Synthesis and Properties of High Oil-Absorbent *4-tert*-Butylstyrene-EPDM-Divinylbenzene Graft Terpolymer

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ABSTRACT: The graft crosslinking polymerization of 4-*tert*-butylstyrene (tBS) and divinylbenzene (DVB) onto ethylene–propylene–diene (EPDM) was carried out in toluene by using benzoyl peroxide (BPO) as an initiator. The synthesized graft terpolymer, tBS-EPDM-DVB (PBED), was extracted with tetrahydrofuran (THF) into gel (called as PBED I) and sol, and then they were identified by infrared (IR) spectroscopy. The effects of solvent amount, molar ratio of DVB to tBS, EPDM content, initiator concentration, reaction temperature, and reaction time on the graft crosslinking polymerization were examined. Among them, solvent amount and molar ratio of DVB to tBS were the important factors for this reaction system. Maximum oil absorbency of PBED I was 84.0 g/g but its oil-absorption kinetic rate was very low. Sol PBED can be reused as oil absorbent (named as PBED II) through photocrosslinking by ultraviolet light irradiation. Although the oil absorbencies of PBED II were lower than those of PBED I in most cases, their oil absorption kinetic rates were higher than oil absorbencies of PBED I. The highest value of oil absorbency of PBED II was 56.0 g/g. The thermal stability of PBED I was studied by TGA. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 2119–2129, 2002

Key words: graft terpolymer; poly(tBS-EPDM-DVB); oil absorbent; gel polymer; photocrosslink

INTRODUCTION

Various polymers have been widely used to absorb oil spilled on water. Among them, alkyl acrylate and aromatic polymers, which have hydrophobicity and gel-type structure consisting of an elastic network and interstitial space, have been attracting much interest in the field of environment.[1–9] However, the oil absorbencies of them were under 50.0 g/g up to now. As known, ethylene–propylene–diene (EPDM) is an artificial rubber, which has high elasticity and outstanding resistance to degradation by heat, light, oxygen, ozone, and water but poor resistance to oil. The butyl radical of 4-*tert*-butylstyrene (tBS) may have some stereo effect to produce the crosslinked polymer with a large cavity in which oil will fill. From this point of molecular design, a new oil absorbent 4-*tert*-butylstyrene-EPDM-divinylbenzene (PBED) was synthesized to obtain high oil absorbency. Here, divinylbenzene (DVB) is a useful crosslinking agent.

PBED was obtained from the reaction of tBS and DVB onto EPDM in toluene under a nitrogen atmosphere using benzoyl peroxide (BPO) as an initiator. The synthesized PBED was extracted by

Table I   Graft Crosslinking Polymerization Conditions Used in the Study

Condition	Description							
Solvent amount (ml/g)[a]	1.7	3.3	5.0	6.7	8.3	10.0	11.7	13.3
DVB/tBS (mol ratio %)	5.0	7.5	10.0	20.0	30.0			
EPDM (wt %)[b]	20	30	40	50				
Initiator (wt %)[b]	0.5	1.0	2.5	5.0	10.0			
Temperature (°C)	60	70	80	90				
Time (h)	24	48	72	96				

[a] Solvent amount was equal to volume of toluene used in feed over total weights of monomers and EPDM.
[b] The concentration was based on the total weights containing monomers and EPDM.

tetrahydrofuran (THF) and separated into two parts, gel and sol. The structures of crosslinked PBED (called PBED I) and sol PBED were identified by infrared (IR) spectroscopy. The effects of synthesis conditions such as solvent amount, molar ratio of DVB to tBS, EPDM content, initiator concentration, reaction temperature, and reaction time were studied in the graft crosslinking polymerization. Sol PBED can be reused as oil absorbent (named PBED II). Sol PBED films were cast from THF solution under air stream at room temperature and then photocrosslinked by using ultraviolet (UV) light irradiation. The oil absorbency of PBED I or of PBED II was evaluated by the ASTM method F726-81.[10] Thermal properties of the PBED I were determined by TGA.

EXPERIMENTAL

Materials

tBS (Aldrich Chemicals) and DVB (Fluka) were purified by standard procedures, as follows: (1) washing DVB or tBS with 10 wt % NaOH aqueous solution three times to remove the inhibitor; (2) neutralizing them with distilled water; (3) drying them used with magnesium sulfate anhydrous; (4) filtering to discard the magnesium sulfate and the filtrate is the purified DVB or tBS.

BPO (Aldrich) was recrystallized from methanol. EPDM, having ethylidene norborene as a termonomer (ethylene-to-propylene ratio of 50/50 by mol %, ML50; 50,500 M_n; 102,000 M_w), was used as received from Aldrich. Ethyl acetate, THF, toluene, dioxane, and n-hexane were distilled prior to use.

Synthesis of PBED

A given weight of EPDM was dissolved in a certain volume of toluene in a flask equipped with a modified Hopkins cooler, thermometer, and nitrogen gas inlet. A mixture of tBS and DVB at a given mole ratio was mixed in toluene and the solution was introduced into EPDM solution with a required amount BPO based on total weights containing monomers and EPDM. The reactions were carried out under various experimental conditions, as shown in Table I.

The obtained product was precipitated in excess methanol with stirring. The precipitate was collected by filtration and then dried in a vacuum oven until a constant weight was reached. The product was further extracted by THF in a Soxhlet extractor for 1 day with a coarse-grade thimble. The sol-free materials were gels including gel PBED, gel poly(tBS-*co*-DVB), and gel PDVB, but for infinite network polymer, only gel PBED (or PBED I) existed. The sol PBED was isolated from soluble mixtures of several homopolymers, copolymers, and nongrafted EPDM, such as poly(*tert*-butylstyrene) (PtBS), poly(divinylbenzene) (PDVB), poly(tBS-*co*-DVB), poly-(EPDM-*g*-tBS), and poly(EPDM-*g*-DVB), by using ethyl acetate, dioxane-to-*n*-hexane (50/50% by volume) cosolvent and ethyl acetate-to-toluene (25/75% by volume)-mixed solvent. Figure 1 shows the scheme of isolation procedure. The total conversion, grafting ratio, and grafting efficiency of graft crosslinking polymerization were estimated by using the following equations[11]:

Total conversion (%)

$$= \frac{\text{Total weight of polymer formed}}{\text{Weight of monomers and EPDM}} \times 100 \quad (1)$$

where polymers formed in the numerator were the all synthesized polymers, including PBED, homopolymers, copolymers, and grafted polymers. Monomers and EPDM in the denominator are monomer tBS, DVB, and EPDM in feed,
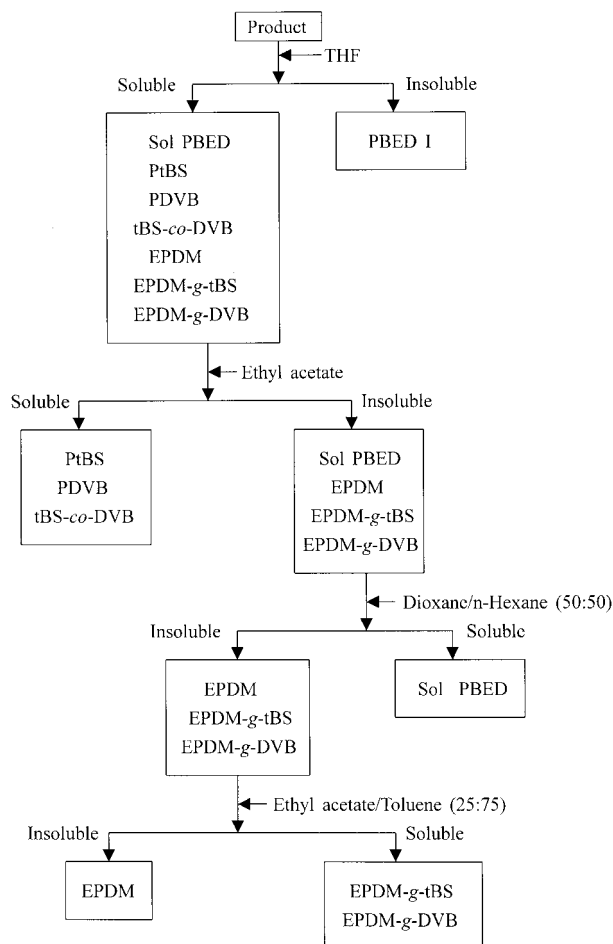
Figure 1 Block diagram of isolation procedure for PBED.

Grafting ratio (%)

$$= \frac{\text{Weight of grafted monomer}}{\text{Weight of nongrafted polymer}} \times 100 \quad (2)$$

where grafted monomer indicated PBED, EPDM-*g*-tBS, and EPDM-*g*-DVB, nongrafted polymer included PtBS, PDVB, tBS-*co*-DVB, and unreacted EPDM;

Grafting efficiency (%)

$$= \frac{\text{Weight of grafted monomer}}{\text{Total weight of polymer formed}} \times 100 \quad (3)$$

Gel fraction (%)

$$= \frac{\text{Weight of dried gel after extraction}}{\text{Weight of polymer before extraction}} \times 100 \quad (4)$$

Photocrosslink of Sol PBED

The sol PBED isolated from the above procedure can be reused as oil absorbent by the photocrosslinking process. The sol PBED films ($3 \times 3 \times 0.3$ cm) were cast from THF solution under air stream at room temperature. The prepared films were photocrosslinked with UV light irradiation (400 W high-pressure mercury lamp: WAKO H-400 A/B, Tokyo, Japan). After irradiation, the films were immersed in THF for a fixed time to remove the residue sol material and then dried in a vacuum oven until a constant weight. The photocrosslinked materials were named PBED II below and the gel fractions were also calculated from eq. 4.

Measurements

Infrared Spectroscopy

The infrared spectroscopy of graft terpolymer was recorded on a Perkin–Elmer 1330 spectrometer.

Thermogravimetric Analysis (TGA)

Thermal stability was examined by a Schimadzu DT 30A TGA instrument at a scanning rate 15°C/min in nitrogen.

Oil-Absorption Test

Oil absorbency of crosslinked polymers PBED I and PBED II were determined by ASTM F726-81; 0.1 g polymer was put in a stainless steel mesh ($4 \times 4 \times 2$ cm) which had been immersed in oil solution (crude oil diluted with toluene, 10 wt % oil) 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 following formula:

Oil absorbency (g/g)

$$= \frac{\text{Weight of absorbed oil in sample}}{\text{Weight of sample before oil absorption}} \quad (5)$$

To study the kinetics of oil absorption, the above measurements repeated from time to time. By way of determination of the maximum oil absorbency, the tests were allowed to stand for 7 days for PBED I and 24 h for PBED II.
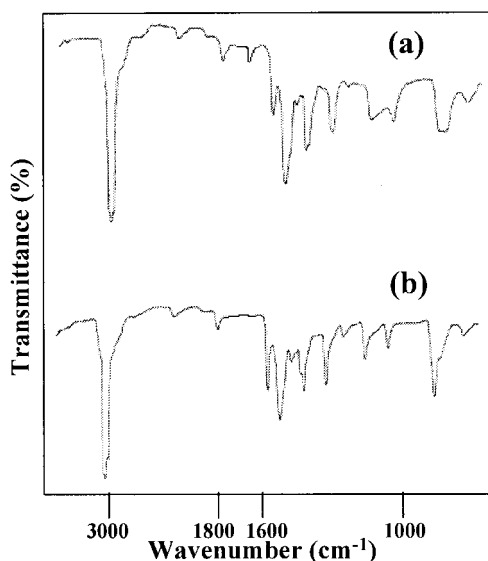
Figure 2 IR spectra of PBED. (a) Sol PBED; (b) crosslinked PBED.

## RESULTS AND DISCUSSION

Characterization

The structure of the synthesized graft polymer PBED was indicated by IR spectra, as shown in Figure 2. The characteristic absorption bands of PBED appeared at 3010 cm^{-1} (stretching vibration of aromatic C—H bond), 2900 cm^{-1} (stretching vibration of aliphatic C—H bond), 1465 cm^{-1} (CH$_2$; scissoring), 1380 cm^{-1} (CH$_3$; bending), 1167 cm^{-1} (propylene methyl groups), and 900–790 cm^{-1} (aromatic = C—H bond; out-of-plane vibration), respectively. The vinyl stretching vibration peak at 1620 cm^{-1} still remained in the sol PBED shown in Figure 2(a), but it was imperceptible in the crosslinked PBED, as given in Figure 2(b).

Effect of Reaction Conditions on Graft Crosslinking Polymerization

Effect of Solvent Amount

The effects of solvent amount on graft crosslinking polymerization are shown in Figure 3. The results were carried out in 0.075 mol ratio of DVB to tBS with 30 wt % EPDM and BPO 2.5 wt % at 70°C for 48 h. As Figure 3 shows, the conversion, the grafting efficiency, and gel fraction decreased and leveled off at 10 mL/g with an increase in solvent amount. The gel fraction had a large slope between 5 and 10 mL/g. These results can been explained by the concentration of polymeric solution.[12,13] Toluene is a good solvent for the polymerization system; 10 mL/g may be a critical value at which polymeric solution becomes so dilute that the hydrodynamic volumes of EPDM macromolecules keep them to a certain distance and some segments of the long chain will curl like coil.[12–14] Monomers, tBS, and DVB, however, can move to them and further polymerize or crosslink with them. In this case, it is easy to form intramo-
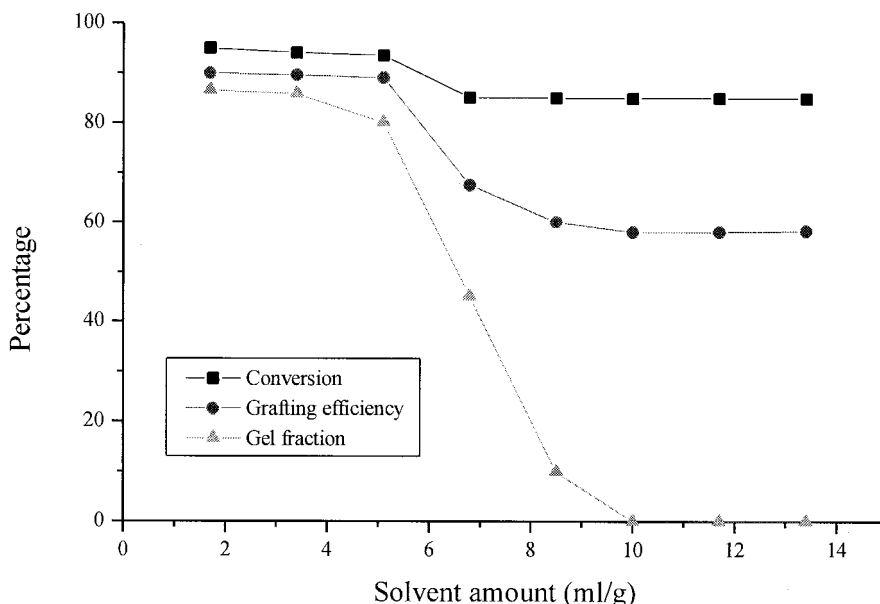
Figure 3 Effect of solvent amount on graft crosslinking polymerization.

Table II   Effect of Molar Ratio of DVB to tBS on Conversion, Grafting Ratio, Grafting Efficiency, and Gel Fraction of Synthesized Polymer

[DVB]/[tBS] in Feed	Total Conversion (%)	Grafting Ratio (%)	Grafting Efficiency (%)	Gel Fraction (%)
0.050	89	196	82	69
0.075	91	216	85	79
0.100	93	283	90	89
0.200	95	309	94	91
0.300	98	327	96	95

lecular crosslinking or intramolecular cyclization. As a result, microgels may be produced that can pass through the thimble during THF extraction, so that the gel fraction remains zero. When solvent amount decreases, the polymeric solution is concentrated and becomes very thick, in which the EPDM macromolecules can touch each other or entangle together. Monomers diffuse and react among these macromolecules. There is more possibility to form intermolecular crosslinking with prepolymer.[14–16] For this graft crosslinking polymerization system, 5 mL/g may be another critical point at which the polymeric solution reaches gelation threshold. The region between 5 and 10 mL/g, however, seems unstable for the gelation process. In this work, 5 mL/g was used to be sure crosslinked PBED was obtained.

Effect of Molar Ratio

Table II shows the mole ratio effect of DVB to tBS on the graft crosslinking polymerization. The reactions were performed in EPDM 30 wt % and BPO 2.5 wt % at 70°C for 48 h. As Table II shows, the total conversion, the grafting ratio, the grafting efficiency, and the gel fraction increased monotonously with an increase in the mole ratio of DVB to tBS in feed. As DVB has two double bonds, the more DVB contents easily make graft polymerization and chemical crosslinking.[17] It is known that the lower the degree of crosslinkage, the more the gel swells,[18] so that all experiments followed adopted a low mole ratio of DVB to tBS.

Effect of EPDM Content

The effect of EPDM content on the graft crosslinking polymerization is shown in Table III. The conversion, the grafting efficiency, and the gel fraction increased with increasing EPDM content. These results are probably caused by the increasing diene contents of graft or crosslinking

sites in EPDM as EPDM contents increase. A slight Trommsdorff effect was observed due to the systematic variation of viscosity (when EPDM was dissolved in toluene with stirring). On the other hand, it seems that the lower the concentration of EPDM, the fewer active centers,[19,20] and thus, the higher degree of homopolymerization of PtBS and copolymerization poly(tBS-*co*-DVB) are produced. Moreover, it may form microgels at very low EPDM content (below EPDM 20 wt %) so the gel fraction is zero. For convenience, however, the EPDM content was fixed at 30 wt % to investigate.

Effect of Initiator Concentration

Table III also shows the effect of initiator concentration on the graft crosslinking polymerization. The grafting efficiency and the gel fraction increased with increasing initiator concentration up to 2.5 wt % but thereafter decreased with further increasing initiator concentration. The decrease in the grafting efficiency at higher initiator concentration is expected because the homopolymer is formed more readily than the graft terpolymer as initiator concentration increases. Maybe more initiators will give more active centers and monomers can move easily and have more chances to be initiated to form homopolymer. A similar observation was made in Voek's[21] and in Cho et al.'s[22] work. The conversion, however, increased monotonously with increasing initiator concentration. The reason is as already mentioned. As Table III shows, the gel fractions were zero when initiator concentration was below 2.5 wt %; it may prefer to form intramolecular crosslinking or intramolecular cyclization at lower active centers system.

Effect of Reaction Temperature

The effect of reaction temperature on the graft crosslinking polymerization is shown in Table III

Table III Effects of EPDM Content, Initiator Concentration, Reaction Temperature, and Reaction Time on Graft Crosslinking Polymerization and on Maximum Oil Absorbency

Changing Condition	Conversion (%)	Grafting Efficiency (%)	Gel Fraction of PBED I (%)	PBED I—Maximum Oil Absorbency (g/g)	PBED II[a]—Maximum Oil Absorbency (g/g)
EPDM (wt %)					
20	85	44	0	—	35.0
30	89	82	69	84.0	32.0
40	92	85	81	73.0	29.0
50	96	90	82	71.0	27.0
Initiator (wt %)					
0.5	76	54	0	—	28.0
1.0	86	58	0	—	30.0
2.5	89	82	69	84.0	32.0
5.0	97	73	66	39.0	41.0
10.0	99	65	64	29.0	43.0
Temperature (°C)					
60	79	58	0	—	56.0
70	89	82	69	84.0	32.0
80	91	73	56	66.0	29.0
90	92	53	42	38.0	23.0
Reaction Time (h)					
24	86	60	0	—	51.0
48	89	82	69	84.0	38.0
72	98	79	69	45.0	32.0
96	99	77	69	36.0	31.0

Besides changed condition, the others were fixed at [DVB]/[tBS]: 0.05; solvent amount: 5 ml/g; EPDM content: 30 wt %; BPO concentration: 2.5 wt %; reaction temperature: 70°C; reaction time: 48 h.

[a] PBED II was obtained from sol PBED photocrosslinked by 48-h UV irradiation and their gel fractions were not listed here.

also. The reactions were carried out at 60, 70, 80, and 90°C, respectively. On increasing temperature, the grafting efficiency and the gel fraction passed through maximums at 70°C. The grafting efficiency depends on the number of active sites available. The increase in temperature is expected to increase the rate of grafting. With increase in temperature, however, the rate of homopolymerization or copolymerization also increases[22,23]; as a result, the grafting efficiency increases initially but on further increase in temperature grafting efficiency decreases. The reason for gel fraction is the same as above, but the value remains zero at very low reaction temperature because of microgel formation. The conversion, however, increased with increasing temperature. It may be related to the decomposition rate of BPO as the function of temperature.[24,25]

Effect of Reaction Time

Table III also shows the effect of reaction time on graft crosslinking polymerization. The polymerization was carried out in toluene for 24, 48, 72 and 96 h, respectively. As reaction time increased, the conversion increased monotonously. The grafting efficiency, however, passed through maximum at 48 h with increasing reaction time. The explanation for the decrease in grafting efficiency may be caused by the formation of homopolymers and copolymers as well as the increase in viscosity of the reaction mass along the reaction path.[23,26,27] The gel fraction increased with reaction time up to 48 h and then leveled off. It is explained that the system may prefer to graft polymerize or to form microgels at the beginning of the reaction so that the gel fraction is zero at 24 h. However, the gel fraction remains constant after 48 h because of the formation of homopolymers and copolymers.

Thermal Stability

At a given molar ratio of DVB to tBS, PBED I decomposition temperature and its weight residue at 500°C were listed in Table IV. The samples

Table IV   Decomposition Temperature and Weight Residue at 500°C of PBED I at Given Molar Ratio of DVB to tBS

Sample	Decomposition Temperature (°C)	Weight Residue at 500°C (%)
[DVB]/[tBS] (mol ratio)		
0.050	439.5	8.49
0.075	441.0	8.68
0.100	441.8	10.12
0.200	453.5	15.84
0.300	460.9	33.02

Heating rate = 15°C/min in nitrogen.

were obtained from reaction conditions as listed in Table II. It was observed that the decomposition temperature and weight residue of PBED I increased in the order of molar ratio 0.050 < 0.075 < 0.100 < 0.200 < 0.300. This means that PBED I with higher DVB content show higher thermal stability. This result may be from more crosslinks produced in the polymer at high level of DVB content.

Effect of Irradiation Time on Photocrosslink of PBED II

The effect of UV irradiation time on the gel fraction of PBED II at given molar ratios of DVB to tBS or given EPDM contents were shown in Table V. The gel fraction increased with increasing UV irradiation time. At the same irradiation time, the gel fraction increased monotonously with increasing molar ratio of DVB to tBS or increasing EPDM content. The reason is as mentioned above.
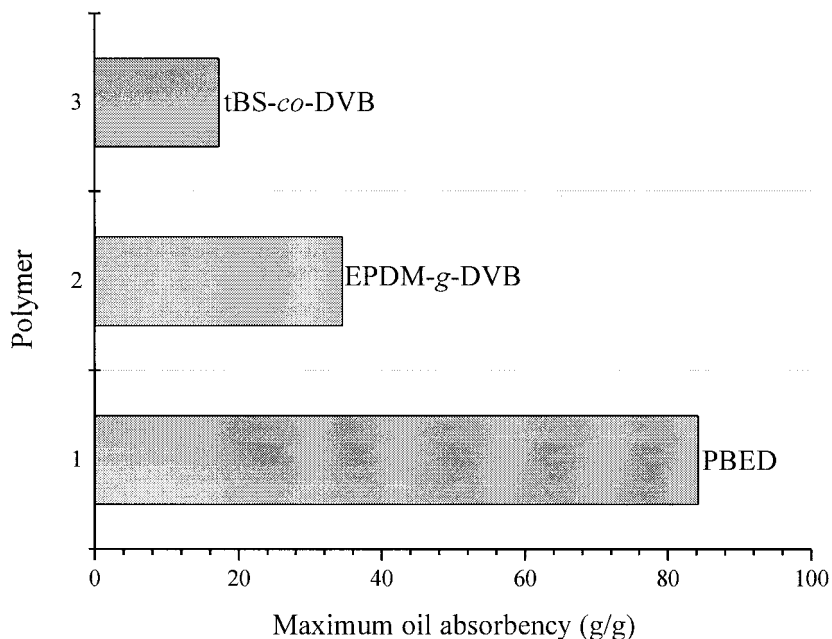
Oil Absorbencies

Comparison of Crosslinked Polymers

Figure 4 shows the maximum oil absorbency of three relative crosslinked polymers. They were produced from solution polymerization in toluene, respectively, and kept other reaction conditions as similar as possible. Their gel fractions were about 70%. Poly(tBS-co-DVB), which had 16.0 g/g maximum oil absorbency, was the lowest value among the three polymers. The next one was graft polymer EPDM-g-DVB; its oil absorbency was 30.0 g/g. The highest maximum oil absorbency was PBED, 84.0 g/g. PBED may have suitable

Table V   Effect of UV Irradiation Time on Gel Fraction and the Maximum Oil Absorbency of PBED II at Given Mole Ratio of DVB to tBS or Given EPDM Content

	Gel Fraction (%)				Maximum Oil Absorbency (g/g)			
	UV Irradiation Time (h)				UV Irradiation Time (h)			
Gel PBED II	24	48	72	96	24	48	72	96
[DVB]/[tBS] (mol ratio)								
0.050	60	75	87	92	35.0 (23.0)[a]	29.0 (20.0)	28.0 (17.0)	22.0 (15.0)
0.075	61	86	88	93	28.0 (22.0)	21.0 (19.0)	16.0 (12.0)	13.0 (10.0)
0.100	64	88	89	95	24.0 (21.0)	19.0 (17.0)	13.0 (10.0)	11.0 (9.0)
0.200	73	89	92	97	21.0 (18.0)	16.0 (13.0)	11.0 (9.0)	9.0 (8.0)
0.300	80	93	94	99	19.0 (16.0)	14.0 (11.0)	10.0 (8.0)	8.0 (7.0)
EPDM content (wt %)								
20	25	44	69	80	39.0 (28.0)	35.0 (25.0)	31.0 (22.0)	23.0 (19.0)
30	60	74	85	91	35.0 (23.0)	29.0 (20.0)	28.0 (18.0)	22.0 (17.0)
40	64	76	87	96	30.0 (19.0)	27.0 (18.0)	24.0 (17.0)	19.0 (14.0)
50	69	78	89	97	26.0 (17.0)	25.0 (15.0)	25.0 (16.0)	18.0 (11.0)

[a]The data in parentheses were measured from the samples immersed in oil solution just 10 min.

Figure 4 Comparison maximum oil absorbencies among three crosslinked polymers. To reach the maximum oil absorbency, it took 24 h immersed in oil for tBS-*co*-DVB, 48 h for EPDN-*g*-DVB, and 96 h for PBED.

molecular structure, such as elasticity and stereo space, into which a large quantity of oil can enter.
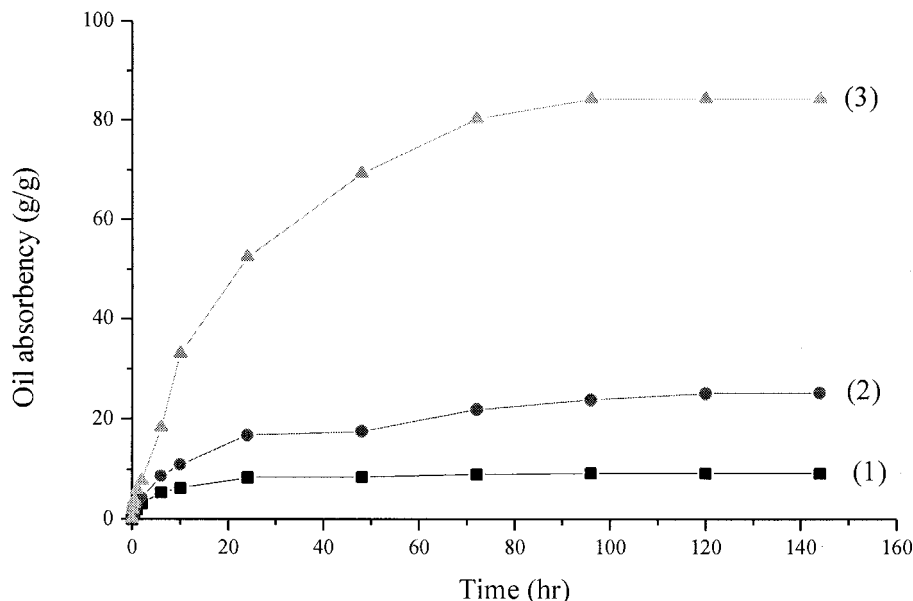
Oil Absorbencies of PBED I

Oil absorbencies of PBED I as a function of oil immersing time are shown in Figure 5. The PBED

I gels were produced from toluene (solvent amount 5 mL/g) with given mole ratio of DVB to tBS, EPDM 30 wt %, and BPO 2.5 wt % at 70°C for 48 h. As Figure 5 shows, all curves increased with increasing immersing time and leveled off at 96 h. The lower the DVB content, the higher the
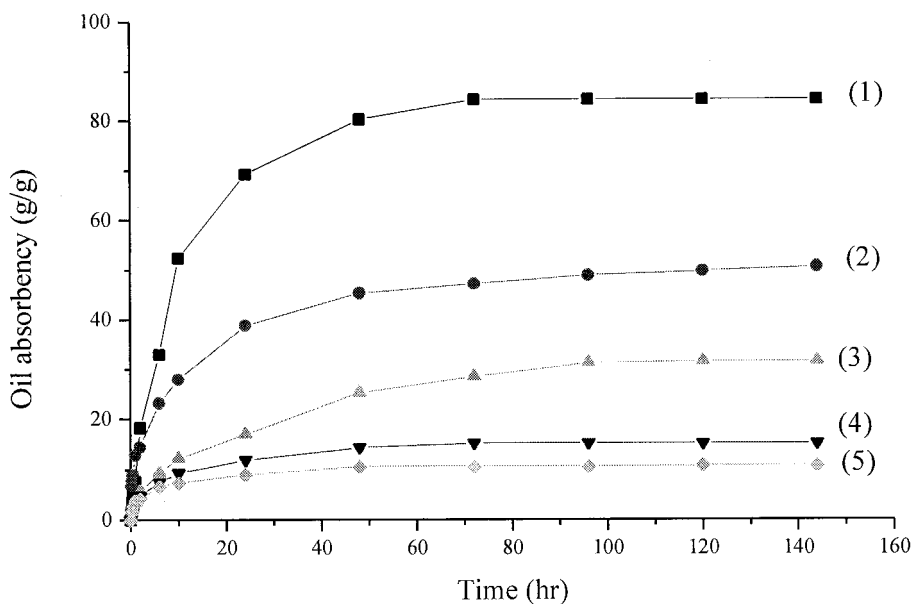
Figure 5 Oil absorbency of PBED I as a function of time (solvent amount: 5 mL/g). Mole ratio of DVB to tBS in feed: (1) 0.050; (2) 0.075; (3) 0.100; (4) 0.200; (5) 0.300.

Figure 6 Oil absorbency of PBED I at given solvent amount as a function of time ([DVB]/[tBS]: 0.050; EPDM: 30 wt %; BPO: 2.5 wt %; temperature: 70°C; time: 48 h). Solvent amount: (1) 1.67 mL/g; (2) 3.33 mL/g; (3) 5.00 mL/g.

oil absorbency is. The highest oil absorbency was 84.0 g/g at 0.050 mol ratio of DVB to tBS after 96 h immersion in oil solution. This behavior can be accounted for that the lower the degree of crosslinkage, the more the gel swells.[18] However, the oil absorption rate was low.

The effect of the solvent amount on oil absorbency of gel is shown in Figure 6. As it shows, the oil absorbencies of gels increased with increasing solvent amount. This may be explained by the fact that the gel obtained from a high quantity of solvent has many large volume cavities, which filled with a lot of solvent during polymerization and crosslinking. After drying, the cavities were still kept in the xerogel, but just shrinkage. They will swell as large as before when they meet suitable solvent.

The effects of other reaction conditions on maximum oil absorbencies of gels were listed in Table III. Except for reaction temperature, the maximum oil absorbencies decreased with increasing EPDM content, or with increasing initiator concentration, or with increasing reaction time. This may be caused by more crosslinkage and small cavities produced from more EPDM, or more initiator, or long reaction time.

Oil Absorbencies of PBED II

Figure 7 shows oil absorbencies of PBED II versus immersing time. The PBED II was obtained from sol PBED, which was produced from given molar ratios of DVB to tBS, solvent amount 5 mL/g, EPDM 30 wt %, and BPO 2.5 wt % at 70°C for 48 h and then photocrosslinked by UV irradiation 12 h. The oil absorbencies of PBED II increased with increasing immersion time and reached a plateau after 12 h immersion in oil. The lower the DVB content, the higher the oil absorbency is. The reason is as described before. It is noteworthy that the oil absorption rates in Figure 7 are larger than those in Figure 5, although the oil absorbencies are lower than theirs in some cases. This phenomenon can be explained by the fact that PBED II sheets seem to produce many cavities *in situ* during photocrosslinking but their volume is small because no solvent was wrapped in it while crosslinking. Maybe the oil absorption rate is determined with the number of pores, but the oil absorbency is dependent not only on the number of the pores but on the size of the cavities as well.

The effect of UV irradiation time on maximum oil absorbency of PBED II at a given mole ratio of DVB to tBS or given EPDM content is shown in Table V. As prolonging irradiation time, maximum oil absorbency decreased at constant DVB concentration or at the same EPDM content. Compared with gel fraction in the same table, it was clear that the higher degree of crosslinkage, the lower oil absorbency. The data in parentheses were measured from the sample immersed in oil
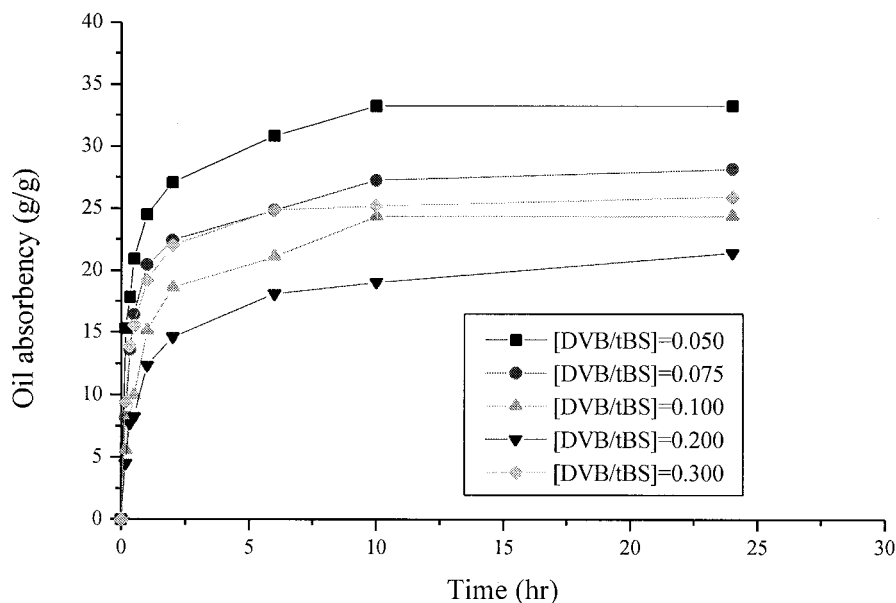
Figure 7   Oil absorbency of PBED II given mole ratio of DVB to tBS and crosslinked by 12 h UV irradiation as a function of time.

only 10 min. It was obvious that over 60% of maximum value had been reached in 10 min. This oil absorption kinetic rate is high enough to suit for commercial application.

Maximum oil absorbencies of PBED II, their sol materials produced from other reaction conditions and then photocrosslinked with 48 h UV irradiation, were listed in Table III. The highest maximum oil absorbency of PBED II was 56.0 g/g at graft polymerization temperature of 60°C. The regularity of maximum oil absorbency of PBED II from various reaction conditions had been found clearly, but their values were lower than those of PBED I in general. It seems that oil absorption is a complex physical process. A lot of factors will impact on oil absorbency. Among them, pore number, cavity size, and its distribution may be very important.

CONCLUSION

High oil-absorbent PBED graft terpolymer was synthesized from reaction of tBS and DVB onto EPDM by using BPO as an initiator by solution polymerization technique. The effects of reaction conditions, such as solvent amount, mole ratio of DVB to tBS, EPDM content, initiator concentration, reaction temperature, and reaction time, were studied in the graft crosslinking polymeriza-

tion. The oil absorption tests of various crosslinked polymers were investigated. The important results were summarized as follows.

1. The solvent amount and the molar ratio of DVB to tBS were the important factors influencing the results of graft crosslinking polymerization.
2. The thermal decomposition temperature of PBED I increased with increasing DVB concentration.
3. Comparison the maximum oil absorbencies, the values of PBED I were higher than those of PBED II in general, but their oil absorption kinetic rates were always lower than those. The highest oil absorbency was 84.0 g/g for PBED I, which obtained from the solvent amount of 5 mL/g with 0.05 mol ratio of DVB to tBS, EPDM 30 wt %, and BPO 2.5 wt % at 70°C for 48 h. The highest oil absorbency was 56.0 g/g for PBED II photocrosslinked with 48 h UV irradiation of sol PBED, which were produced from the same reaction conditions as above except for temperature of 60°C.
4. The oil absorbency of PBED II, only immersed in oil 10 min, had reached over 60% of its maximum value. This rate is large enough to agree with commercial usage.
5. Among three relative crosslinked polymers,

poly(tBS-*co*-DVB), EPDM-*g*-DVB, and PBED, PBED has the highest oil absorbency because of its suitable molecular structure.

6. Xerogels PBED, either PBED I or PBED II, are white plastics and their relative densities are about 0.89, which is smaller than water's density so that it will float on the surface of water and can absorb oil spilled on water readily.

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