Kinetic Modeling of Oil Absorption by Waste Tire Granules

Pongrapee Kaeomani, Duangkamol Danwanichakul and Panu Danwanichakul*

Abstract— **A study of oil absorption by using waste tire granules was investigated and modeled. It was found that the kinetics of oil absorption of waste tire granule depended on oil type, tire granule size, and temperature. Gasoline was absorbed to reach equilibrium with the highest rate, followed by diesel, soybean oil (cooking oil) and motor oil. Gasoline absorbability of tire granule with the size of 10 mesh had the highest value of 1.2 times tire's weight at 50°C. Considering the size of waste tire granule, the oil absorbability was greater when the size was smaller. In addition, tire granules were able to absorb more oil at higher temperature because both rubber and oil molecules had higher kinetic energy to move inside the rubber particle. Moreover, the diffusion coefficient could be estimated from the diffusion equation (long-time kinetic model) for a spherical particle by using the experimental swelling data. It was seen that the diffusion coefficient was increased when oil temperature was higher or when the tire granule was smaller.**

Keywords—**kinetics, oil, absorption, waste tire granule, diffusion**

I. Introduction

Currently, oil contamination in water is an important environmental problem harming both human and other organisms. The problem of oil spill may be alleviated by using dispersants or applying absorbents. This work concerns the latter in which many materials such as polypropylene [1], polystyrene nanofiber and activated carbon were tested for their oil absorbability. Electrospun polystyrene nanofibers could absorb motor oil up to 113.87 g/g [2] while activated carbon with surface area of $615 \, \mathrm{m^2/g}$ could absorb crude oil as much as 5.90 g/g at $40 \, {}^\circ\mathrm{C}$ [3].

Another environmental problem, which is the increasing number of waste tires, is raising much concern since they are highly durable and difficult to be reclaimed. Applying them as oil absorbents is reasonable as to handle both problems at the same time.

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A tire is mainly composed of rubber which is non-polar so it is compatible with oils. 20-mesh recycled waste tire powder for the recovery of oil spills was reported [4]. It was found that 1 g waste tire powder could absorb 2.2 g motor oil [4]. Later, its absorption capacity could be boosted to 7.78 g/g by using composite of 40-mesh waste tire powder and polypropylene fiber [5]. In addition, it was reported that tire rubber particle with average diameter of 1.4 mm could absorb cooking oil about 0.87 g/g [6]. However, there is only a few works studying oil absorption kinetics. For example, Aisien *et al.* investigated the absorption kinetics of crude oil by using scrap tire [7]. In this work, we focused on absorption kinetics of different oils including gasoline, diesel, motor oil and soybean oil or cooking oil by using waste tire granules and based the kinetic modeling on diffusion of oil into the matrix of tire granules.

II. Methodology

A. Material

The size-reduced tire waste was investigated. The chosen average particle sizes are 1.651 mm (Mesh 10; M10) and 2.794 mm (Mesh 7; M7). It was supplied by the Union Pattanakij Co., Ltd. (Thailand). Gasoline 91 and diesel were purchased from Ptt PCL, Thailand. Soybean oil as cooking oil was supplied by Morakot Industries PCL, Thailand while motor oil (SAE 20W-50) was obtained from Bangchak Petroleum Public Co., Ltd.

B. Waste tire Granule Characterization

The composition of waste tire granule was analyzed by thermogravimetric analysis (TGA). In the experiment, a sample was placed in a platinum crucible and heated at the rate of $20 \, {}^\circ\mathrm{C}/\mathrm{min}$ under the ambient temperature to $500 \, {}^\circ\mathrm{C}$ with continuous N_2 flow of 20 ml/min. After that, the heating process was continued under the air atmosphere until the system reached the final temperature of $850 \, {}^\circ\mathrm{C}$. The tests were performed in triplicate.

C. Determination of Crosslink Density

The crosslink density of waste tire granules, which is the rubber vulcanizate, was determined by saturating tire granules in toluene for 78 hrs at $30 \, {}^\circ\mathrm{C}$. The assessment of the crosslink density was done by using the Flory-Rehner equation [8]. The typical Flory-Rehner equation is shown below.

$$-\ln(1-V_r) - V_r - \chi V_r^2 = V_0 n (V_r^{1/3} - V_r/2) \tag{1}$$

where V_r is the volume fraction of rubber in the swollen gel at equilibrium, V_0 is the molar volume of swelling agent (105.9 ml/mol for toluene), and n is the physical degree of

crosslink. χ is a characteristic parameter of the interaction between the rubber network and the swelling agent, which could be calculated through solubility parameters [8] by

$$\chi = 0.34 + (\delta_s - \delta_r)^2 V_0/RT. \qquad (2)$$

Here, δ_s and δ_r are the solubility parameters of the swelling agent and the rubber network, respectively. R is the universal gas constant (1.987cal/mol-K) and T is the absolute temperature (K). The volume fraction of rubber, V_r, in the swollen gel at equilibrium can be written as

$$V_r = \frac{\dfrac{m_0 \Phi (1 - \alpha)}{\rho_r}}{[\dfrac{m_0 \Phi (1 - \alpha)}{\rho_r} + \dfrac{(m_1 - m_2)}{\rho_s}]} \qquad (3)$$

where m_0, m_1 and m_2 are the weights of the tire granules in air, in swollen state and after drying in a vacuum oven at 90^oC for 32 hrs, respectively. Φ is the mass fraction of rubber in the vulcanizate, α is the mass loss of the gum rubber vulcanizate during swelling, and ρ_r and ρ_s are the rubber and the solvent densities, respectively.

D. *Absorption Experiments*

Four types of oil, which are gasoline 91, diesel, soybean oil (cooking oil) and motor oil, were used to evaluate the absorption kinetics and equilibrium. First, 1 g of waste tire granules was packed in a small bag and the bag was then sealed. After that it was soaked in the beaker containing 50 ml oil at 30^oC and 50^oC. The waste tire granules were weighed during absorption at many intervals using an analytical balance with 4 decimal numbers to obtain the kinetic data. The equilibrium absorption was achieved when the weight of tire granules was constant. The experiments were done in triplicate. The absorption ability, Q, and %sorption of waste tire granules can be calculated according to Eq. (4) and (5), respectively.

$$Q_{sorption} = \left(\frac{W_f - W_i}{W_i}\right) \qquad (4)$$

$$\% Sorption = \left(\frac{W_f - W_i}{W_i}\right) \times 100 \qquad (5)$$

Where $Q_{sorption}$ is the absorption ability (g/g$_{rubber}$), W_i (g) and W_f (g) are initial and final weights of waste tire granules in the absorption experiments.

III. **Results and Discussion**

A. *Composition Analysis*

The compositions of M10 and M7 waste tire granules obtained from TGA are shown in Table 1. It was found that both compositions were slightly different. They contained mostly hydrocarbon or rubber up to 53.45-59.22%. Carbon content of those samples was found to be 26.18-30.17% which was from carbon black as the reinforcing filler. Ash contributes 3.11-6.56% of waste tire mass. Ash usually includes silica which is the reinforcing filler, zinc which is from the activator for vulcanization and sulfur which is used to vulcanize the rubber composite. The volatile matter which

is from other additives was found to be 9.82-11.49%.

TABLE I. WASTE TIRE GRANULE COMPOSITIONS

Tire Sample	Weight (%)			
	Volatile matter	Hydrocarbon (rubber)	Carbon	Ash
M10	9.82	53.45	30.17	6.56
M7	11.49	59.22	26.18	3.11

It was expected that the large amount of non-polar part which is the rubber matrix, either natural rubber or synthetic rubber, should contribute to the oil absorbability of waste tire granules.

B. *Crosslink Density*

As shown in Table II, the crosslink density of M10 is slightly lower than that of M7 probably because more mechanical forces exerted while grinding the tire to smaller granules can break more crosslinks of the rubber leading to lower crosslink density.

TABLE II. CROSSLINK DENSITIES OF WASTE TIRE GRANULE

Tire Sample	Crosslink Density (mol/m^3)
M7	0.492 x 10^{-5}
M10	0.432 x 10^{-5}

C. *Absorption kinetics*

Absorption abilities of tire granules, M7 and M10, over time for gasoline, diesel, motor oil and cooking oil were shown in Figures 1-4, respectively. It was found that when the absorbent size was smaller, the absorption ability for every oil type could reach its equilibrium faster because the absorption rate depends on transfer area. The smaller rubber granules (M10) have higher surface area and lower crosslink density which could facilitate the transfer of oil inside the granules. Moreover, at a higher temperature, absorption ability could reach the equilibrium faster due to higher kinetic energy of oil molecules. Obviously, absorption for gasoline, diesel and motor oil reached their equilibrium at 120, 240 and 1800 min, respectively corresponding to their kinematic viscosities which in turn dependent on molecular weight as shown in Table III, whereas for cooking oil, it reached equilibrium at 240 min. The equilibrium sorption capacities of M10 for gasoline, diesel, motor oil and cooking oil at 50^oC were 1.207, 1.141, 0.921 and 0.664 g/g, respectively, dependent on molecular weight and polarity of oil molecules.
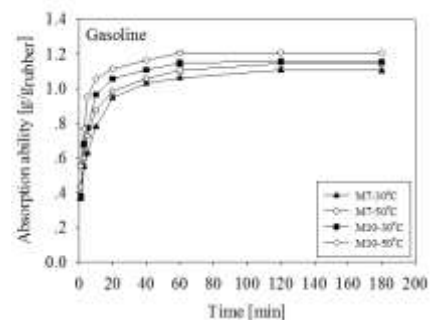

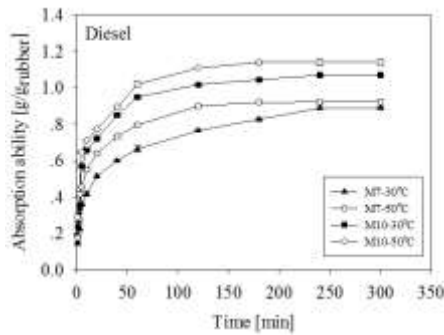Figure 1. Absorption ability for gasoline
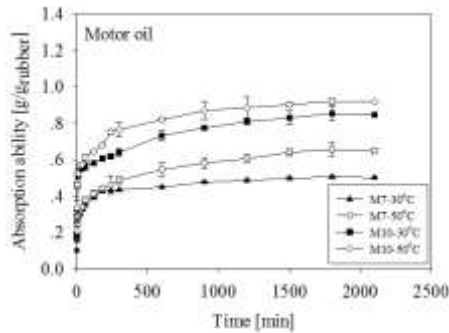
Figure 2.   Absorption ability for diesel

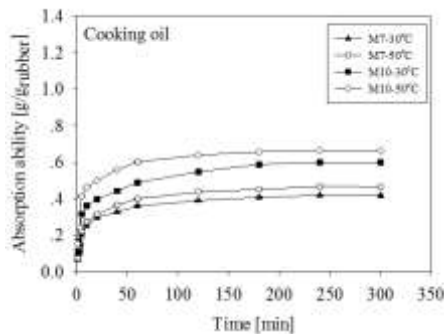Figure 3.   Absorption abiliity for motor oil

Figure 4.   Absorption ability for cooking oil

TABLE III.   PROPERTIES OF GASOLINE, DIESEL, MOTOR OIL AND SOYBEAN OIL

Oil Type	Chemical Formula	Density (kg/m^3)	Kinematic Viscosity at 40 ℃ (mm^2/sec)
Gasoline	$C_5 - C_8$	722	0.55
Diesel	$C_{12} - C_{15}$	800	2.38
Motor oil	$C_{20} - C_{34}$	892	154.63
Soybean oil (Cooking oil)	It is composed of various fatty acid such as oleic acid ($C_{18}H_{34}O_2$) and Linoleic acid ($C_{18}H_{32}O_2$)	850	57.2

D. *Equilibrium Absorption*

The equilibrium sorption percentages of M7 and M10 for gasoline, diesel, motor oil and cooking oil were reported in Figure 5. It is clearly seen that the %sorption for gasoline was the highest followed by diesel, motor oil and cooking oil, respectively. Although, the kinematic viscosity of cooking oil is lower than that of motor oil, the %sorption of cooking oil was lower because the cooking oil is composed of some carboxylic acids such as oleic acid and linoleic acid which have hydrophilic functional groups incompatible with hydrophobic nature of rubber in tire granules.
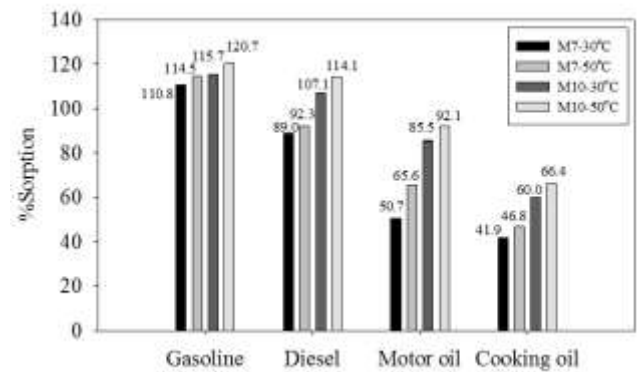

Figure 5.   %Sorption for different oil types

E. *Transport Mechanism of Sorption in Adsorbents*

Sorption mechanism can be studied using the short-time kinetic relation [9],

$$\log\left(\frac{Q_t}{Q_e}\right) = \log k + n \log t \qquad (6)$$

Where Q_t and Q_e are the absorption ability at any time (t) and at equilibrium (g/g$_{rubber}$), respectively. The parameter k describes interaction between rubber and the oil while n indicates the mechanism of molecules of oil diffusing in the rubber matrix. The plots between $\log(Q_t/Q_e)$ and t are shown in Figure 6 of which the values of n and k were obtained as shown in Table IV, with R^2 greater than 0.844.
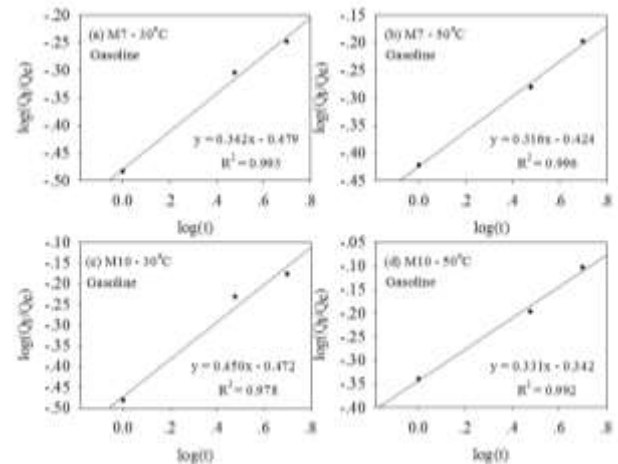

Figure 6.   log (Q_t/Q_e) vs. log (t) of gasoline

For any pair of oil-rubber, the value of n is close to 0.50, a theoretical value, implying that the transport mechanism is Fickian diffusion. The diffusion into most rubbery polymers tends to behave according to Fick's law of diffusion while glassy polymers exhibit "anomalous" or "non-Fickian" behavior because polymers in rubbery state respond quickly to changes while the properties of glassy polymers are time-dependent [10].

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TABLE IV. PARAMETERS n AND R^2

Oil Type	Tire Sample	Sorption Temperature (°C)	n	R^2
Gasoline	M7	30	0.342	0.993
		50	0.316	0.996
	M10	30	0.450	0.978
		50	0.331	0.992
Diesel	M7	30	0.527	0.949
		50	0.561	0.940
	M10	30	0.513	0.925
		50	0.469	0.935
Motor oil	M7	30	0.599	0.926
		50	0.304	1.000
	M10	30	0.561	0.997
		50	0.486	0.991
Cooking oil	M7	30	0.638	0.924
		50	0.639	0.952
	M10	30	0.628	0.844
		50	0.592	0.940

Because the transport mechanism into the rubber is Fickian diffusion, the diffusion coefficient, D_{ab} of oil molecules into the rubber matrix could be estimated by using the equation for mole uptake during a short-time period of absorption [10],

$$D_{ab} = \left[\sqrt{\pi} \left(\frac{\Theta D_p}{12 Q_e} \right) \right]^2 \qquad (7)$$

Here, Θ is the slope of the linear portion of the curve of Q_t versus $t^{1/2}$, where t is the absorption time. D_p is the average diameter of rubber granules. In this case, we assume the shape of granules to be spheres. The D_{ab} of short-time kinetic model calculated from Eq. (7) was shown in Table V.

TABLE V. D_{AB} CALCULATED FROM SHORT-TIME KINETIC MODEL

Oil Type	Tire Sample	Sorption Temperature (°C)	D_{ab} (mm²/min)
Gasoline	M7	30	6.5 x 10⁻³
		50	7.4 x 10⁻³
	M10	30	6.7 x 10⁻³
		50	6.1 x 10⁻³
Diesel	M7	30	6.2 x 10⁻³
		50	9.8 x 10⁻³
	M10	30	5.2 x 10⁻³
		50	5.2 x 10⁻³
Motor oil	M7	30	1.4 x 10⁻²
		50	3.3 x 10⁻³
	M10	30	5.8 x 10⁻³
		50	4.2 x 10⁻³
Cooking oil	M7	30	1.1 x 10⁻²
		50	1.1 x 10⁻²
	M10	30	4.0 x 10⁻³
		50	8.3 x 10⁻³

The comparison between the experimental data of adsorption ability and those obtained later from short-time kinetic model can be done. The consistency between the two sets of data is expressed by R^2 and RMSE which are defined according to Eq. (8) and (9), respectively.

$$R^2 = 1 - \frac{\sum_{i=1}^{N} ((Q_{pred,i}/Q_{pred,e}) - (Q_{exp,i}/Q_{exp,e}))^2}{\sum_{i=1}^{N} ((\overline{Q}_{pred}/Q_{pred,e}) - (Q_{pred,i}/Q_{exp,i}))^2} \qquad (8)$$

$$RMSE = [\frac{1}{N} \sum_{i=1}^{N} ((Q_{pred,i}/Q_{pred,e}) - (Q_{exp,i}/Q_{exp,e}))^2]^{1/2} \qquad (9)$$

Where $Q_{exp,i}$ and $Q_{pred,i}$ are absorption abilities at any time, which were obtained from experimental data and those from short-time kinetic model (g/g), respectively. $Q_{pred,e}$ and $Q_{exp,e}$ are the equilibrium ones obtained from experimental data and from short-time kinetic model (g/g), respectively. $\overline{Q}_{pred}$ is the average value of absorption ability (g/g).

The Q_t/Q_e vs. time of gasoline obtained from experimental data and short-time kinetic model is shown in Figure 7 while R^2 and RMSE obtained from experimental data and short-time kinetic model are shown in Table VI. Considering values of R^2 and RMSE, the absorption for diesel and cooking oil can be fit with the short-time kinetic model better than those for gasoline and motor oil.
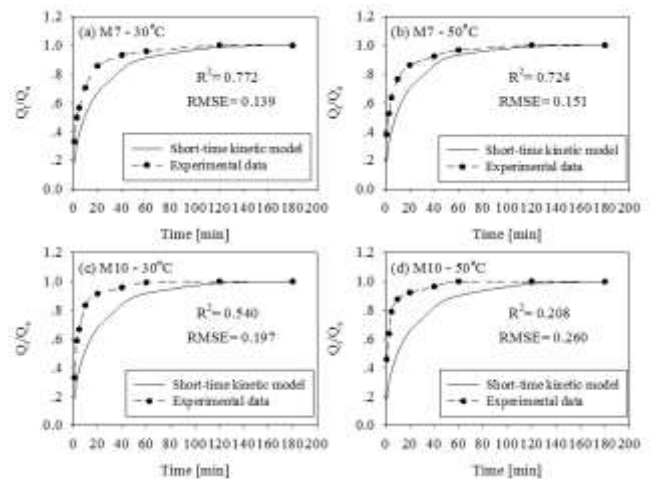

Figure 7. Q_t/Q_e vs. time for gasoline obtained from experimental data and short-time kinetic model

TABLE VI. R^2 AND RMSE OBTAINED FROM EXPERIMENTAL DATA AND SHORT-TIME KINETIC MODEL

Oil Type	Tire Sample	Sorption Temperature (°C)	R^2	RMSE
Gasoline	M7	30	0.772	0.239
		50	0.724	0.151
	M10	30	0.540	0.197
		50	0.208	0.260
Diesel	M7	30	0.925	0.082
		50	0.956	0.084
	M10	30	0.935	0.078
		50	0.909	0.092
Motor oil	M7	30	0.558	0.155
		50	0.699	0.170
	M10	30	0.648	0.168
		50	0.793	0.136
Cooking oil	M7	30	0.914	0.077
		50	0.910	0.079
	M10	30	0.856	0.092
		50	0.916	0.075

Another kinetic model is based on the long-time transport of oil molecules through the interface and along the radial axis of the granule which is assumed to be a

sphere. By fitting the experimental data with series in Eq (10), one could determine the value of D_{ab}. The results are shown in Table VII. The values of R^2 and RMSE were obtained from experimental data and the long-time kinetic model as provided in Table VIII.

$$\frac{Q_t}{Q_e} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{4D_{ab}n^2\pi^2 t}{D_P^2}\right) \qquad (10)$$

Considering the values of R^2 and RMSE in Table VIII and in Table VI, the results expressed that the absorption for all oil types could be better fit with the long-time kinetic model than with the short-time kinetic model. This is obviously seen in Figure 8. However, some discrepancy is still seen since the assumptions of spherical shape and uniform size of tire granules are not wholly valid.

The results of D_{ab} obtained from long-time kinetic model was considered further. As shown in Table VII, D_{ab} of gasoline is the highest implying that it was absorbed to reach equilibrium with the highest rate, followed by diesel, cooking oil and motor oil. Moreover, D_{ab} increased with higer oil temperature and an increase in the tire granule size.

TABLE VII. D_{AB} CALCULATED FROM EQUATION 10

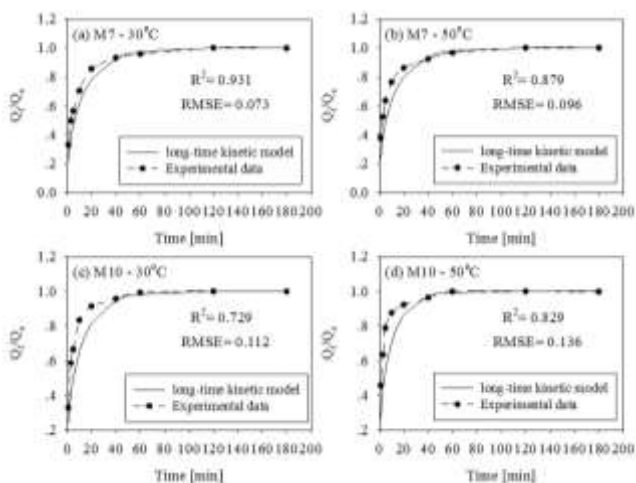| Oil Type	Tire Sample	Sorption Temperature (ºC)	D_{ab} (mm²/min)
Gasoline	M7	30	1.0×10^{-2}
		50	1.1×10^{-2}
	M10	30	1.2×10^{-2}
		50	1.5×10^{-2}
Diesel	M7	30	3.7×10^{-3}
		50	6.9×10^{-3}
	M10	30	9.3×10^{-3}
		50	1.0×10^{-2}
Motor oil	M7	30	1.7×10^{-3}
		50	1.7×10^{-3}
	M10	30	2.3×10^{-3}
		50	2.6×10^{-3}
Cooking oil	M7	30	5.0×10^{-3}
		50	5.1×10^{-3}
	M10	30	6.4×10^{-3}
		50	9.6×10^{-3}

Figure 8 Q_t/Q_e vs. time for gasoline obtained from experimental data and long-time kinetic model

TABLE VIII. R^2 AND RMSE OBTAINED FROM EXPERIMENTAL DATA AND LONG-TIME KINETIC MODEL

Oil Type	Tire Sample	Sorption Temperature (ºC)	R^2	RMSE
Gasoline	M7	30	0.931	0.073
		50	0.879	0.096
	M10	30	0.729	0.112
		50	0.829	0.126
Diesel	M7	30	0.974	0.051
		50	0.977	0.044
	M10	30	0.959	0.057
		50	0.946	0.064
Motor oil	M7	30	0.821	0.141
		50	0.805	0.147
	M10	30	0.735	0.166
		50	0.822	0.135
Cooking oil	M7	30	0.924	0.068
		50	0.945	0.058
	M10	30	0.922	0.071
		50	0.936	0.066

IV. Conclusion

Oil absorption of waste tire granules depends on interaction between oil and rubber matrix. So any factor enhancing the rate of oil diffusion will boost the absorption capacity. It was found that when the absorbent size was smaller, absorption ability reached equilibrium faster. The absorption capacities at equilibrium of gasoline, diesel, motor oil and cooking oil using M10 at 50ºC were 1.207, 1.141, 0.921 and 0.664 g/g, respectively. The kinetic models show that the long-time kinetic model can describe the transport mechanism better than short-time one.

Acknowledgment

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