Original article



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Abstract

The novel renewable source precursors from hydroxyl liquid natural rubbers (HLNRs) with various secondary hydroxyl content of 22% (HLNR22), 35% (HLNR35), and 50% (HLNR50) (or naming macro-hydroxyl polyols) were used to prepare rigid polyurethane foam. The aim of this study was to investigate the effect of hydroxyl content of HLNR precursors and the ratio of HLNRs and commercial polyols on physico-mechanical properties of rigid polyurethane foams in comparison to foams made from commercial polyols. The increase in hydroxyl content of HLNRs resulted in the foams with larger cell size while the increase in the HLNR portion caused a small and more uniform cell size, which is related to their density and compressive strength. Thermal stability of polyurethane foams was analyzed by thermogravimetric analysis and the results have demonstrated that the use of HLNR polyols improved thermal stability of polyurethane foams in commercial foam.

Keywords

rigid polyurethane foam, hydroxyl liquid natural rubber, polyol, physico-mechanical properties, thermal stability

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Introduction

Polymeric foams play an important role in everyday life. The most important attributes of polymeric foams are their light weight and relatively high strength per unit weight when compared to solid polymers. Polyurethane foam is one of the synthetic cellular polymers characterized by the presence of urethane linkages. The global polyurethane foam market continues to grow.¹ The main types of polyurethane foams can be categorized into flexible foams and rigid foams. The major markets for flexible polyurethane foams are cushioning materials in furnishings, transportation, and packaging applications while rigid polyurethane foams are particularly useful in the industrial products for thermal insulation and construction, for example, insulating materials, core composite sandwich structures, and sealants. This is due to their outstanding thermal insulation and their unique physical properties.^{2,3} The fundamental aspects of the production and properties of polyurethane foams have been reviewed.^{4,5} Polyols play an important role in the urethane industries as a starting materials. Conventionally, a majority of them are derived from petrochemical crude oil and coal. Nowadays, as the price of petroleum oil grows rapidly, costs of polymeric raw materials have risen steadily as a result of the rising feedstock price. Additionally, it has been reported recently that petroleum-based polyurethane foams do not biodegrade for several hundred years under anaerobic conditions found in landfills.⁶ Therefore, there current need is to develop an eco-friendly polyurethane foam from renewable sources. Hence, in view of the environmental and sustainability aspects, many research groups have been developing polyurethane foams from biomaterial-based polyols such as cooking oil polyols,⁷ soy bean oil polyols,^{8–11} tung oil polyols,¹² palm oil polyols,^{13–15} castor oil polyol,¹⁶ rapeseed oil polyol,^{14,17} and canola oil polvols.¹⁸ The resulting products not only exhibit improved thermal stability but also show comparable mechanical properties with polyurethane foams made from petroleum-based polyol.14,17,19

One of the most promising possibilities is the replacement of petrochemical derived polyols in polyurethane foam synthesis by modified natural rubber (NR) as NR is a renewable bio-resource material, which has many advantages such as low cost, abundant supply, and environmental amity. Hence, it is called "green material." Moreover, from an economical point of view, such material is gaining more and more interest due to the rising cost of synthetic polymers from petrochemicals. Another feature of natural rubber is its inherent unsaturated structure, which is reactive and can be chemically modified due to the double bonds present in the polymeric backbone.^{20,21} Chemically modified natural rubber can increase the potential number of applications in particular for polyurethane foams based on natural rubber. Hydroxyl terminated natural rubbers (HTNRs), one type of the telechelic oligo-isoprenes, were successfully prepared by the selective and controlled degradation of natural rubber.^{22–24} It can be used as a starting material to replace the petroleum products for flexible polyurethane foam synthesis.

In the present work, natural rubber was modified with the aim of generating secondary hydroxyl groups along the rubber chain (hydroxyl liquid natural rubber, HLNR) rather than primary hydroxyl groups at chain ends. Previously, the attempts to utilize HLNR as a

polyol source for polyester and polyurethane synthesis have been reported. Most applications of these reported materials are for coatings and adhesives.^{25,26} The most significant effort to be highlighted is that the inherent hydroxyl functionality along the HLNR chains plays an important role in the production and properties of rigid polyurethane foams. To control the reactivity of the foaming process and prevent the cell wall brittleness, the rigid polyurethane foams were also prepared from mixtures of polyols containing HLNRs and a commercial polyol. The effect of hydroxyl content of HLNRs and HLNRs/commercial polyol ratio were investigated. Based on the observed positive and beneficial effects, it can be stated that the use of HLNR as a polyol in polyurethane foams can constitute a new application path for converting natural rubber into valuable resources for producing a new class of green materials.

Experimental

мaterials

Polymeric 4,4-diphenyl methane diisocyanate (p-MDI) (Cosmonate HL) was sourced from Mitsui Takeda Chemicals Inc. Hydroxyl liquid natural rubber (HLNR) was prepared via three reaction steps: epoxidation of natural rubber via *in-situ* epoxidation, chain scission by periodic acid, and ring-opening with hydrogen peroxide as described in the literature.^{21,26,27} The hydroxyl contents of HLNR on the rubber chain compared with the isoprene unit determined by ¹H-NMR were 22% (HLNR22), 35% (HLNR35), and 50% (HLNR50), respectively. The hydroxyl numbers of these HLNRs were 1045, 1662, and 2375 mgKOH/g, respectively. The viscosity average molecular weights (\overline{M}_{ν}) of these modified rubbers measured by dilute-solution viscometry were in the range of 19,000–20,000 g/mol.²⁶ and have viscosities in the range of 100–120 Pa.s at 25°C. Thamol-HL-456, a commercial petroleum-based polyether polyol with the hydroxyl number of 183–223 mgKOH/g and the viscosity of 1.12–1.63 Pa.s at 25 °C produced by Thai Mitsui Specialty Chemicals Co Ltd, silicone surfactant (Tegostab B 8871, Evonik Nutrition & Care GmbH), amine catalyst (Tegoamin 33, Evonik Nutrition & Care GmbH), and Dibutyl tin dilaurate DBTDL (Aldrich) were used as received.

Preparation of polyurethane foam and foaming time determination

The polyurethane foams were prepared using a one-step method by adding p-MDI to the polyol mixture, which consisted of a polyether polyol (Thamol-HL-456), different types of HLNRs, distilled water, and catalysts. The isocyanate index was kept constant at 110. Table 1 gives the detailed information on the formulations of p-MDI and polyols. The mixture was stirred for 20 s at 1500 rpm and then poured into an open mold and allowed to rise freely. The characteristic foaming times, that is, cream time (the time from mixing to initiation of foaming), full rise time (the time from mixing to full expansion of foaming), gel time, and tack free time were recorded. After that, the foam was removed from the

Components (php) ^a	PU0	PUAI	PUA2	PUA3	PUBI	PUB2	PUB3	PUCI	PUC2	PUC3
Thamol-HL-456	100	71	52	29	80	63	39	85	71	48
HLNR 22		29	48	71	_	_	_	_		_
HLNR 35	_	_	_	_	20	37	61	_	_	_
HLNR 50	_	_	_	_	_	_	_	15	29	52
p-MDI	120	186	228	279	198	264	357	207	288	420
Water					4	4.0				
DBTDL					0.	175				
Tegomin 33 0.175										
Tegostab B 8871						1.5				

Table I. Formulation of polyurethane foams.

^aThe amount of all components is denoted by parts per hundred parts of polyol, which dictates that the total polyols add up to 100 parts.

mold and allowed to post-cure for 48 h at room temperature before cutting into test specimens.

Characterization of polyurethane foams

IR spectra were recorded on FTIR Perkin–Elmer spectrophotometer (ax series), equipped with a diamond ATR (attenuated total reflection) device, and a resolution of 4 cm^{-1} .

The morphology of polyurethane foams was determined by scanning electron microscopy (Camscan). Rectangular pieces of approximately 2.5 mm were cut with a razor blade at the middle of each specimen and were mounted on an aluminum stub. The samples were scanned in the free-rise direction at the accelerating voltage of 10 kV. At least 4–5 micrographs were taken for each foam formulation. The cell diameter of the polyurethane foam cells was measured based on $20 \times$ magnified micrographs using Image J version 1.52a free software, and the statistical analysis of the average cell size and distribution were calculated using MS. Excel. The 10–50 cells were considered for each foam micrograph. Only whole cells were used for measurement.

The densities of the polyurethane foams were measured according to the ASTM D 1622 method. The compressive strength of the foams was determined using a Universal Testing Machine (LLOYD L500) with a load cell of 1.5 kN. The test was performed according to ASTM D 1621-00 method. The size of the specimen was $50 \times 50 \times 25$ mm (width × length × thickness), and the crosshead speed was 2.5 mm/min. The compressive strength for each foam was obtained using the average value from five measurements. Dimensional stability was measured at 80°C and -2° C for the duration of 72 h following ASTM D 2126. Thermal analyses of thermogravimetry were carried out using thermogravimetric analysis (TGA) (TGA 7, Perkin Elmer). For the thermogravimetric analysis, an accurately weighed sample (approx. 1 mg) was heated from 30 to 600°C at the rate of 10°C/min with N_2 gas purging.



Figure I. Typical ATR-FTIR spectra of (a) p-MDI; polyurethane foams prepared from, (b) HLNR22, (c) commercial polyol, and (d) mixture of commercial polyol with HLNR22.

Results and discussion

Structural characterization of rigid polyurethane foams

The ATR-FTIR spectra found in Figure 1 show the disappearance of the strong peak at 2277 cm⁻¹ of the isocyanate group of p-MDI (Figure 1(a)) upon its conversion to the polyurethane products. On the other hand, a number of new peaks observed in Figures 1(b) to (d) may be assigned to the newly formed urethane linkages. The characteristic signals for N–H stretching were observed at 3325–3340 cm⁻¹ and N–H bending in plane of amide (urethane bonded) took place at 1595 cm⁻¹ instead. The signals at 1707–1709 cm⁻¹ could be due to hydrogen bonded urethane carbonyl group.²⁵ The band at 1506 belonging to N–H bending of urethane bond was detected as well. The other bands in the range of 1220–1225 cm⁻¹ and 1060–1070 cm⁻¹ were assigned to asymmetric and symmetric stretching of N–CO–O and C–O–C, respectively.^{25,26,28,29} It can be seen that the spectra of products prepared from HLNR22 (Figure 1(b)) and mixture of commercial polyol with HLNR22 (Figure 1(d)) showed the similar characteristics of peaks in the

range of 2800–3000 cm^{-1} assigned to the C–H stretching mode of methylene and methyl groups of HLNR.

The intensity of specific signals observed during FTIR analysis confirmed the high content of urethane linkages in the produced rigid polyurethane foams made from HLNR, and the mixture of commercial polyol and HLNR. These results confirmed the accomplished reaction between polyol and isocyanate.

Effect of HLNRs on foaming times

The foaming times of polyurethane foams made from commercial polyol (PU0) and mixtures of commercial polyol with HLNR polyols (PUA, PUB, and PUC) are illustrated in Table 2. A reaction occurred between water and the isocyanate group to form an amine and carbon dioxide gas in the form of small bubbles giving the mixture a creaming appearance. The time taken for the appearance to change, as measured from the initial mixing, is known as the cream time. It could indicate a time needed for obtaining a homogeneous mixture. As more carbon dioxide is generated, the bubbles expand and the foam begins to rise. While the bubbles are expanding, a polymerization reaction takes place in the liquid phase and the viscosity starts to increase. At full rise time, the reactions generating the gas stop. All polyurethane foams prepared from mixtures of polyols showed longer foaming time than PU0 and the foaming times (cream time, gel time, rise time, and tack free time) increased with the increase in the proportion of HLNRs. This could be explained by the slower reactivity of HLNRs due to the lower reactivity of the secondary hydroxyl groups existing in the HLNRs. The similar results have been reported in other studies.^{7,11,15,30} In addition, this might be due to the higher viscosity of HLNRs with the greater \overline{M}_{v} in comparison to commercial polyol.²⁵ Comparing the different hydroxyl content of HLNRs (PUA-PUC series), the HLNRs with higher hydroxyl content would have more hydrophilicity and might mix better with water. Additionally, foams from HLNRs with the greater content of secondary hydroxyl groups led to the less HLNR portion by its formulation (Table 1) giving rise to lower viscosity of the system. These made the higher rate of polyurethane formation and hence shorter foaming time.

Samples	PU0	PUAI	PUA2	PUA3	PUBI	PUB2	PUB3	PUCI	PUC2	PUC3
Cream time (s)	28	35	40	57	33	35	41	29	31	37
Gel time (s)	93	172	250	287	165	222	250	159	207	240
Rise time (s)	102	320	345	375	312	330	342	203	247	325
Tack free time (s)	114	410	568	878	384	435	593	324	383	524

 Table 2. Characteristic foaming times.



Figure 2. SEM micrographs of polyurethane foams.

Effect of HLNR content on morphology of polyurethane foams

The cross-sectional surfaces of the polyurethane foams observed with scanning electron microscope (SEM) are shown in Figure 2 and the analyzed cell size distribution is illustrated in Figure 3. SEM micrographs in Figure 2 show that all of the foams consisted of well-defined closed cells.

Figure 3 reveals that the cell sizes increase in the sequence of PUA, PUB, and PUC. This could be explained by assuming that the cell sizes depend on the viscosity of the reactive system. On the basis of the formulation in Table 1, the higher content of hydroxyl functionality of the HLNRs used in the sequence of PUA, PUB, and PUC, the less HLNR content in the formulation leading to the reduced viscosity, which in turn causes the cell size to be larger. However, increasing the HLNR proportion in the reactive mixture resulted in smaller cell size. This finding might be related to the fact that the higher viscosity of HLNR reacting liquid system at the initial foaming stage can reduce the



Figure 3. Cell size distributions of polyurethane foams.

coalescence among bubbles, and therefore lead to a smaller average cell size. The decrease in cell size with increasing viscosity of mixture was also observed in previous reports.^{8,11,16,31,32}

It should be noted that PUA3 are characterized by the smallest cell size foam with the narrowest distribution of cell size. This may be because of the highest viscosity of polyol mixture of PUA3 from the highest HLNR22 content. Nevertheless, the largest cell size was obtained with PUC3. This is mainly due to the use of the HLNR50 with highest hydroxyl content, which caused the small amount of HLNR50 to be equivalent to the used weight of p-MDI and distilled water used in the formulation. The small amount of HLNR50 further brought about the decrease in the viscosity which subsequently resulted in coalescence into largest cell size. The widest distribution of cell size and some of irregular-shaped cells were also observed in case of PUC3. Such result confirms the occurrence of cell coalescence during foam expansion. In this process, neighboring bubbles might expand in such a way that the intervening polymeric films between these bubbles became so thin and stretched that they might rupture as the polymeric cell wall is brittle and exhibits insufficient strength due to high crosslinking. If the cell wall ruptures, neighboring cells may merge randomly to form a larger and irregular-shaped cell. Similar observation was also made in the case of poly (3-hydroxybutyrate-co-3-hydroxyvalerate) with variable amount of blowing agent.³³

Effect of HLNR content on physical properties of polyurethane foams

The physical properties of foams were analyzed and shown in Table 3. With the partial replacement of commercial polyol with HLNRs, most of foams from mixtures of commercial polyol and HLNRs exhibited better compressive strength than the foam made from commercial polyol. It was also obvious that PUA3 exhibited the most suitable

Samples	PUO	PUAI	PUA2	PUA3	PUBI	PUB2	PUB3	PUCI	PUC2	PUC3
Cell size (µm)	453±16	375±16	242±5	I 89±3	506±25	468±19	411±15	560±29	484±28	631±86
Density (kg/m ³)	43±2	44±I	50±2	52±I	43±I	46±I	48±I	42±I	45±I	41±2
Compressive strength (kPa)	0I ∓ 96I	200±12	260±20	318±30	194±18	243±24	245±20	197±13	232±10	190±13
Volume change (%) @80°C	0.2	0.2	0.4	0.2	0.3	0.2	0.3	0.3	0.3	0.3
Volume change (%) $@-2^\circ C$	0.2	0.3	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.1

Table 3. Physical properties of polyurethane foam from HLNRs and a commercial polyol.

properties with the greatest compressive strength. This is related to the smallest cell size and narrowest size distribution and highest density while PUC3 showed inferior compressive strength due to the larger cell size and wide size distribution as a result of coalescence during foam expansion. The relationship between physical properties and cell size agrees with other reports.^{8,16,34,35} The foams were dimensional stable under the testing conditions. The largest of volume change is less than 1%. The small volume change would be due to the high crosslink from high hydroxyl number of HLNR.

Effect of HLNR content on thermal stability of polyurethane foams

The thermal stability of polyurethane foams is important from the scientific and technological points of view with respect to thermal insulation applications. The prepared



Figure 4. (a) TGA and (b) DTG results of PU0, PUA1, PUA3, PUC1, and PUC3.

	l st stage			2 nd stage			
Samples	T _i ¹ (°C)	T _P ^{−1} (°C)	T _f ^I (°C)	T _i ² (°C)	T _P ² (°C)	T _f ² (°C)	
PU0	230	324	363	364	401	470	
PUAI	274	351	399	524	555	624	
PUA3	262	329	384	507	542	625	
PUBI	253	312	393	510	566	625	
PUB3	243	308	367	444	540	624	
PUCI	224	313	394	458	564	624	
PUC3	227	323	382	437	531	625	

 Table 4. TGA results of polyurethane foams from HLNR and commercial polyols investigated under nitrogen atmosphere.

 T_i : initial decomposition temperature. T_p : maximum rate of decomposition temperature. T_f : final temperature.

polyurethane foams were thermally analyzed by TGA and differential thermogravimetry (DTG). It was found that polyurethane degraded in two weight loss stages as revealed in the TGA and DTG curves in Figure 4 and the main temperature peaks of weight loss can be described in Table 4. The first decomposition occurred at 300-330°C and can be ascribed to the decomposition of the urethane linkage, and the second stage occurred at 450-500°C it is attributed to the decomposition of fragments associated with the polyol. These phenomena are consistent with many previous findings.^{24,29,36,37} It was seen that the second stage decomposition temperature was remarkably shifted to higher values, and thus, it can be implied that the HLNRs help improve the thermal stability of the polyurethane foams.

Conclusions

In summary, natural rubber was modified by hydroxylation to generate HLNRs with the secondary hydroxyl groups along the rubber chain. The water-blown rigid polyurethane foams were successfully prepared by blending these HLNRs and commercial polyol (Thamol-HL456). The influence of the HLNR and commercial polyol ratio on physico-mechanical properties and morphology of rigid polyurethane foam was established. The results indicated that the foaming time increased with increasing amount of HLNRs but decreased with hydroxyl content in HLNRs due to the slower reactivity of the secondary of hydroxyl group existing in HLNRs and their inherent high viscosity. Higher content of HLNR in the reaction mixture resulted in the polyurethane foams with smaller and more uniform cell size due to the higher viscosity of the polyol mixture. However, the use of the HLNR with high hydroxyl content caused the less amount of HLNR in the mixture and lower viscosity, which in turn led to coalescence into larger irregular-shaped cells. The use of HLNRs gave the high compressive strength of polyurethane foam. Polyurethane foams made from commercial polyol and HLNR22 (PUA3) were found to exhibit the greatest density and compressive strength. It was found that the HLNR also helped to improve the

thermal stability of the polyurethane foams. The best thermal stability was found in PUA3. Therefore, it was found that the foam from 29% of commercial polyols and 71% of HLNR22 exhibited the most suitable mechanical properties of rigid polyurethane foam in line with the observed cell morphology. The suggested item to be studied in the future is the thermal conductivity which is related to the important properties of insulating materials.

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