Polyisoprene modified poly(alkyl acrylate) foam as oil sorbent material

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ABSTRACT: Biorenewable polyisoprene latex obtained from natural rubber, *Hevea brasiliensis*, was used to prepare the reusable polyisoprene–poly(alkyl acrylate) foam for petroleum-based liquid absorption. The foam was produced via latex vulcanization and cured by steaming. The effect of various types of poly(alkyl acrylate) such as poly(methyl methacrylate) (PMMA), poly(butyl methacrylate) (PBMA), and poly(butyl acrylate) (PBA) on oil sorption capacity of the foam were studied. Scanning electron microscope (SEM) images showed interconnected open-cell macrostructure with the foam porosity greater than 75% and good compression set. The oil sorption capacity of the foam was in the range of 2.0–16.6 g g^{-1}. The addition of poly(alkyl acrylate) enhanced hydrophobicity and oil sorption capacity of the foam. The absorbed oil was easily recovered by squeezing and the foam can be reused up to 30 sorption–desorption cycles and still preserve high quality sorption. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42688.

INTRODUCTION

Oil spills and chemical leakage often result in both immediate and long-term environmental damage and post health hazard to both animals and human. The conventional methods for oil spill cleanup are booms, *in situ* burning, dispersant, oil skimmers, and sorbent materials according to the variation in oil types, locations, and weather conditions.[1–6] Oil spill cleanup by sorbent material is the simplest method for surrounding oil spill area by transformation spilled liquid into semisolid phase or solid phase.[7] The important properties of an ideal sorbent material for oil spill cleanup are oleophilicity and hydrophobicity, excellent oil/water selectivity, floatable before and after oil sorption, and reusable.[8–10] Oil sorbent can be prepared from synthetic polymer, plants, agricultural waste, and also mineral. However, their oil sorption capacities have been reported on poor buoyancy, relatively low oil sorption capacity, and low hydrophobicity.[11–14] Some cellulosic materials such as milkweed floss, cotton, and kenaf achieved the crude oil sorption capacity up to 40 g g^{-1}, however, the recovery of the absorbed oil required mechanical retrieval equipment.[15] Several works reported on oil sorbent materials from synthetic polymer. It can be prepared as fiber, resin, gel or foam. For example, butyl methacrylate (BMA)/lauryl methacrylate (LMA)

copolymer fiber was prepared and its oil sorption capacity of the fiber was in range from 8–35 g g^{-1}.[16,17] The blend of BMA/LMA fiber with polypropylene (PP) exhibited maximum sorption capacity of 35 g g^{-1}, which was greater than that of conventional PP fiber about 5 times. For resin such as BMA/methyl methacrylate (MMA) copolymer, BMA/hydroxyethyl methacrylate (HEMA) copolymer, and BMA/octadecyl acrylate (OA) copolymer, the maximum oil sorption capacity was approximately 24 g g^{-1}.[18–20] The strong hydrophobicity and superoleophilicity depended on cross-linked network stability of polymer. However, the limitations of fiber and resin are slow sorption rate, unrecoverable absorbed oil, and poor reusability. Therefore, the macroporous gel or absorbent foam has been discovered to involve these limitations. Various macroporous gels from synthetic polymer such as butyl rubber (BR), *cis*-polybutadiene (CBR) or styrene–butadiene rubber (SBR) were reported.[21–23] The oil sorption capacity of these macroporous gels were achieved up to 38 g g^{-1}. The macroporous gel was prepared by freeze dry technique, which require large amount of organic solvent to dissolve synthetic polymer. Moreover, the reusability of macroporous gel sorbent was significantly decreased after initial oil sorption according to the crack propagation in the gel network. Foam absorbent provides huge space for oil storage regarding to its large pore volume,

which is very useful for oil recovery and reusability. The example of absorbent foam are polyurethane (PU) foam coated with poly(lauryl methacrylate) (PLMA),[4,24] silica sol, and gasoline treated PU foam,[25] carbon soot (CS) foam,[26] and poly(dimethylsiloxane) (PDMS) foam.[27,28] Most synthetic polymers as mentioned above are obtained from petroleum-based resources, a non-renewable resource. Therefore, a biorenewable polymer is becoming viable alternatives to petroleum-based polymer.

Natural rubber (NR), *Hevea brasiliensis*, is an important biorenewable polymer due to its outstanding flexibility and excellent mechanical property. The chemical structure of NR is $cis-1$, 4-polyisoprene which is hydrophobic polymer from biorenewable resource. NR is easily produced as NR foam, a highly porous material, light weight, buoyancy, hydrophobic property, and good mechanical property.[29,30] Our previous work has been reported on the modified NR foams with poly(methyl methacrylate) (PMMA) and poly(butyl methacrylate) (PBMA). The addition of PMMA or PBMA (0.1–1.0 part per hundred part of rubber, phr) performed the petroleum-based liquid sorption capacity in the range of 1.5–12 g g^{-1}.[31] In the present work, NR foam was prepared by latex mixing and steam vulcanization method as described in the previous work. To extend the scope of research, the wide range of poly(alkyl acrylate) emulsion addition has been studied (0.5–5.0 phr). The improvement hydrophobicity and oleophilicity of NR foam with various types of poly(alkyl acrylate) such as poly(methyl methacrylate) (PMMA), poly(butyl methacrylate) (PBMA) or poly(butyl acrylate) (PBA) were observed by contact angle measurement. The effect of foam density and oil viscosity on oil sorption capacity and reusability of foam were discussed. The foam characteristics such as morphology, functionality, thermal stability, and hydrophobicity of foam were characterized.

EXPERIMENTAL

Materials

High ammonia natural rubber latex (60% dry rubber content), potassium oleate dispersion, sulfur dispersion, zinc oxide (ZnO) dispersion, zinc diethyldithiocarbamate (ZDEC) dispersion, zinc 2-mercaptobenzothiazole (ZMBT) dispersion, poly(dicyclopentadiene-co-p-cresol) dispersion (Wingstay®L), diphenylguanidine (DPG) dispersion, and sodium silicofluoride (SSF) were supplied by Rubber Research Institute, Thailand. Methyl methacrylate (MMA), butyl methacrylate (BMA), butyl acrylate (BA), and sodium dodecyl sulfate (SDS) were acquired from Sigma–Aldrich while potassium persulfate (KPS) from Ajax Finechem. Alkyl acrylate monomer was purified by washing with 10% w/v NaOH solution to remove inhibitor and then neutralized with distilled water. The purified acrylate monomer was dried over anhydrous sodium sulfate and stored at temperature below 4°C.

Preparation of Poly(alkyl acrylate) Emulsion

Poly(alkyl acrylate) (PMMA, PBMA, and PBA) were primed by emulsion polymerization.[32,33] About 0.108 g of KPS and 0.625 g of SDS were dissolved in 100 mL deionized water and transferred to a 500 mL three-neck flask equipped with dropping funnel, a reflux condenser, and a nitrogen gas inlet. The mixture was purged from nitrogen gas for 30 min, heated up to 70°C, and drop wised acrylate monomer (MMA, BMA or BA) and

polymerized for 6 h under nitrogen atmosphere. Poly(alkyl acrylate) emulsion were obtained (solid content about 30±2%). Number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity index (PDI) of poly(alkyl acrylate) were determined by gel permeation chromatography (GPC) using Waters 2414 refractive index detector (RID) equipped with Waters styragel HR5E columns 7.8 × 300 mm (molecular weight resolving range = 2,000–4,000,000 Daltons). The GPC columns were eluated using high-performance liquid chromatography (HPLC) grade tetrahydrofuran (THF) at a flow rate of 1.0 mL min^{-1} and operated at 40°C. Sample of 0.2% (w/v) poly(alkyl acrylate) solution in THF was filtered through a 0.45 μm pore size filter and then 100 μL of the filtered sample was injected into the GPC. Waters' Breeze 2 Software was used for data collection and data processing.

Preparation of Rubber Foam

About 167 g of high ammonia NR latex (60% dry rubber content) and 1.5 phr of potassium oleate were charged into a 500 mL glass container and stirred at 1200 rpm. Various types of poly(alkyl acrylate) emulsion (PMMA, PBMA, and PBA), 2.0 phr of sulfur dispersion, 1.0 phr of ZDEC dispersion, 1.0 phr of ZMBT dispersion, 1.0 phr of Wingstay®L dispersion, 5.0 phr of ZnO dispersion, 0.67 phr of DPG dispersion, and 1.0 phr of SSF dispersion were added to the latex mixture and stirred at room temperature for 1 min at 300 rpm. Un-gelled NR was swiftly emptied into an aluminum mold and cured by steaming for 15 min. The vulcanized foam was thoroughly washed with water to remove potassium oleate and non-reacting elements and dried until constant weight. The foam contained poly(alkyl acrylate) named as modified NR foam and the foam without poly(alkyl acrylate) named as unmodified NR foam.

Characterization

Relative density (RD) of the foam can be calculated from foam density ratio (ρ_{foam}) to solid rubber density ($\rho_{solid\ rubber}$) and porosity (ϕ) is the fraction of air void in the rubber foam.[34–36]

$$\text{Relative density (RD)} = \frac{\rho_{foam}}{\rho_{solid\ rubber}} \qquad (1)$$

$$\text{Porosity } \phi = \left(1 - \frac{\rho_{foam}}{\rho_{solid\ rubber}}\right) \times 100 \qquad (2)$$

In this research, the average relative density and porosity of all NR foams were controlled at 0.22±0.04 and 78±4, respectively.

Morphology was observed by scanning electron microscope (SEM JEOL JSM 6510 LV, Japan) under an electron beam with an accelerating voltage of 20 kV. The average cell size of the foam was evaluated from the SEM image. Fourier transform infrared (FTIR) spectra were obtained by Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectrometer (Perkin Elmer) over the wavenumber of 3500 and 400 cm^{-1} with 32 scans.

Foam thermal stability was carried out by thermogravimetric analysis instrument (Perkin Elmer TGA 7) under nitrogen atmosphere with the heating rate of 10°C min^{-1} and operated at 40–700°C. The initial decomposition temperature (T_{id}) and the maximum degradation temperature (T_{max}) were determined from thermogram.
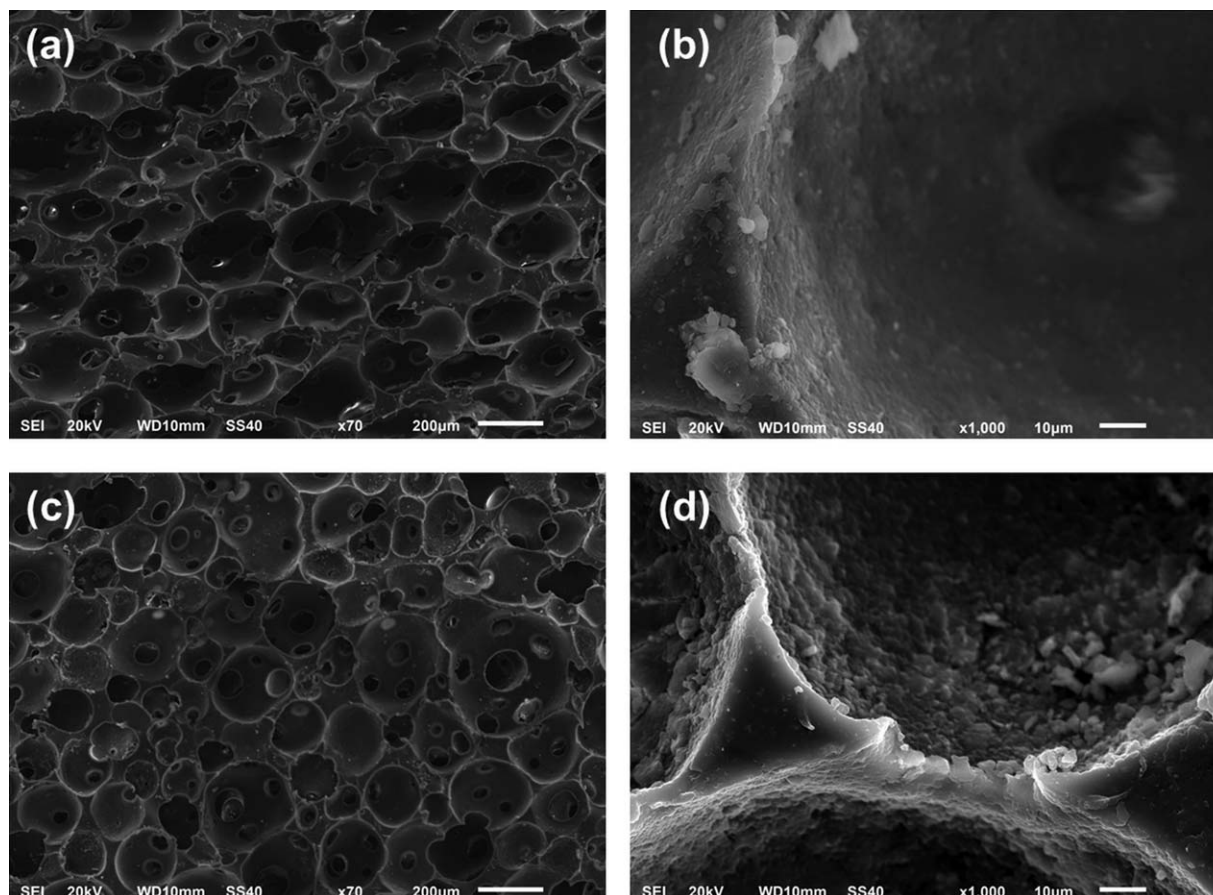
Figure 1. SEM images (70× and 1000× magnifications) of (a–b) NR foam and (c–d) PBMA modified NR foam.

Contact angle measurements were performed by standard contact angle goniometer (Ramé-hart Instrument Co.). The sessile drop technique was used to measure the contact angle where a 1.0 μL drop of liquid in a syringe was dropped on the sample surface at room temperature. The images of a liquid droplet were recorded by a CCD camera and analyzed the contact angle by the DROP image standard software.

The static compression set test was followed ASTM D395 Method B (under a constant deflection in air). Samples with initial thickness (t_0) of 1.25 cm were deflected to 50% and conditioned in an oven at 70°C for 24 h. The recovery time was allowed at room temperature for 30 min at ambient prior to measure the final thickness (t_i). t_s is the spacer thickness used for compression set. The compression set (%) can be expressed in eq. (3).[37]

$$\text{Compression set}(\%) = \frac{t_0 - t_i}{t_0 - t_s} \times 100 \qquad (3)$$

Oil sorption test was followed ASTM F726-12. A cubic shape foam sample (0.7 cm × 0.7 cm × 0.7 cm) was immersed into petroleum-based liquid for 15 min±20 s, then drained for 30±3 s and weighed. The various types of petroleum-based oil were used for the oil sorption test. The viscosity (v) of the oil was measured by automatic viscometer (CANNON miniAV, Korea) and the surface tension was measured by digital tensiometer (EasyDyne K20, Kruss, Germany) using Du Noüy ring

method. For water sorption test, a foam sample was placed into the Erlenmeyer flask filled with deionized water (15 mL) and horizontal shaking at 150 rpm for 15 min±20 s. The foam was removed, drained for 30±3 s and weighed. The sorption capacity (Q) of the foam was determined from the initial weight of the foam (W_0) and the fully absorbed weight of the foam (W_1) as follows:[38]

$$Q(g\,g^{-1}) = \frac{W_1 - W_0}{W_0} \qquad (4)$$

Foam reusability was determined by investigation of sorption capacity for each sorption–desorption cycle. The liquid contained in fully absorbed foam was desorbed by squeezing and evaporating. Oil recovery efficiency (RE) is a percentage of mass ratio of the total amount of absorbed oil and weight of fully absorbed foam for each cycle.

$$RE(\%) = \frac{W_1 - W_0}{W_1} \times 100 \qquad (5)$$

RESULTS AND DISCUSSION

Physico-Chemical Properties of NR Foam

The formation of macropore structure or air void was generated during latex mixing process. Morphology of NR foam and PBMA modified NR foam ($\phi = 78\pm4\%$, RD = 0.22±0.04) characterized by SEM are presented in Figure 1. SEM images illustrated interconnected open-cell structure with the pore size
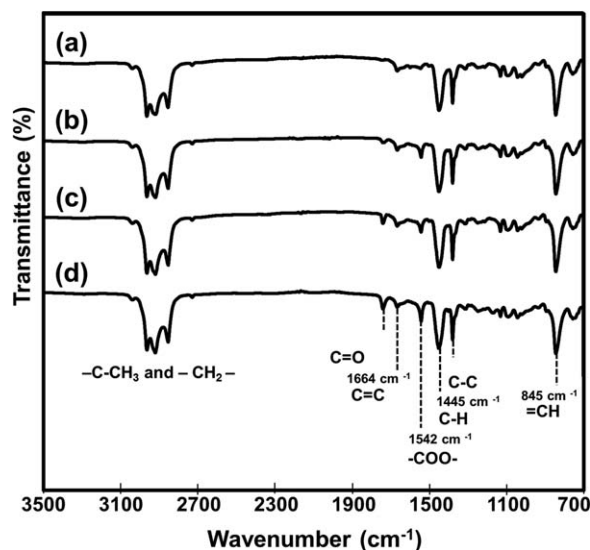
Figure 2. FTIR spectra of (a) unmodified NR, (b) PMMA modified NR, (c) PBMA modified NR, and (d) PBA modified NR.

Figure 3. DTG curves of NR foam and poly(alkyl acrylate) modified NR foams.

range of 50–250 μm. The interconnected open-cell structure of NR foam was initiated during the bubble formation and then the PBMA emulsion possibly diffused through the interconnected pore. Thus, PBMA molecules were entrapped into the rubber matrix. At 1000× magnification [Figure 1(b,d)], the cell wall of macropore structure showed surface roughness and the dispersion of fine particles around interconnected network which possibly referred to the dispersion of PBMA in the rubber matrix.

Compression set test was used to characterize the foam ability to maintain elastic properties after prolonged compressive stress. From the test, the compression set of unmodified NR foam and PBMA modified NR foam was 22.5±3.1% and 15.6±3.8%, respectively. The compression set of PBMA modified NR foam was lower than that of unmodified NR foam which indicated the flexibility and elasticity of PBMA modified NR foam was higher than that of unmodified NR foam.

The presence of poly(alkyl acrylate) in the modified NR foam was characterized by ATR-FTIR spectroscopy. Figure 2 showed FTIR spectra of unmodified and modified NR foam with various types of poly(alkyl acrylate) (PMMA, PBMA, and PBA). All vulcanized NR foams illustrated strong absorption peaks of asymmetric and symmetric stretching of C–H groups (–C–CH$_3$ and –CH$_2$–) (3090–2805 cm^{-1}), C=C stretching (1664 cm^{-1}), and =CH out of plane bending (845 cm^{-1}) of cis−1,4-polyisoprene structure. The chemical structure of crosslinked natural rubber indicated that C–S stretching vibration (760 cm^{-1}), C–C stretching (1375 cm^{-1}), and C–H stretching (1445 cm^{-1}) were related with chemical structure of cross-linked NR after vulcanization.[39] By addition of poly(alkyl acrylate), FTIR spectra presented two new peaks at 1745 cm^{-1} and 1543 cm^{-1} which attributed to carbonyl (C=O) stretching and carboxylate (–COO–) stretching of acrylate group.[40] This result implied to presence of poly(alkyl acrylate) (PMMA, PBMA, and PBA) in the NR foam matrix.

Thermal stability of unmodified NR foam and poly(alkyl acrylate) modified NR foam were evaluated by thermal gravimetric analysis
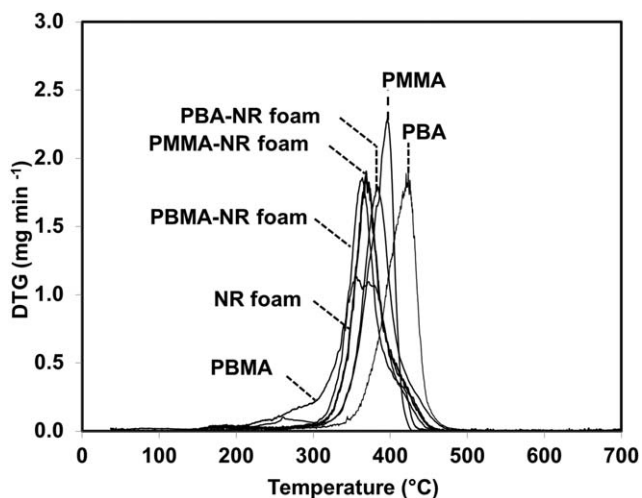
(TGA). The initial degradation temperature (T$_{id}$) and maximum weight loss temperature (T$_{max}$) were obtained from differential thermal analysis (DTG) curves (Figure 3) and summarized in Table I. All DTA curves showed single step degradation. The weight loss from 137°C to 460°C corresponded to the decomposition of the foam samples. T$_{max}$ of unmodified NR foam and poly(alkyl acrylate) modified NR foam were not significantly difference where the addition of PBA showed highest thermal stability at T$_{max}$ of 370°C. Thermal stability of poly(alkyl acrylate) modified NR possibly related with molecular weight of polymer. From GPC results in Table II, the molecular weight of PBA was lower than that of PMMA and PBMA, therefore, PBA molecules were easily penetrated with cis−1,4-polyisoprene chain and formed stronger polymer network than PMMA and PBMA.

Hydrophobicity and Oleophillicity of NR Foam

A water droplet and a diesel droplet were used to investigate the sorption characteristics of unmodified NR foam and poly(alkyl acrylate) modified NR foam. In this study, PBMA modified NR foam was used as a representative of poly(alkyl acrylate) modified NR foam. The contact angle measurement results are shown in Figure 4. A water droplet (surface tension of 71.5 mN m^{-1}) was allowed to contact the foam surface. The water contact angle of

Table I. Thermal Analysis of Foam Samples

Sample	Initial Degradation Temperature (°C)	Maximum Degradation Temperature (°C)
Unmodified NR foam	137	370
PMMA-NR foam	137	366
PBMA-NR foam	137	363
PBA-NR foam	137	380
PMMA (M$_w$ 9.50 × 10^{-5} Da)	150	395
PBMA (M$_w$ 17.1 × 10^{-5} Da)	150	392
PBA (M$_w$ 8.17 × 10^{-5} Da)	150	421

Table II. Molecular Weight of Poly(alkyl acrylate)

Polymer	Molecular weight		Polydispersity Index(PDI)
	$M_n \times 10^{-5}$ (Daltons)	$M_w \times 10^{-5}$ (Daltons)	
NR	3.75	11.60	3.09
PMMA	3.82	9.50	2.49
PBMA	5.80	17.1	2.94
PBA	2.60	8.17	3.14

unmodified NR foam (117.5°) and PBMA modified NR foam (133.5°) were over 90° which referred to hydrophobic characteristic (contact angle, $\theta > 90°$).[41] The water contact angle of PBMA modified NR foam was slightly higher than that of unmodified NR foam about 16° or 13.7% compared to unmodified NR. This result implied to improvement of the foam hydrophobicity. On the contrary, a diesel droplet (surface tension of 27.3 mN m^{-1}) was immediately absorbed into the foam and the foam surface swollen which indicated the oleophilicity of the material (contact angle close to 0°).[28] The observation on volume expansion of the foam surface after the diesel sorption indicated the solvation of polymer networks after diesel oil filled into the pore channels.[22] Therefore, the presence of poly(alkyl acrylate) can improve hydrophobicity and oleophilicity of the NR foam and selectively absorb petroleum-based liquid.

To ensure the selective absorption in petroleum-based liquid, dynamic water sorption was investigated. The water sorption capacity of various types of poly(alkyl acrylate) modified NR foam were compared to unmodified NR foam as presented in Figure 5. The water sorption capacity of unmodified NR foam was 1.32 g g^{-1}, while the water sorption capacity of poly(alkyl acrylate) modified NR foams were in the range of 0.60–0.92 g g^{-1} for PMMA modified NR foam (PMMA-NR), 0.44–0.76 g g^{-1} for PBMA modified NR foam (PBMA-NR), and 0.31–0.72 g g^{-1} for PBA modified NR foam (PBA-NR). The variation of the amount of poly(alkyl acrylate) in modified NR
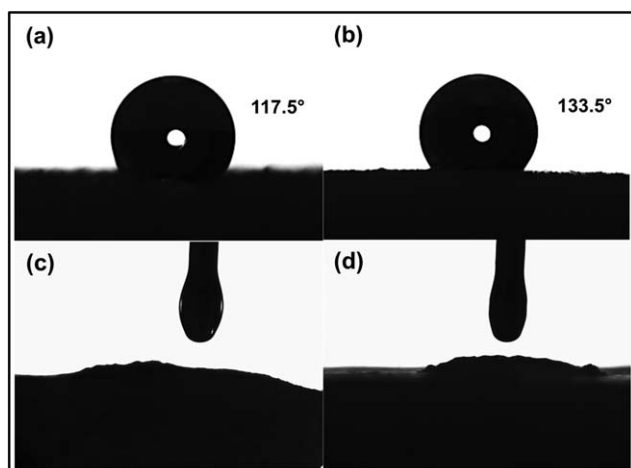
Figure 4. Water contact angle of (a) unmodified NR foam and (b) PBMA modified NR foam. Oil contact angle of (c) unmodified NR foam and (d) PBMA modified NR foam.
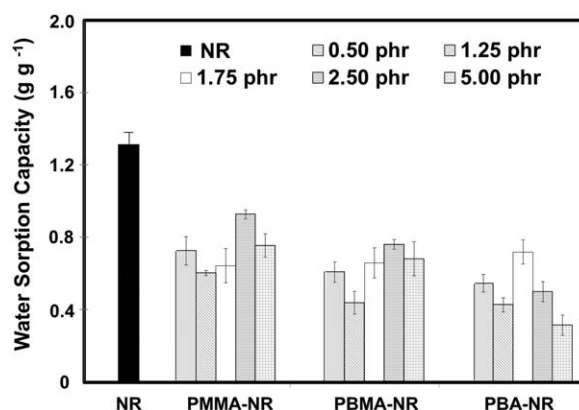
Figure 5. Water sorption capacity of unmodified NR (■) and poly(alkyl acrylate) modified NR foam at different the amount of PMMA, PBMA, and PBA.

foam slightly effected to the water sorption capacity, which decreased about 30–76% compare to the water sorption capacity of unmodified NR foam. These results can be implied to improvement of hydrophobicity and oleophilicity of the NR foam after modified with poly(alkyl acrylate).

Oil Sorption Capacity of Unmodified and Modified NR Foam
In this study, unmodified NR foam and PBMA modified NR foam were used as a sorbent material. The different types of common petroleum-based liquids with different viscosities (0.49–37.0 cSt) were used for oil sorption test. The characteristics of each petroleum-based liquid are summarized in Table III. The effect of the foam density (0.22–0.56 g cm^{-3}) onto the sorption capacity was also investigated. The results of oil viscosity and the foam density on the oil sorption capacity are presented in 3D surface plots as shown in Figure 6. The oil sorption capacity was depended on both foam density and oil viscosity. It can be seen that the decreasing in the oil viscosity and foam density increased the oil sorption capacity as well and reached the maximum value. The further increasing in the oil viscosity and foam density decreased the oil sorption capacity. For the range of study, the PBMA modified NR foam performed higher oil sorption capacity than unmodified NR foam. This result implied that the presence of poly(alkyl acrylate) can improve oil sorption capacity which can enhance the foam hydrophobicity and oleophilicity. However, the addition of poly(alkyl acrylate) emulsion affected to the dry rubber content of NR latex during latex mixing process and the foam stability in latex. Since all chemical reagents were added into the latex

Table III. Viscosity (v) and Surface tension (γ) of Petroleum-based Liquids

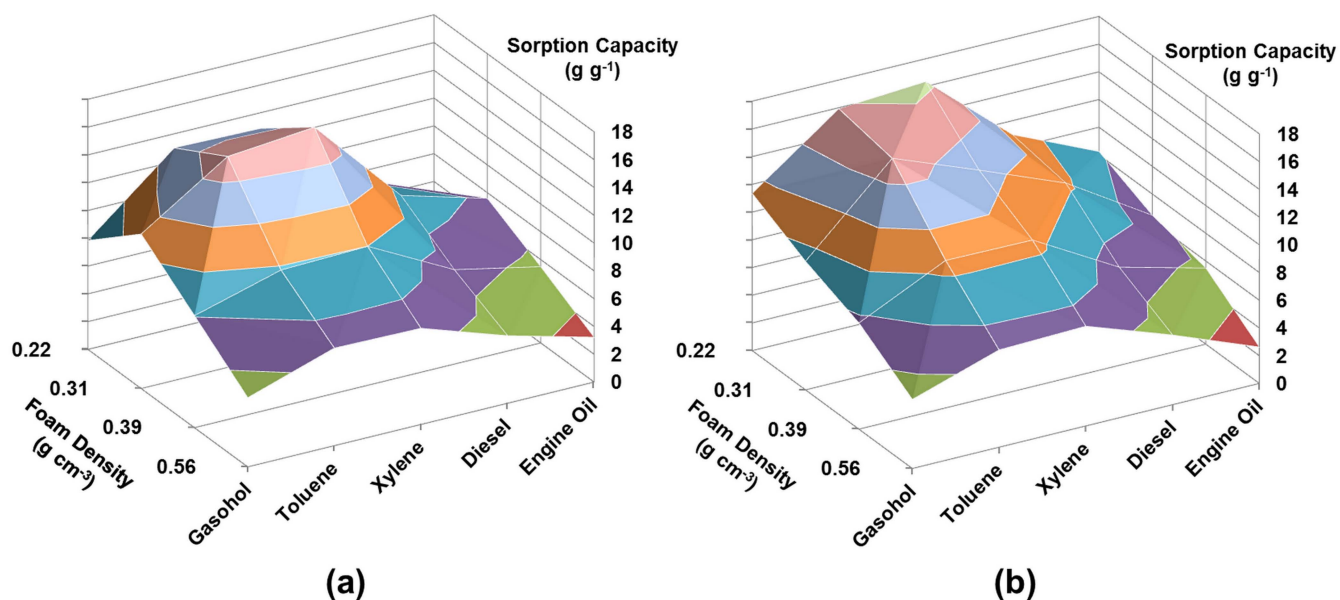| Petroleum-based Liquids	Viscosity at 40°C (cSt)	Surface tension (mN m^{-1})
Xylene	0.65	27.5
Toluene	0.55	27.0
Gasohol	0.49	20.4
Diesel	3.0	27.3
Engine Oil	37.0	29.6

Figure 6. Effect of foam density and oil viscosity on oil sorption capacity of (a) unmodified NR foam and (b) PBMA modified NR foam. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

system as emulsion or dispersion, therefore at high amount of poly(alkyl acrylate) emulsion directly affected to the rubber solid content. Conventionally, the suitable solid content of natural rubber foam process should contain as low as 55% which are strong enough when first gelled. Thus, the tiny fibrils cohere and shrink from the mold rather than collapsing during cure.[42] Therefore, this is the limitation of poly(alkyl acrylate) emulsion loading in the NR foam process.

Reusability of Modified NR Foam

One of the most concerns for oil spill cleanup application is the reusability of sorbent material. In reusability study, the PBMA modified NR foam was absorbed with various types of petroleum-based liquid (xylene, toluene, gasohol, diesel oil, and engine oil) and recorded the oil sorption capacity for each sorption–desorption cycle. The results are presented in Figure 7. Oil sorption capacities of the PBMA modified NR foam in the first
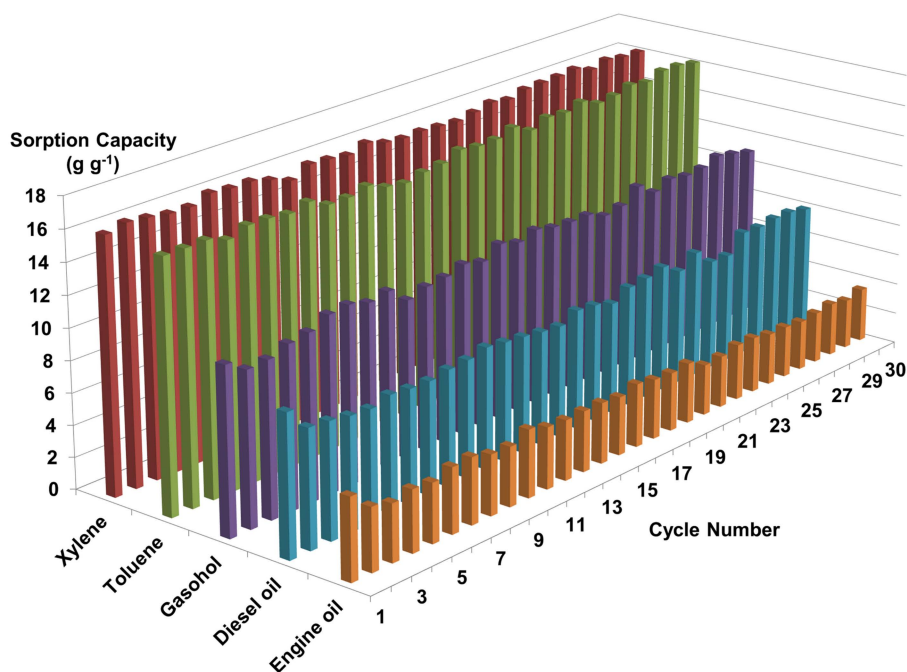

Figure 7. Reusability of PBMA modified NR foam. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. Comparison of Oil Sorbent Materials

Type of sorbent	Detail	Oil	Q (g g^{-1})	Number of cycle	Desorption method	Ref.
Foam	Modified NR foam	Xylene	16.6	30	Squeeze	This study
		Toluene	16.7			
		Gasohol	11.3			
		Diesel	11.0			
		Engine oil	8.2			
Fiber	P(BMA-co-LMA)	Kerosene	8	-	-	16
		Toluene	15			
		Chloroform	35			
Fiber	PP	Trichloroethylene	7	-	-	17
	PP-blend-P(LMA-co-BMA)	Trichloroethylene	35			
Resin	P(MMA-co-BMA)	Toluene	17.6	-	-	18
Resin	P(BMA-co-HEMA)	Kerosene	1.17	-	-	19
		Toluene	12.59			
		Trichloroethylene	24.03			
Resin	P(BMA-co-OA)	Toluene	23.5	-	-	20
Gel	BR	Diesel	23	30	Squeeze	22
		Crude oil	20			
Gel	CBR or SBR	Olive oil	27	20	Squeeze	23
		Crude oil	38			
Foam	PU coated LMA	Diesel	46.98	-	-	4, 24
		Kerosene	41.42			
Foam	PU coated silica sol (or gasohol)	Motor oil	103	15	Squeeze	25
		Peanut oil	108			
		Diesel	95			
Foam	Carbon soot	Toluene	50	10	Squeeze	26
		Hexane	25			
		Engine oil	33			
Foam	Swellable porous PDMS	Chloroform	34	20	Squeeze or wash	27
		Toluene	18.7			
		Gasoline	22			
		Diesel	12			
		Crude oil	9			
Foam	PDMS	Chloroform	11	19	squeeze or wash	28
		Toluene	5.0			
		Motor oil	5.2			

cycle were approximately 16 g g^{-1} for xylene and toluene, 10.5 g g^{-1} for gasohol, 8.8 g g^{-1} for diesel, and 5.1 g g^{-1} for engine oil. After reused, the modified NR foam performed similar oil sorption capacity up to 30 cycles. For low viscosity liquid (xylene, toluene, and gasohol), oil recovery efficiency (RE) was over 95% whilst the recovery efficiency of high viscosity liquid (diesel and engine) was 45–68%. A decreasing in oil recovery efficiency caused by the small amount of oil residual which was trapped inside pores and NR network after swollen. In this case, the PBMA modified NR foam after swelling should be washed with alcohol and dried before reuse for best results. However,

PBMA modified NR foam can be reused over 30 times of sorption–desorption cycles, which confirmed the reusability performance of the foam for oil sorption. Because of reusability, it decreased the cost of oil cleanup.

The comparison of oil sorption capacity and reusability of several oil sorbent materials, which were reported in previous literatures, are summarized in Table IV. NR foam performed higher oil sorption capacity than fiber or resin according to porosity of the foam. However, the oil sorption capacity of modified NR foam was lower than macroporous gel, PU foam, and carbon
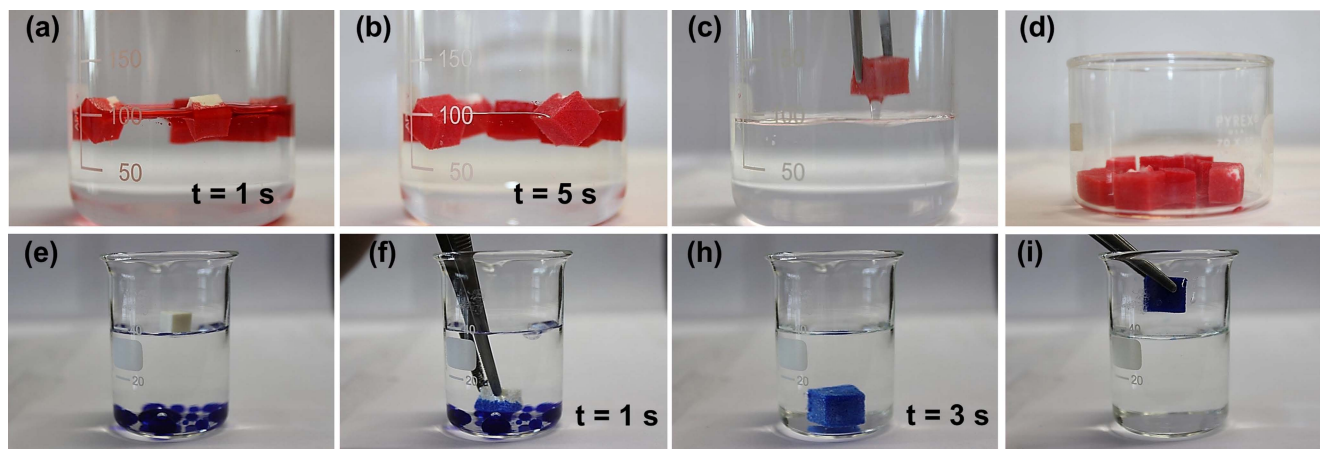
Figure 8. Demonstration of oil/water separation using PBMA modified NR foam (a–d) diesel sorption test and (e–i) dichloromethane sorption test (dyed with blue color). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

foam while the reusability of the modified NR foam was greater than other sorbent materials including fiber, resin, macroporous gel, PU foam, and carbon foam because of flexibility and elasticity of PBMA modified NR foam as reported in compression set testing.

Application as Oil Sorbent Material

For practical applications, oil sorbent should float on the water surface before and after oil sorption to prevent the contamination of oil and ecology system under water. In order to investigate the oil/water separation, the demonstration of petroleum-based liquid removal was observed as illustrated in Figure 8. About 10 mL of diesel (dyed with red color) was poured into a beaker containing 100 mL of water. The diesel quickly parted to the top due to its lower density than water. One gram of modified NR foam was placed on top of diesel–water mixture. Diesel rapidly saturated PBMA modified NR foam and absorbed all diesel within 5 sec. The saturated diesel foam was removed and examined. It can be clearly seen that the modified NR foam removed only diesel and no water was absorbed. To prove the finding, a high-density organic solvent (dichloromethane, density 1.33 g cm^{-3}) was used for oil sorption test with the same procedure as described above. A piece of modified NR foam was submerged in the water until exposed to dichloromethane layer (dyed with blue color). The foam quickly absorbed dichloromethane within 3 sec and no water sorption.

CONCLUSIONS

Polyisoprene–poly(alkyl acrylate) foam were successfully prepared by latex vulcanization and cured by steaming process. The addition of poly(alkyl acrylate) (PMMA, PBMA, and PBA) enhanced the hydrophobicity and oleophilicity, decreased water sorption capacity and increased oil sorption capacity of NR foam. The foam density and petroleum-based liquid viscosity were directly affected to the oil sorption capacity. The modified NR foam can be used as petroleum-based oil sorbent and reused up to 30 times.

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