intervalos para cada etapa de proceso, por lo que la persona versada en la materia ve improbable la obtención de espumas con dos propiedades completamente diferentes a partir de un solo método de obtención y más si se tiene en cuenta que las demás solicitudes fraccionarias y la solicitud parental reclaman los mismos productos a partir de métodos completamente diferentes, lo que va en contra de los resultados mostrados en la descripción más específicamente la tabla comparativa de procedimientos realizados y productos obtenidos.

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.



JESUS FERNEL GARCÍA GARCÍA
Director de Nuevas Creaciones (E)

El anterior requerimiento fue notificado por fijación en lista, de fecha 2014-12-09

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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 1Mono-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.

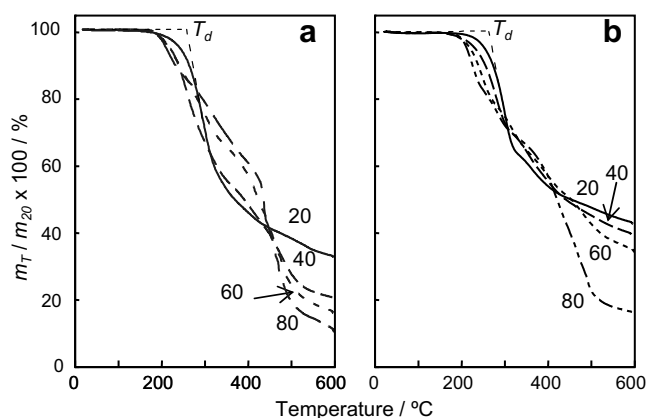


Fig. 1. TG curves of the PEG- or DEG-contained foams having various PO-p contents as indicated on each curve (%): (a) PEG; (b) DEG.

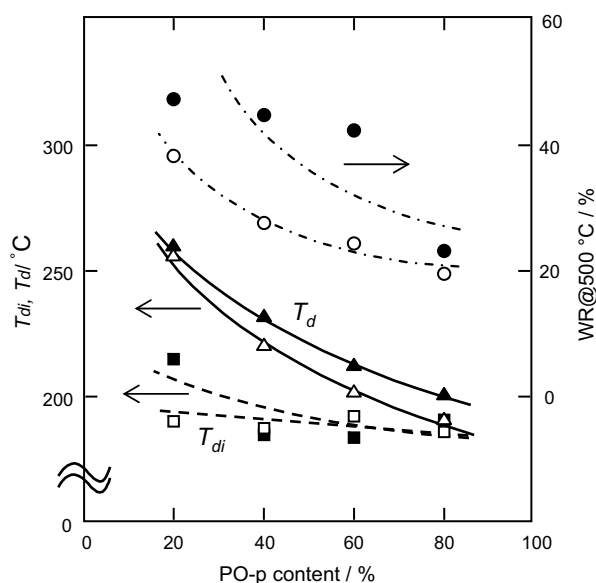


Fig. 2. Starting (T_{di}) and thermal decomposition (T_d) temperatures and weight residues (WR@500 °C) of PU foams having various PO-p content; PEG series: open symbols; DEG series: closed symbols.

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

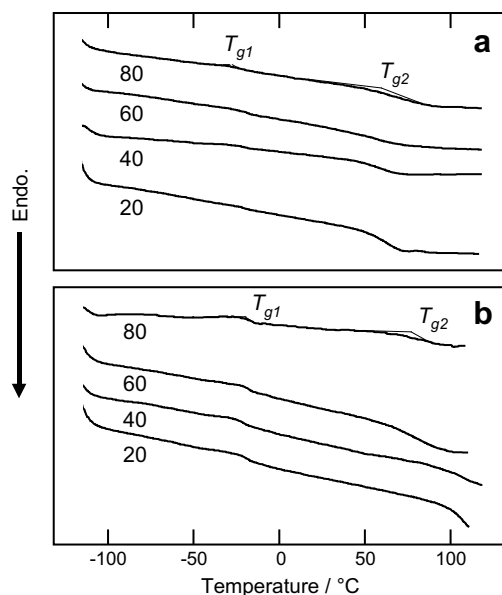


Fig. 3. DSC curves of the PEG- or DEG-containing foams having various PO-p contents as indicated on each curve (%): (a) PEG; (b) DEG.

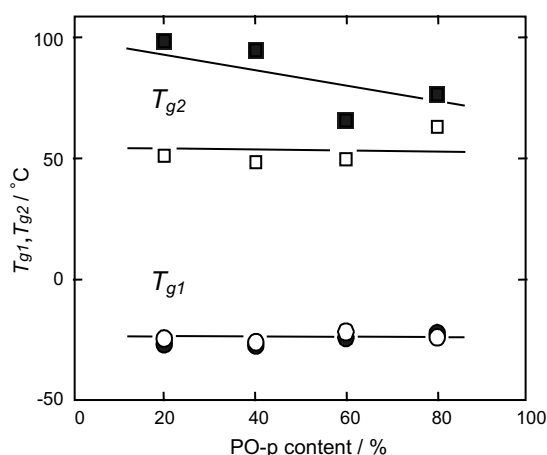


Fig. 4. Relationship between glass transition temperatures (T_{g1} and T_{g2}) and PO-p content; PEG series: open symbols; DEG series: closed symbols.

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

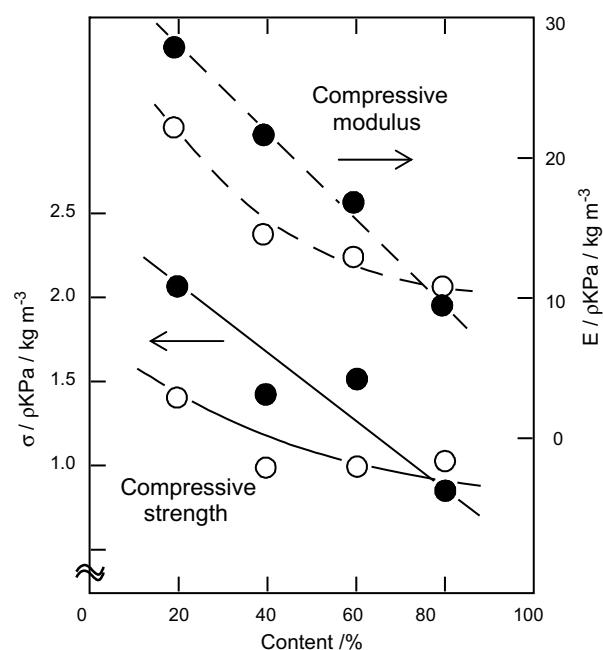


Fig. 5. Changes of compressive strength (σ/ρ) and compressive modulus (E/ρ) along PO-p content; PEG series: open symbols; DEG series: closed symbols.

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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