Oil-Absorption Function of Physical Crosslinking in the High-Oil-Absorption Resins

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ABSTRACT: The concept of physical crosslinking was introduced into the research field of oil-absorption resins, which were traditionally synthesized only by chemical crosslinking. Specifically, the partially physical crosslinking acrylic series for high-oil-absorption resins were prepared in the suspension process, and the swelling behavior of the samples was observed and recorded online. This demonstrated that a kind of relaxing three-dimensional network was indeed formed by the introduction of polybutadiene (PB). The effects of monomer feed ratios, crosslinking agent concentration and type, particle size, and temperature on the oil absorbency and oil-absorption speed were investigated. The results indicated that there were an optimum monomer feed ratio and an optimum amount of ethylene glycol dimethacrylate or PB. In addition, the particle size and temperature had a serious influence on the oil-absorption speed in comparison with the monomer feed ratio and the crosslinking agent concentration and type. The results also showed that particle size affected oil absorbency to a great degree and that the effect of temperature on oil absorbency was complex. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3945–3950, 2003

Key words: resins; crosslinking

INTRODUCTION

The pollution caused by oil spills has been noted for its tremendous and lasting harm, and various methods[1] for the treatment of spilled oil have been tried. Recently, trials of spilled oil treatments have focused on oil absorbents. A kind of absorbent whose basic material is a highly oil-swelling polymer with a gel structure, has attracted the interest of many researchers and has provided promise for an efficient solution to the oil pollution problem. However, the disadvantages of a low oil absorbency and the irreversibility of oil-releasing have impeded its development.

Hence, an approach was attempted to resolve these disadvantages and improve its properties. According to Flory's swelling theory,[2] oil absorption behavior is a process in which an oil molecule penetrates into a network continually and expands it to cause swelling. This swelling behavior is mainly affected by two opposite factors: resin–oil affinity and the forbidding force of the three-dimensional network. It is known that alkyl acrylate monomers with a long-chain alkyl group have a good affinity to oil and nonpolar solvents, and various long-chain alkyl acrylates have been discussed by many research groups.[3] Therefore,

we do not discuss resin–oil affinity here any more, and we used dodecanol methacrylate (DMA) or octanol methacrylate (OMA) as one of our comonomers. In this study, we examined mainly the structure of the resin and hoped to form a kind of network with a lower forbidding force for oil absorption.

As is well known, the structure of a resin is a three-dimensional network that is traditionally formed through chemical crosslinking. Because of covalent bonds the resin is crosslinked so tight that it is radically impossible to form a kind of relaxing structure with a low barrier for oil penetration. To improve this condition, we introduced a concept, physical crosslinking, into the research field of oil-absorption resins.

Physical crosslinking, according to Irzhak,[4] is mainly with nodes of topological features. By these topological nodes, an entanglement structure is formed. Compared with the structure formed by chemical crosslinking, this entanglement structure is easy to move. Ross-Murphy[5] pointed out that chemical crosslinking has junction points and that physical crosslinking has junction zones. Junction points are formed by the interaction of covalent bonds with a strong force forbidding the extension of the network. On the contrary, junction zones are not points on chains but involve more extended zones or even particular structures. In many cases, the nature of the junction zones is not known unambiguously. However, one may be sure that the interaction of physical crosslinking is much weaker than that of chemical

TABLE I
Materials and Reagents

Material	Function	Source
St	Monomer	Purification by distillation under reduced pressure
OMA	Monomer	Synthesized by direct esterification
DMA	Monomer	Synthesized by direct esterification
EGDMA	Chemical crosslinking agent	Purification by distillation under reduced pressure
PB	Physical crosslinking agent	Beijing Yanhua Co.
Benzoyl peroxide	Initiator	Purification by recrystallization
Hydroxypropyl methylcellulose (chemical pure)	Dispersant	Japan Chemosynthesis
Vinyl trichloride (chemical pure)	Testing agent	Shanghai Chemical Factory

crosslinking. Hence, we considered the use of weak physical crosslinking to loosen the network which was crosslinked tightly by chemical crosslinking, and to improve its oil absorbency and reversible oil-releasing ability.

Strictly speaking, physical and chemical crosslinking coexist in gelation and cannot be classified accurately. Krakovsky et al.[6] studying the elastic and swelling behavior of crosslinked copolymers of 2-hydroxyethyl methacrylate, diethylene glycol methacrylate, and methacrylic acid, found that the concentrations of the elastic network chains determined from the Young's modulus of swollen networks were higher than those calculated from stoichiometry. They attributed this effect to the presence of additional physical crosslinks along with the chemical crosslinks. So, physical crosslinking exists in the traditional gelation synthesized by a chemical crosslinking agent, but its quantity is very small.

Therefore, we introduced polybutadiene (PB) which is a physical crosslinking agent relative to a traditional chemical crosslinking agent, into the high-oil-absorption-resin molecular chain to increase the quantity of its physical crosslinking. In addition, we hoped to form a kind of relaxing three-dimensional network that would be easily swollen and to produce more space to absorb oil and increase oil absorbency.

This article presents the studies on the oil-absorption properties of crosslinked styrene(st)—acrylate copolymers for oil-absorbency application. The oil absorption process was recorded online, and the effects of copolymer composition, crosslinking agent concentration and type, particle size, and temperature on the oil absorbency and absorption speed were also investigated.

EXPERIMENTAL

Polymerization was carried out in a suspension process with a free-radical mechanism. All of the materials used in experiment are given in Table I. A mixture of monomers, initiator, crosslinking agent, dispersant, and water at a given molar ratio was introduced into

a 500-mL reactor and was then polymerized at 80°C for 8 h. The copolymer was obtained as beads. After the polymerization, the beads were decanted, washed with distilled water, and dried in a vacuum oven for 2 days at 50°C.

The swelling behavior of the samples was observed and recorded by an online microscope and computer. To easily evaluate the swelling behavior of the samples, we used vinyl trichloride with a proper boiling point as the testing agent. The oil absorbency (W) and oil absorption speed (v) were calculated according to the following equations:

$$W(g/g) = \frac{(r_1^3 - r_0^3)}{r_0^3} \frac{\rho_2}{\rho_1}$$

$$v(mm^3/s) = \frac{4\pi(r_1^3 - r_0^3)}{3t}$$

where r_0 and r_1 are the prime radius and the first equilibrium radius of a particle, respectively; ρ_2 and ρ_1 are the densities of the testing agent (1.4–1.47 g/cm^3) and the sample (0.9–0.95 g/cm^3, measured by density method), respectively; and t is the oil absorption time.

The gel fraction was measured by an extraction method. A weighed quantity of dried sample was put into a weighed filter paper bag, and the bag was put into a Soxhlet's extractor whose bottom was a distillation flask with tetrahydrofuran solvent in a water bath at about 70°C. The sample was washed with tetrahydrofuran for 24 h, and then, the filter paper bag was weighed after drying in a vacuum oven for 2 days at 50°C. The gel fraction (G) was calculated according to the following equation:

$$G = \frac{G_a}{G_b} \times 100\%$$

where G_a and G_b are the weights of the resin after and before suction, respectively.
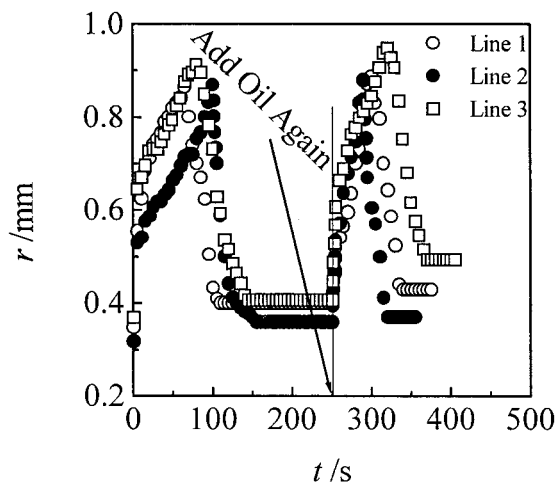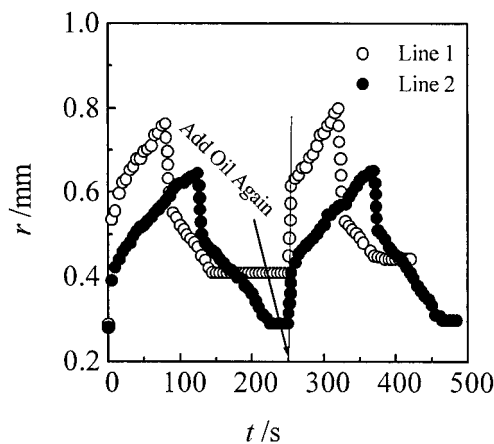
Figure 1 Variation of the radius of the particle with time (St/DMA = 3 : 1 and T = 293 K). (○) EGDMA = 0.375% and PB = 2.5%, (●) EGDMA = 0.625% and PB = 6%, and (□) EGDMA = 0.625% and PB = 14.58%.

RESULTS AND DISCUSSION

Effect of PB

We observed online the swelling behavior of the St–DMA copolymer gel particles with partial physical crosslinking, and the results are given in Figure 1. Line 3 in the illustration is used to explain the process. At $t = 0$, the prime radius of the particle was 0.3691 mm. As soon as vinyl trichloride was added, the particle began to swell. After about 80 s, the polymer network achieved swelling equilibrium, and the first equilibrium radius of the particle was 0.9124 mm. Because of the release of the network and the vaporability of vinyl trichloride, the particle retracted to 0.4082 mm. It was named the first release radius, which was larger than the prime radius of 0.3691 mm. When we added vinyl trichloride to the particle again, a new swelling equilibrium was obtained, and a larger radius of the particle, a second equilibrium of 0.9484 mm was obtained. At last, after retraction, the second release radius of the particle was 0.4948 mm, which was not only larger than 0.3691 mm, the prime radius, but was also larger than 0.4082 mm, the first release radius.

From these phenomena of the swelling process, we concluded that the particles indeed had a kind of relaxing three-dimensional network. However, was it the result of the introduction of PB or not? When we compared the swelling process of the partially physical crosslinking particle with the totally chemical crosslinking particle, we obtained the conclusion. As shown in Figure 2, line 2, without PB, after swelling, the second equilibrium radius was no larger than the first equilibrium radius. After retraction, the first and second release radii were no larger than the prime radius either. This difference between the totally chemical crosslinking particle and the partially phys-


Figure 2 Variation of the radius of the particle with time (St/DMA = 3 : 1 and T = 293 K). (○) EGDMA = 0.625% and PB = 0.42% and (●) EGDMA = 1.04%.

ical crosslinking particle demonstrated that the introduction of PB indeed resulted in the formation of a kind of relaxing three-dimensional network.

Effect of St concentration

The effect of St concentration on oil absorbency is depicted in Figure 3. The monomer feed ratios (weight percentage of St/weight percentage of DMA or OMA) were 33.3 : 66.7, 50 : 50, 60 : 40, 66.7 : 33.3, 75 : 25, 86.7 : 13.3, and 100:0. Compared with DMA or OMA, the hydrophobicity of St was smaller. It seems that when there was a larger amount of DMA or OMA, the oil absorbency of the particle was higher. However, this was not the case, as shown in Figure 3. There was an optimum monomer feed ratio of about 75 : 25 in this
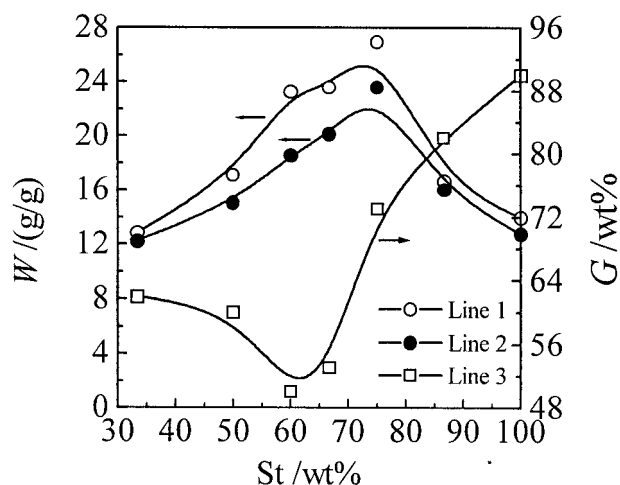
Figure 3 Variation of the oil absorbency and gel fraction with the percentage of St (T = 293 K, r_0 = 0.25 mm, EGDMA = 0.3%, and PB = 2%). (○) and (□) St/DMA, and (●) St/OMA.

system because the three-dimensional network structure had an important influence on the oil-absorption process, as mentioned before, along with the hydrophobicity of the monomers. Also, the existence of St contributed to the formation of a kind of structure that both had a rigid backbone and was easily extended. In fact, it was similar to the introduction of PB into the copolymer particle, which was crosslinked tightly by chemical crosslinks.

Line 3 of Figure 3, indicating the variation of gel fraction with different monomer feed ratios, shows that an optimum gel fraction was a critical condition for high oil absorbency.

Table II gives the oil-absorption speed of particles that were prepared with different monomer feed ratios, with all other variables constant. The value varied from 5 mm^3/s to 20 mm^3/s. Relative to the value, several hundred, obtained by the effects of the radius of the particle or the temperature of oil absorption, which is mentioned later, it was relatively small. Therefore, we think that the influence of the monomer feed ratio on the oil-absorption rate was rather small.

Effect of the concentration of the chemical crosslinking agent

To investigate the effect of the chemical crosslinking agent concentration on the oil absorbency, we prepared various copolymers with different ethylene gylcol dimethacrylate (EGDMA) contents (from 0.3 to 2.29% of the total monomer weight), with all other variables constant. Figure 4 illustrates the relationship
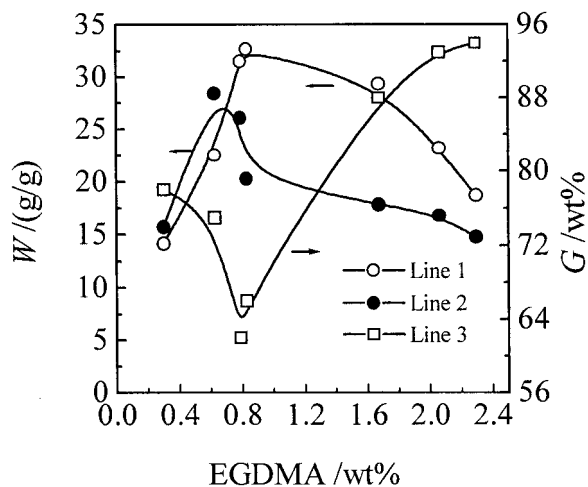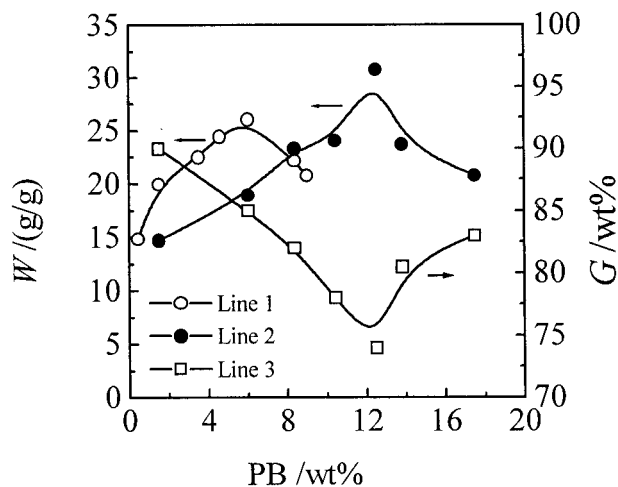

Figure 4 Variation of the oil absorbency and gel fraction with the content of the chemical crosslinking agent (T = 293 K, r_0 = 0.2 mm, and St/DMA = 3 : 1). (○) and (□) PB = 12.5%, and (●) PB = 8.33%.

between oil absorbency and the amount of EGDMA at a certain amount of PB. As shown in Figure 4, there was a maximum point. When the amount of EGDMA was smaller than that at the maximum point, the oil absorbency increased with increasing EGDMA. However, the oil absorbency decreased with increasing EGDMA when the amount of EGDMA was larger than that at the maximum point. The amount of EGDMA at the maximum point of 12.5% of the PB amount, 0.83%, was higher than that of 8.33% of the PB amount, 0.625%.

It is well known that an increase in the amount of a chemical crosslinking agent causes the formation of a denser network of the copolymer and reduces the chain length between crosslinks. However, when we added the physical crosslinking agent (PB) to partially replace the chemical crosslinking agent, we softened the strengthening effect of EGDMA. Because the interaction of physical crosslinking was weaker than that of chemical crosslinking, as mentioned before, we introduced PB. The result was satisfying. As shown in Figure 4, the higher the amount of PB was added, the higher the amount of EGDMA at the maximum point was, and the oil absorbency at it was higher.

However, the amount of PB could not be too large because it increased the solubility of the resin. At the same time, the amount of EGDMA could not be too large, also, because the crosslinking density of the particle was high, and the crosslinking network was so tight that there was no use of PB any more when the amount of EGDMA was too large.

Table II gives the oil-absorption speed at different amounts of EGDMA and shows that the oil-absorption speed varied to a slight degree when the amount of EGDMA was varied.

TABLE II
Oil Absorption Speed of the Various Copolymers
(T = 293 K, r_0 = 0.22 mm)

Polymerization recipe			
St/DMA	PB(%)	EGDMA (%)	v(mm^3/s) × 10^3
3 : 1	12.50	0.300	10.7125
		0.625	7.0893
		0.790	11.7777
		0.830	22.3049
		1.670	15.7192
		2.058	7.5048
		2.290	5.0239
	8.33	0.300	4.3123
		0.625	20.6627
		0.790	19.5436
		0.830	17.3217
		1.670	15.1715
		2.058	12.0699
		2.290	11.0543
1 : 2	2	0.30	6.1676
1 : 1			5.9372
3 : 2			6.6996
2 : 1			4.7712
6.5 : 1			6.0799
St = 100%			7.0964

Figure 5 Variation of the oil absorbency and gel fraction with the content of the physical crosslinking agent ($T = 293$ K, St/DMA = 3 : 1, and $r_0 = 0.3$ mm). (○) EGDMA = 0.625% and (●) and (□) EGDMA = 1.25%.

Effect of the concentration of the physical crosslinking agent

We investigated the effect of the chemical crosslinking agent (EGDMA) concentration on resin and know that the amount of physical crosslinking agent (PB) had an influence on the amount of EGDMA at the maximum point. However, how did the amount of PB affect the character of the resin? As shown in Figure 5, there was also an optimum amount point, and it (PB = 6% when EGDMA = 0.625%, and PB = 12.5% when EGDMA = 1.25%) also varied with different amounts of EGDMA. This behavior was due to the fact that the barrier to oil penetration efficiently could be decreased and the oil absorbency of resin could be increased when PB was added at certain amounts of EGDMA. However, the solubility of resin increased with increasing PB at the same time. When the decrease of oil absorbency for the increase of solubility of resin was higher than the increase by decreasing the barrier, the oil absorbency of resin decreased. Therefore, there was an optimum amount of PB, and the increase in the solubility of the resin was slower when the amount of EGDMA was higher. So, the higher the amount of EGDMA was, the higher the optimum amount of PB was.

Table II also gives the oil-absorption speed at different amounts of PB and shows that the oil speed varied to a slight degree when the amount of PB was varied.

Effect of particle size

The effect of the particle radius was investigated. The polymerization of the St–DMA copolymer was carried out at the optimum monomer feed ratio (St/DMA = 75 : 25) and the optimum PB and EGDMA amount accordingly. Figure 6 shows that the oil absorbency of the copolymer decreased and the oil absorption speed increased to a great degree when the radius of particle increased. The reason was that the surface area of the particle varied greatly with the variation in radius. As is well known, oil absorption is a diffusion process from the external surface of the samples into the internal space of the networks. Therefore, the influence of the radius of the particle was explicit.

On the whole, this behavior was considered serious but not essential because for common use, we can synthesize copolymer particles as small as possible, and this was not our object in this study.
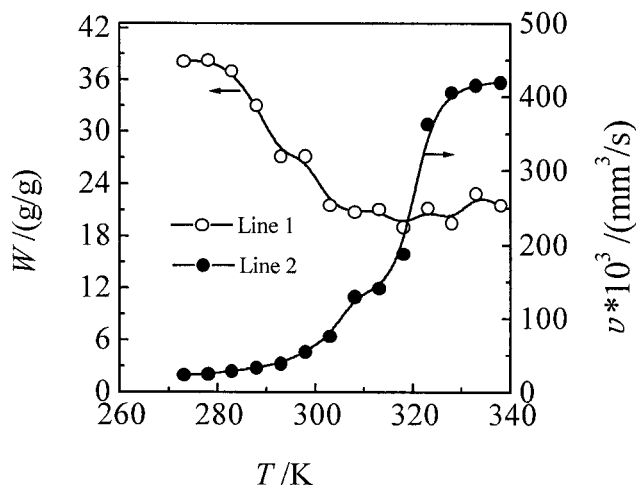
Effect of oil absorption temperature

Figure 7 shows the effect of temperature on the oil-absorption speed and oil absorbency. As shown in Figure 7, line 2, the oil-absorption speed increased with increasing temperature. This can be easily explained by the fact that the molecules of vinyl trichloride moved faster at higher temperatures and so speeded the whole process of swelling.

The effect of temperature (T) on the oil absorbency was complex. As shown in Figure 7, line 1, the oil absorbency was approximately equal to a stable value (21) at temperatures higher than 302 K, whereas oil absorbency decreased rapidly with increasing temperature when the temperature was lower than 302 K.

The effect of temperature on the absorbency was a swelling equilibrium problem for the three-dimensional network. Many research groups have presented theoretical models, but so far, there no theory has been thoroughly considered and accepted by most scien-
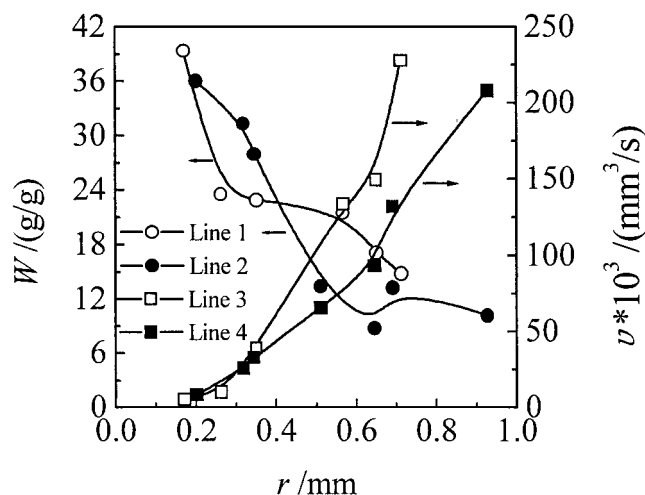
Figure 6 Variation of the oil absorbency and oil-absorption speed with the radius of the particle ($T = 293$ K and St/DMA = 3 : 1). (○) and (□) EGDMA = 0.375% and PB = 2.5%, and (●) and (■) EGDMA = 0.625% and PB = 6%.

Figure 7 Variation of the oil absorbency and oil-absorption speed with temperature (St/DMA = 3 : 1, r_0 = 0.35 mm, EGDMA = 0.375%, and PB = 2.5%).

tists. The classical Flory–Huggins equation[2] of Flory's swelling theory does not consider the effect of composition on the interaction parameter and neglects entanglement structures, which are formed by physical crosslinking and indeed exist in a three-dimensional network more or less. Choi and coworkers[7,8] extended Flory–Huggins theory, considering the interaction parameter as a function of both temperature and composition and also the effect of physical crosslinking. However, our results deviated to a certain degree from the expected tendency from Choi et al. So, the theoretical model presented by Choi et al. may be inaccurate, and the swelling equilibrium problem of partially physical crosslinking networks should be studied further.

CONCLUSIONS

The swelling behavior of various copolymer gel particles were observed online, and the effects of various parameters on the oil absorbency and oil-absorption speed were investigated. From the oil-absorption records, we found that a kind of relaxing three-dimensional network was indeed obtained, and it was the result of the introduction of a physical crosslinking agent (PB).

Due to the functional difference between St and DMA or OMA in the formation of the network, there existed an optimum monomer feed ratio (weight percentage of St/weight percentage of DMA or OMA), and 75 : 25 was the resultant value that we obtained. There was an optimum amount of EGDMA (0.625 when PB = 8.33%, and 0.83% when PB = 12.5%) that increased with increasing PB and an optimum amount of PB (6% when EGDMA = 0.625%, and 12.5% when EGDMA = 1.25%) that increased with increasing EGDMA, either. However, the amount of PB or EGDMA could not increase infinitely. The radius of the particle had a serious influence on the oil absorbency, and the effect of the oil-absorption temperature on the oil absorbency was complex.

With regard to oil-absorption speed, we found that the radius of the particle and the oil-absorption temperature had a more important influence in comparison with the effects of the monomer feed ratio and the amounts of EGDMA and PB. With increasing oil-absorption temperature or radius of the particle, the oil-absorption speed increased rapidly. For common use, we should prepare a smaller copolymer particle for practical use.

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