

Synthesis and Characterization of a Novel High-Oil-Absorbing Resin

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Received 30 March 2009; accepted 3 September 2009

DOI 10.1002/app.31384

Published online 3 November 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A high-oil-absorbing resin, which was a low crosslinking resin, was synthesized by conventional suspension copolymerization in this study. The effects of the monomer ratio, crosslinker, initiator, ratio of water to oil, and defined optimum reaction conditions were studied. The highest oil absorptivity of the resin was about 11.5 g/g in diesel and the oil-absorption saturation time was 3 days when the best process conditions were as follows: ratio of styrene to ethylene-propylene-diene terpolymer = 40/60 w/w, amount of crosslinker divinylbenzene = 1.0 wt %, amount of benzoyl peroxide = 1.0 wt %; proportion of gelatin to calcium phosphate = 0.2 g/0.1 g, stirring speed = 500 r/min, and proportion of water to oil

= 15 : 1. By using such methods as infrared spectroscopy, thermogravimetric analysis, and other methods, we studied the oil-absorbing resin structure, oil-absorption rate, oil-absorption saturation time, and oil-absorption rate twice. The oil-absorbing resins were used repeatedly through the extraction of ethanol. The experiment results show little effect on the oil-absorption properties. The oil-absorption rate constant was evaluated for diesel, and the oil-absorption process obeyed the first-order kinetics equation. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 3321–3325, 2010

Key words: resins; rubber

INTRODUCTION

The ever-increasing volume of petroleum products used worldwide has brought with it a proportionate increase in the number of accidental and deliberate hydrocarbon oil spills. In open bodies of water, such as rivers, harbors, lakes, and oceans, oil is a serious pollutant. Large spills can be positively disastrous to birds and perimarine life, and even small spills can foul beaches. There is an exigent need to develop an adequate and efficient process for removing this oil. Various materials, such as brick clay, silicon dioxide, activated carbon, paper pulp, polypropylene fiber, polyurethane foam, and oil-absorbing resin have been used widely to absorb oil spilled on water. Among them, the capability of oil-absorbing resin is seen to be superior to other ordinary materials.^{1–4} This resin can be made granular, sheeted, or as an emulsion and can be applied not only in environmental protection but also in agriculture, medicine, and industry. It is this broad range of possible applications that has led to recent interest in this system. In this study, we synthesized a high-oil-absorbing

resin by suspension copolymerization. It was hydrophilic and had a gel-type structure consisting of an elastic crosslinking three-dimensional network and interstitial space that did not dissolve in oil but swelled in oil. To improve the general structure of the surface of the oil-absorbing resin, reduce the crosslinked network of space resistance, and enhance the oil absorbency and poor mechanical properties, in this study, from the perspective of molecular design, we selected the flexible macromolecular ethylene-propylene-diene terpolymer (EPDM) and rigid molecule styrene (St) as monomers. To overcome the viscosity of EPDM, which is easily bonded and sensitive to temperature changes and other issues, we selected divinylbenzene (DVB) as the crosslinker, benzoyl peroxide (BPO) as the initiator, toluene and cyclohexane as the solvents, and gelatin, calcium phosphate, and sodium dodecyl sulfate as the dispersants. We designed the optimal proportions and used the suspension polymerization method to synthesize an olefin type high-oil-absorbing resin. By using such methods as infrared (IR), thermogravimetric analysis (TGA), and other methods, we found the double bond in the EPDM side chain to indeed react with the monomers and act as a chemical crosslink. Because with current organic syntheses, oil-absorbing materials are difficult to degrade, because their burning pollutes the environment, and because of their higher cost, in this study, we sought to facilitate the oil-absorbing resin recovery through the extraction of ethanol to use the

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Contract grant sponsor: Tianjin University of Science and Technology; contract grant number: 20060429.

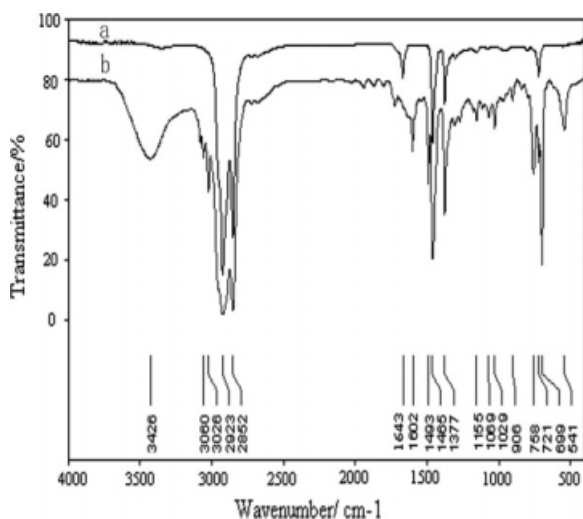


Figure 1 FTIR spectra of (a) EPDM and (b) the EPDM-DVB-St oil-absorbing resin.

resin. The experiments were generally repeatable more than 10 times with little effect on the oil-absorption properties.

EXPERIMENTAL

Materials

EPDM (Shanghai Rubber Institute, Shanghai, China) and BPO (Tian-Lian Chemical Reagent Factory, Shanghai, China) were dissolved in CHCl_3 (Tian-Tai Chemical Reagent Factory, Tianjin, China) and precipitated by the addition of an equal volume of MeOH. Gelatin and calcium phosphate (Yong-Da Chemical Reagent Factory, Tianjin, China), toluene and cyclohexane (Chemical Reagent Co., Tianjin, China), diesel (market seller, Tianjin, China), St (Guang-Cheng Chemical Reagent Factory, Tianjin, China), and DVB (North Chemical Reagent Co., Tianjin, China) were purified by washing with 5% aqueous sodium hydroxide (Tian-Tai Chemical Reagent Co., Tianjin, China), dried by anhydrous CaCl_2 (Tian-Tai Chemical Reagent Factory), and distilled under a vacuum.

Measurements

IR spectroscopy

Fourier transform infrared (FTIR) spectra of the oil-absorbing resin were taken with a Vector 22 IR spectrophotometer (Bruker Co., Germany). The KBr pressed-disc technique (ca. 2 mg of sample and 200 mg of KBr) was used.

Oil-absorption test

Test 1. The oil-absorbing resin crosslinking density was determined by ASTM F726-81; 0.1 g of sample

was put in stainless steel mesh ($4 \times 4 \times 2 \text{ cm}^3$) that had been immersed in diesel and weighed beforehand. The sample and the mesh were together picked up from oil, drained for 20 s, tapped with filter paper to remove excess oil from the bottom of the mesh, and then weighed on a balance. The oil absorbency was calculated by the following formula:

Oil absorbency(g/g)

$$= \frac{\text{Weight of absorbed oil in the sample/}}{\text{Weight of the sample before oil absorption}}$$

Test 2. TGA was carried out with a TA Instruments Co. thermal analysis system (TGAQ500). About 10 mg of the oil-absorbing resin before oil absorption (sample I) and after oil absorption (sample II) were weighed into an aluminum crucible, the profiles were recorded from room temperature to 600°C at a heating rate of $20^\circ\text{C}/\text{min}$, and then, the oil absorbency was calculated by the TGA curves.

Recovery of the oil-absorbing resins

The oil-absorbing resins after oil absorption were recovered by the extraction of ethanol and used repeatedly. The oil absorbency was measured by tests 1 and 2.

Preparation of the oil-absorbing resin

A given weight of gelatin glue was dissolved in a known volume of distilled water in a 250-mL round-bottom flask equipped with a thermometer, a stirrer, a gas inlet pipe, and a reflux condenser. The mixture of EPDM and St with DVB crosslinker was then

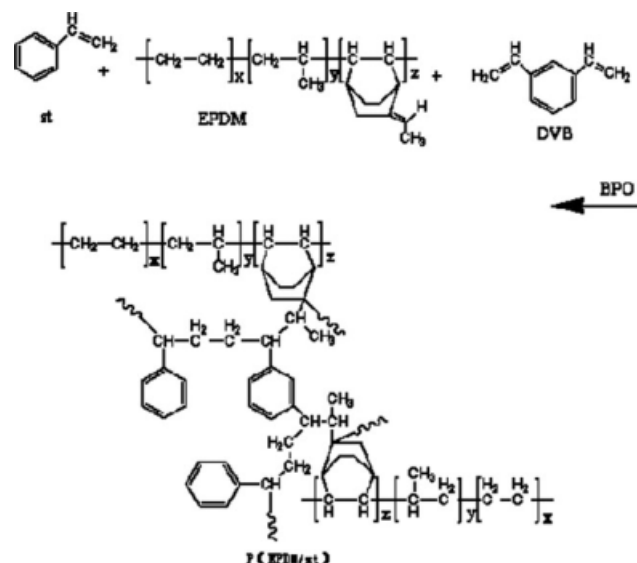


Figure 2 Possible chemical reaction mechanism for the oil-absorbing resin.

TABLE I
Graft Crosslinking Polymerization Conditions

Reaction condition	Description						
	I	II	III	IV	V	VI	VII
EPDM/St (wt %)	60/40	40/60	20/80	60/40	60/40	60/40	60/40
DVB (wt %) ^a	1	1	1	1.5	2	1	1
BPO (wt %) ^a	1	1	1	1	1	0.5	1.5
H ₂ O/oil (mL/mL) ^b	15	15	15	15	15	15	15
Gelatin/calcium phosphate (g/g)	2	2	2	2	2	2	2
Temperature (°C)	80	80	80	80	80	80	80
Time (h)	8	8	8	8	8	8	8
Stirring speed (rpm)	500	500	500	500	500	500	500
Highest oil absorptivity (g/g) ^c	11.5	9.8	8.2	9.1	8.2	9.6	7.9
Oil-absorption saturation time (days)	3	5	5	4	3	3	4

^a The concentration was based on the total weights of the monomers and EPDM.

^b The amount of oil was equal to the volume of toluene and cyclohexane used.

^c The highest oil absorptivity was measured in test 1 when the oil-absorbing resin was immersed in diesel.

added to the flask with BPO. After 8 h of suspension reaction at a stirring speed of 500 rpm under a nitrogen atmosphere at 80°C, the prepared oil-absorbing resin was collected by filtration; then, the solution was cooled, extracted with tetrahydrofuran, and dried in a vacuum oven until a constant weight was reached.

RESULTS AND DISCUSSION

Characterization

The structure of the synthesized oil-absorbing resin and EPDM were indicated by the IR spectra, as shown in Figure 1. As shown in Figure 1(a), characteristic absorption bands of EPDM appeared at 2923 cm⁻¹ (stretching vibration of aliphatic C—H bond), 2852 cm⁻¹ (stretching vibration of aliphatic C—C bond), and 1155 cm⁻¹ (propylene methyl groups). The aromatic vinyl stretching vibration peak at 1602 cm⁻¹ of St monomer is shown in Figure 1(b), but it

is imperceptible in Figure 1(a). At same time, the aliphatic vinyl stretching vibration peak at 1643 cm⁻¹ is not shown in Figure 1(b). Therefore, we concluded that crosslinking oil-absorbing resin was gained through the chemical reaction of EPDM, St, and DVB. A possible chemical reaction mechanism for the oil-absorbing resin is shown in Figure 2.

Effect of the reaction conditions on the maximum oil absorbcency

The reactions were carried out under various experimental conditions, as shown in Table I. The effect of EPDM content on the highest oil absorptivity is shown in Table I. The highest oil absorptivity increased with increasing EPDM content. These results were probably caused by the increasing diene content of the graft or crosslinking sites in EPDM as the EPDM content increased. On the other hand, it seemed that the lower the concentration of EPDM

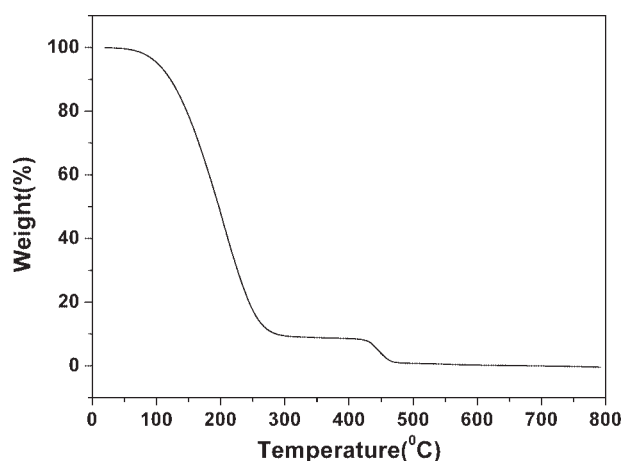


Figure 3 TGA curve for the oil-absorbing resin after the absorption of oil.

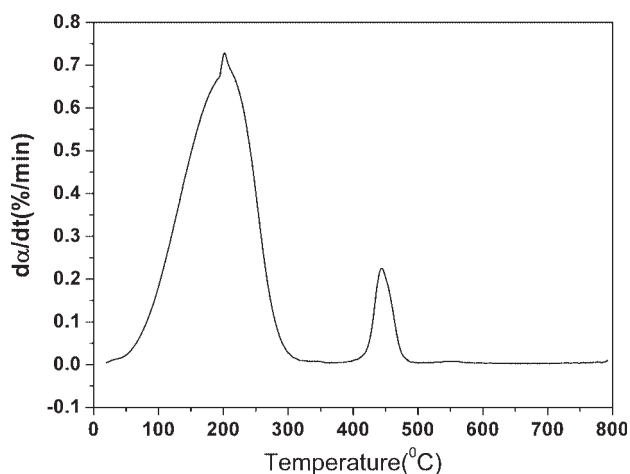


Figure 4 DTG curve for the oil-absorbing resin after the absorption of oil.

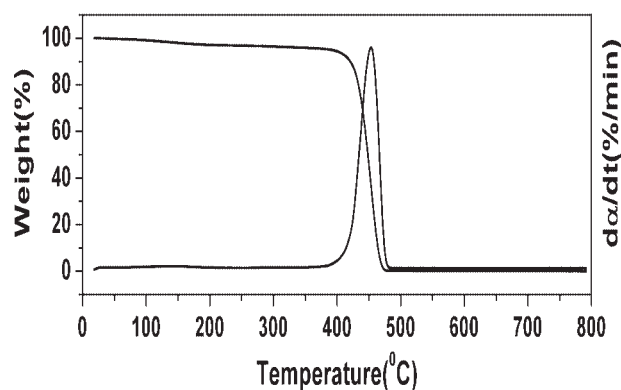


Figure 5 TG and DTG curves for the oil-absorbing resin before the absorption of oil.

was, the fewer active centers there were,^{5,6} and thus, higher degrees of homopolymerization of St and copolymerization poly(St-co-DVB) were produced. For convenience, however, the EPDM content was fixed at 60 wt % to investigate. Table I shows the effect of the concentration of DVB on the graft crosslinking polymerization. The reactions were performed in EPDM/St (60/40 wt %) and BPO (1 wt %) at 80°C for 8 h. As Table I shows, the highest oil absorptivity decreased monotonously with increasing content of DVB. As DVB had two double bonds, the higher DVB content easily allowed graft polymerization and chemical crosslinking.⁷ It is known that the lower degree of crosslinking is, the more a gel swells,⁸ so in all of the experiments, we adopted a low molar ratio of DVB content. Table I also shows the effect of the initiator concentration on the graft crosslinking polymerization. The highest oil absorptivity increased with increasing initiator concentration up to 1 wt % but, thereafter, decreased with further increasing initiator concentration. The decrease

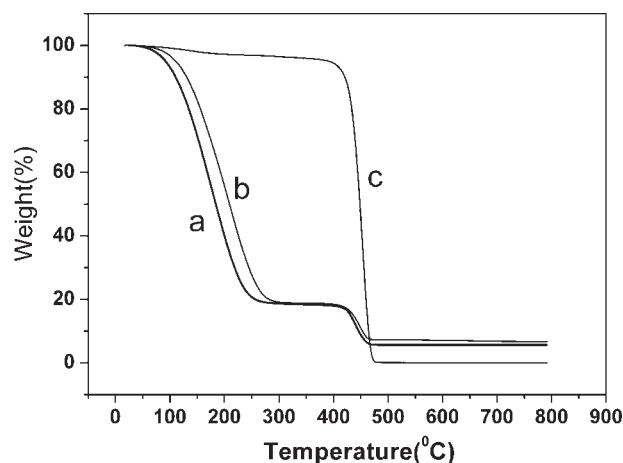


Figure 6 TGA curves of the oil-absorbing resin: (a) the oil-absorbing resin used repeatedly through the extraction of ethanol, (b) the oil-absorbing resin after the absorption of oil, and (c) the oil-absorbing resin before the absorption of oil.

in the grafting efficiency at higher initiator concentrations was expected because the homopolymer was formed more readily than the graft terpolymer as the initiator concentration increased. Maybe more initiator gave more active centers, and monomers could move easily and have more chances to be initiated to form homopolymer. Similar observations were made in Voek's⁹ and Cho et al.'s¹⁰ articles. Accordingly, when the initiator concentration was below 1 wt %, intramolecular crosslinking or intramolecular cyclization may have been preferred at lower active center systems.

TGA of the oil-absorbing resin

The thermogravimetry (TG) curve of the oil-absorbing resin that absorbed diesel is shown in Figure 3. The corresponding differential thermogravimetry (DTG) curves (see Fig. 4) showed a first degradation stage at a low temperature, immediately followed by another second stage at a higher temperature. We attributed the degradation to diesel for the first DTG peak, whereas the degradation at the second DTG peak was attributed to random chain scission of the oil-absorbing resin. As shown in Figure 2, the absorbed diesel began degrade from 50 to 300°C. Accordingly, the TG and DTG curve of the oil-absorbing resin before diesel absorption is shown in Figure 5 and confirms our conclusion. The pure oil-absorbing resin began to degrade from 380°C, which showed that the oil-absorbing resin could be used under higher temperature conditions. TGA curves of the ordinary oil-absorbing resin and the oil-absorbing resins used repeatedly through the extraction of ethanol are given in Figure 6. The oil-absorbing resin could be used repeatedly, and the recovery of oil-absorbing resin had little effect on the oil absorptivity.

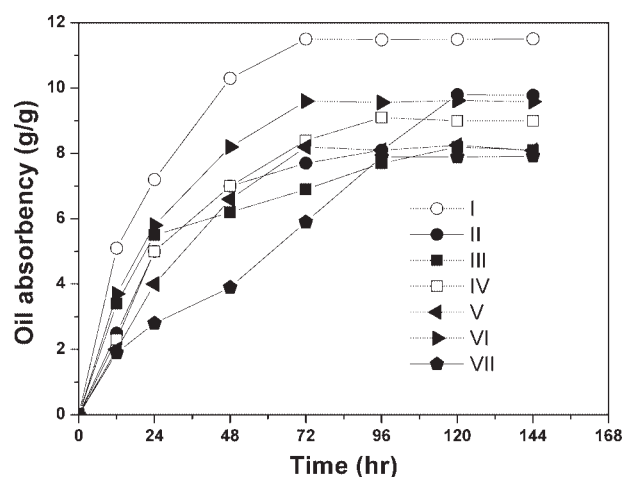


Figure 7 Oil absorptivity of the oil-absorbing resins versus the immersion time.

TABLE II
Oil-Absorption Rate Constant (K) Values for the Seven Synthetic Resins

Resin	I	II	III	IV	V	VI	VII
$K \times 10^{-3} \text{ (h}^{-1}\text{)}$	60.2	48.6	49.2	45.8	40.2	59.4	32.5

Kinetic analysis of the oil-absorbing resin

Under these experimental conditions, we choose diesel to study the oil-absorbing kinetic process. Figure 7 shows the oil absorbencies of the oil-absorbing resin versus immersion time. The oil-absorbing resins are shown Table I. The oil absorbencies of the oil-absorbing resin increased with increasing immersion time and reached a plateau after 3–5 days of immersion in diesel. The lower the DVB content was, the higher the oil absorbency was. The reason was described previously. The oil absorbencies in oil-absorbing resin I were larger than other those of the other resins shown in Table I, and the oil absorption rates were higher than the those of the other resins shown in Table I. This phenomenon was explained by the fact that oil-absorbing resin I seemed to produce many large-sized cavities during the reaction. Maybe the oil absorbency and the oil absorption rate were dependent not only on the number of the pores but also on the size of the cavities. We used the oil absorptivity–time relation curve to determine the kinetic constant (K) associated with the first kinetic equation.¹¹

$$dQ/dt = K(Q_{\max} - Q_t) \quad (1)$$

where $d\alpha/dt$ is the differential of the weight loss of sample vs time; Q is the oil absorptivity; Q_{\max} is the highest oil absorptivity; and Q_t is the oil absorptivity at time t . Equation (1) can be changed into eq. (2):

$$\ln\left(\frac{Q_{\max}}{Q_{\max} - Q_t}\right) = Kt \quad (2)$$

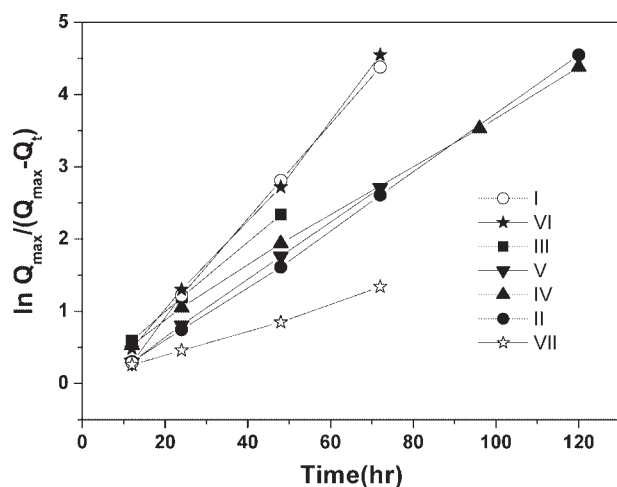


Figure 8 Kinetic parameter curves of the seven synthetic oil-absorbing resins.

Thus, the K value can be determined through the linear relation in eq. (2). The K values of the seven synthetic oil-absorbing resins are given in Table II. The results of Table II show that the prepared oil-absorbing resin I in this experiment had a higher oil-absorption rate than other oil-absorbing resins. Figure 8 shows the kinetic analysis curves of the seven synthetic oil-absorbing resins.

CONCLUSIONS

High-oil-absorbent resins were synthesized from the reaction of St, DVB, and EPDM with BPO as an initiator by the suspension polymerization technique. The effects of the reaction conditions, such as solvent amount, molar ratio of DVB to St, EPDM content, initiator concentration, reaction temperature, and reaction time, were studied in the graft crosslinking polymerization. The best reaction conditions were as follows: ratio of St to EPDM = 40/60 w/w, amount of crosslinker DVB = 1.0 wt %, amount of BPO = 1.0 wt %, proportion of gelatin to calcium phosphate = 0.2 g/0.1 g, stirring speed = 500 r/min, and proportion of water to oil = 15 : 1. The highest oil absorptivity of the resin was about 11.5 g/g in diesel, and the oil-absorption saturation time was 3 days under the best processing conditions. The recovery test of the oil-absorbing resins showed that oil absorption through the extraction of ethanol kept the oil absorbency constant.

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