

Studies of Crosslinked Styrene–Alkyl Acrylate Copolymers for Oil Absorbency Application. II. Effects of Polymerization Conditions on Oil Absorbency

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ABSTRACT: Crosslinked styrene–acrylate copolymers were synthesized and evaluated by swelling properties for oil-absorbency application. The effect of various polymerization conditions (crosslinking agent concentration, initiator concentration, monomer concentration, and polymerization temperature) were studied through oil-absorption tests using kerosene oil. The oil absorbency was influenced mainly by the degree of crosslinking and the hydrophobicity of the copolymer units. The effect of moisture and the types of acrylate were also investigated. The copolymer with a longer alkyl acrylate had higher oil absorbency in the order of stearyl acrylate (SA) > lauryl acrylate (LA) > 2-ethylhexyl acrylate (EHA). The oil absorbency of the lauryl methacrylate (LMA) copolymer was higher than that of the LA copolymer. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 914–920, 2000

Key words: crosslinked styrene–acrylate copolymer; swelling property; oil absorption

INTRODUCTION

As environmental pollution by oil spills increases, oil absorbents have gained considerable interest. In developing highly efficient cleanup materials for spilt oil, the desirable characteristics are as follows: (1) fast oil-absorption rate, (2) large oil-absorption capacity, (3) good absorption selectivity of oil over water, (4) convenient shipping and storage, (5) lower density compared to water to float with or without oil absorbed, etc. The existing oil absorbents, polypropylene fiber or fabrics, melt-blown polyesters, polyurethane foam sheets, and so on, have unsatisfactory oil-absorbing capability. What is worse, they have difficulty in

shipping and storage because of their bulkiness. To overcome these disadvantages, we suggested a new concept in manufacturing oil absorbents. Prior to manufacturing, compressed spongelike materials, base materials with high oil-absorption capability, were prepared by copolymerizing the styrene monomer with various long-chain alkyl acrylates. Four kinds of acrylate monomers, 2-ethylhexyl acrylate (EHA), lauryl acrylate (LA), lauryl methacrylate (LMA), and stearyl acrylate (SA), were employed in this study. These acrylates with long-chain alkyl groups are generally known as hydrophobic materials. Therefore, a highly oil-absorbing property can be obtained by controlling the composition and the crosslinking density of the copolymer. EHA, LA, and SA were chosen to evaluate the effect of hydrophobicity with varying the length of alkyl groups. LMA, on the other hand, was chosen to find the difference between acrylate and methacrylate. In the first

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part of this series, various crosslinked and uncrosslinked styrene-acrylate copolymers were synthesized and characterized.¹ The basic properties of the copolymers were also studied in the previous article.¹

In this article, we conducted a detailed study on the swelling properties of the crosslinked copolymers. The influence of synthetic variables (monomer feed ratio, amount of crosslinking agent, amount of initiator, polymerization temperature, and type of acrylate monomer) of the crosslinked copolymers on the oil-absorption capacity were examined for oil-absorbency application. The effect of moisture was also investigated through a series of oil-absorption tests. In our next experiment, spongelike materials using crosslinked styrene-acrylate copolymers will be prepared and their oil-absorption capacity will be evaluated.

EXPERIMENTAL

The main procedure for the synthesis of crosslinked styrene-acrylate copolymers is similar to those previously described.¹ All samples for the oil-absorption tests were immersed in oil directly after drying in a vacuum oven for 2 days. To investigate the effect of moisture, air-equilibrated samples were prepared by keeping the dried samples in air for 2 days. Oil absorbency was measured by a suction-filtration method.² A weighed quantity of the crosslinked copolymer was immersed in oil at room temperature until equilibrium was reached, and the residual oil was then removed by a suction aspirator for 1 min (filter paper type: TOYO 5C). The equilibrium time was determined by measuring the oil absorbency at each time until it reached a limiting value. The oil absorbency, Q , was determined by weighing the swollen gel and calculated according to the following equation:

$$Q(\text{g/g}) = \frac{\text{weight of swollen gel} - \text{weight of dried sample}}{\text{weight of dried sample}}$$

The primary objective of the swelling test is to evaluate the influence of the styrene/acrylate ratios, the type of acrylate, crosslinking agent concentration, initiator concentration, and polymerization temperature on the swelling behavior of the synthesized copolymers. The various compo-

sitions of the samples were reported in the preceding article. In each set of measurements, five samples of each composition were tested. The average of three data with the exception of the maximum and minimum values was used, and the scatter was within 5% of the average absorbency. After the oil-swelling test, each sample was dried in a 60°C vacuum oven for about 5 days and weighed. The content ratio of the remaining polymer, R , was calculated according to the following equation:

$$R(\text{wt } \%) = \frac{\text{weight of dried sample after swelling test}}{\text{weight of dried sample before swelling test}} \times 100$$

The oil used in this experiment is kerosene oil (LG-Caltex Oil Co.). For the real application to clean up an oil spill, the oil-absorption test has to be operated using not only light or medium oil but also heavy oil, because the spilt crude oil has a high viscosity. But the materials used in this test to absorb the oil do not have a spongelike structure with open pores yet. It has only a micronetwork structure formed by the crosslinking reaction. Therefore, heavy oil with a high viscosity, like bunker-C, cannot easily diffuse from the external surface of the samples into the internal space of networks. For this reason, we used kerosene oil, having a lower viscosity than bunker oil in this experiment so that the swelling behavior of the samples could be easily evaluated.

RESULTS AND DISCUSSION

Effect of Crosslinking Agent Concentration

According to Flory's swelling theory,³ swelling behavior is affected by three factors: rubber elasticity, affinity to the solution, and crosslinking density. The swelling behavior of gels with different amounts of the crosslinking agent was studied. Various copolymers were prepared with different divinylbenzene (DVB) contents (from 0.2 to 5% of the total monomer weight). Figure 1 illustrates the relationship between oil absorbency and the amount of the crosslinking agent (DVB). Oil absorbency decreased with increase in the amount of DVB due to the restricted relaxation of the polymeric chain. An increase in the amount of the crosslinking agent forms a denser network of the

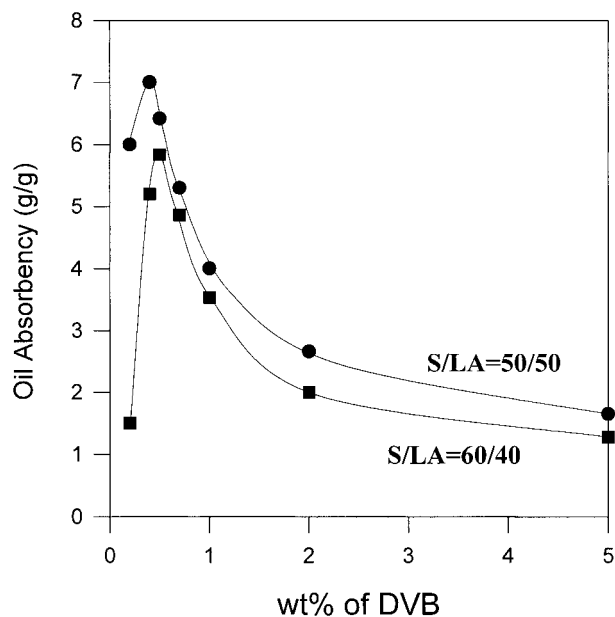


Figure 1 Variation of oil absorbency with content of crosslinking agent (DVB): 0.5 g BPO; 90°C; (●) S/LA = 50/50; (■) S/LA = 60/40 copolymer.

copolymer and reduces the \bar{M}_c , the average molecular weight, between crosslinks.⁴ Generally, the higher \bar{M}_c decreases the swelling ratio.⁵ This can be seen from the region with a high DVB concentration in Figure 1. However, oil absorbency decreased with a decrease in the amount of the crosslinking agent at low DVB concentration. This behavior is due to the existence of soluble materials including linear, branched materials and a very lightly crosslinked copolymer. By decreasing the amount of the crosslinking agent, soluble materials increase and dissolve in the oil during the swelling experiment. This can be supported by weighing the remaining polymer dried after the swelling experiment. Figures 2 and 3 show the content ratio of the remaining polymer in the S/LA = 50/50 and 60/40 copolymers, respectively. As shown in the figures, the content ratio of the remaining polymer increases with decreasing the amount of the crosslinking agent, as mentioned above. Oil absorbency of the crosslinked polymer, that is, insoluble materials, was calculated by subtracting the weight of the soluble materials and is also depicted in Figures 2 and 3. These show the effect of the crosslinking density on the oil absorbency regardless of the soluble materials; the higher the concentration of the crosslinking agent, the lower the oil-absorbing capacity.

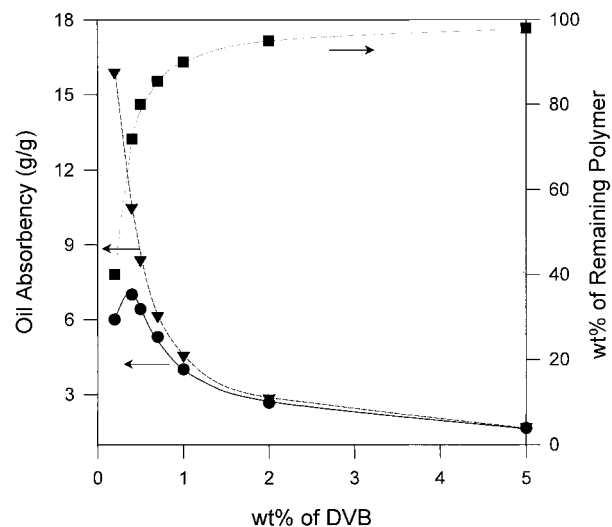


Figure 2 Variation of oil absorbency with content of crosslinking agent (DVB) in S/LA = 50/50 copolymer: (●) oil absorbency of soluble + insoluble materials; (▼) oil absorbency of insoluble materials; (■) weight fraction of insoluble materials.

Comparing the case of the S/LA = 50/50 copolymer with the 60/40 copolymer in Figure 1, the content of DVB to endow the maximum absorbency in the S/LA = 50/50 copolymer (0.4 wt % DVB) is smaller than that in the S/LA = 60/40 copolymer (0.5 wt % DVB). This is probably due to the side reaction, the crosslinking by LA. This can

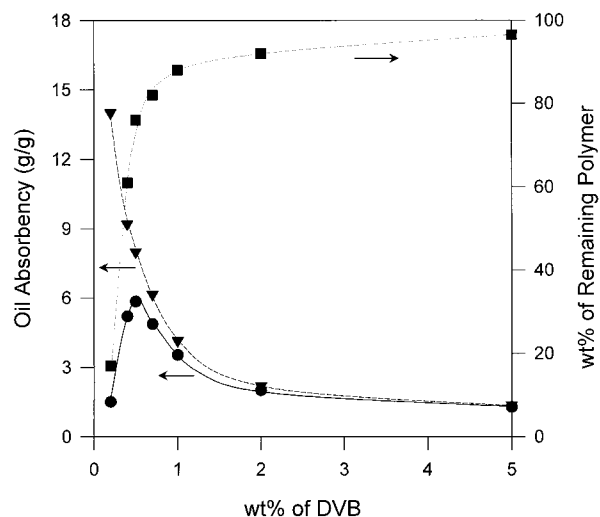


Figure 3 Variation of oil absorbency with content of crosslinking agent (DVB) in S/LA = 60/40 copolymer: (●) oil absorbency of soluble + insoluble materials; (▼) oil absorbency of insoluble materials; (■) weight fraction of insoluble materials.

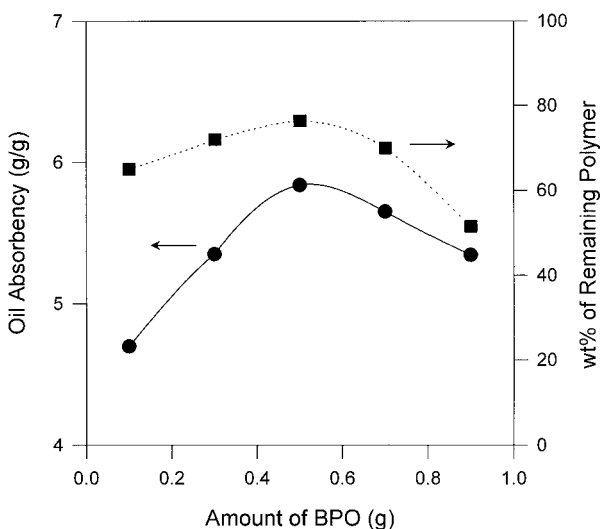


Figure 4 Variation of oil absorbency with content of initiator (BPO) in S/LA = 60/40 copolymer: (●) oil absorbency of S-LA copolymer; (■) weight fraction of insoluble materials.

be supported by our previous work, reporting that S-LA copolymers without adding a crosslinking agent are crosslinked and swollen to some extent in the case of the copolymer with the higher ratio of LA.¹

Effect of Initiator Concentration

To investigate the effect of the initiator concentration on the oil-absorption capacity, various S-LA copolymers (S/LA = 60/40) were synthesized, keeping all other variables constant. Added amounts of BPO as an initiator were 0.1, 0.3, 0.5, 0.7, and 0.9 g. The results of the oil-absorption test are shown in Figure 4. It is well known that in free-radical-chain polymerization the initiation efficiency and conversion will be as high as the increasing initiator concentration. However, a further increase in the initiator concentration makes the radical concentration excessive, causing the rate of termination reactions to increase, the conversion to decrease, and the chain length between each crosslink to decrease. These can affect the oil-absorption capacity of the polymer. As shown in Figure 4, there is a maximum point at 0.5 g (4.13×10^{-2} M) of BPO. When the amount of BPO is smaller than that at the maximum point, the oil absorbency increases with an increasing amount of the initiator. This arises from an increase in the concentration of radicals formed through the decomposition of the initiator.

When the amount of BPO is larger than that at the maximum point, however, the oil absorbency decreases with an increasing amount of the initiator due to the excessive radicals. This can be also explained by the concept of the relative amount of the polymer chain ends.⁶ The number-average degree of polymerization is inversely proportional to the square of the initiator concentration.⁷ When the initiator concentration increases, the molecular weight decreases and the polymer chain ends increase. Since the polymer chain ends do not contribute to the oil-absorption capacity, the oil absorbency decreases.

Effect of Polymerization Temperature

The effect of the polymerization temperature on the oil absorbency was investigated. The polymerization of the S-LA copolymer (S/LA = 60/40) was carried out at 70, 75, 80, 85, and 90°C, keeping all other variables constant. Figure 5 shows that the oil absorbency of the copolymer decreases to a slight degree when polymerization temperature increases. This is due to a decrease of the molecular weight with an increase in the polymerization temperature. In radical polymerization induced by thermal decomposition of an initiator, generally, as the polymerization temperature increases, the dissociation rate of the initiator and the rates of initiation, propagation, and termination are enhanced.⁸ All these factors except the

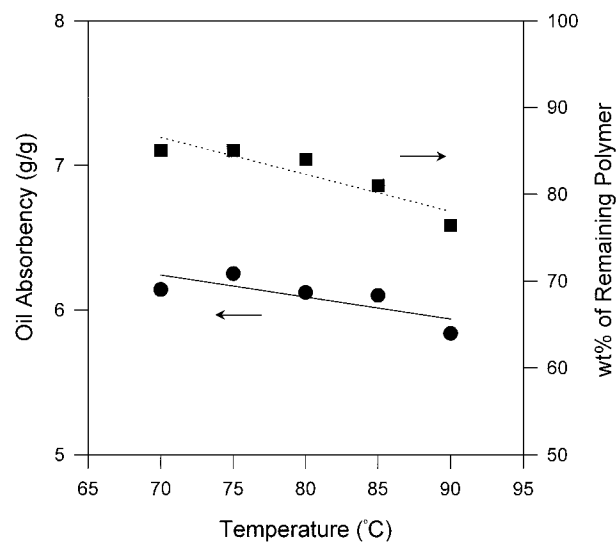


Figure 5 Variation of oil absorbency with polymerization temperature in S/LA = 60/40 copolymer: 0.5 wt % DVB; 0.5 g BPO; (●) oil absorbency of S-LA copolymer; (■) weight fraction of insoluble materials.

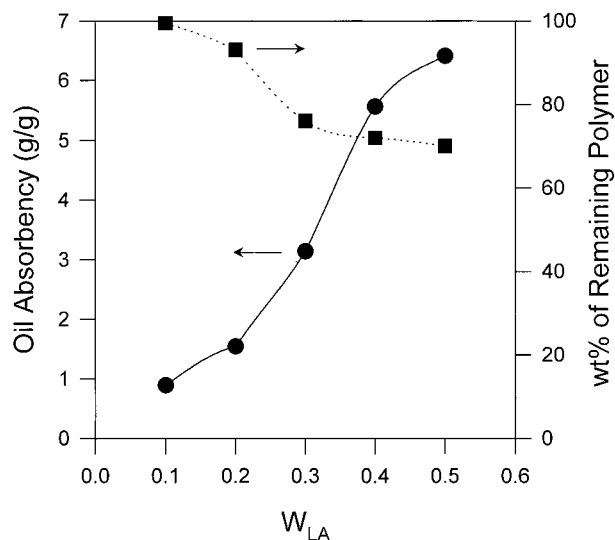


Figure 6 Variation of oil absorbency with concentration of LA (W_{LA}): 5 wt % DVB; 0.5 g BPO; 90°C; (●) oil absorbency of S-LA copolymer; (■) weight fraction of insoluble materials.

rate of termination increase the rate of polymerization. However, a further increment in the polymerization temperature reduces the molecular weight of the polymer, due to an increase of the rate of termination and chain transfer, and increases the relative amount of the polymer chain end, which does not contribute to the oil absorption as mentioned before. Therefore, increasing the polymerization temperature results in decrease of the oil absorbency. However, the degree of the decrease in oil absorbency is slight and negligible, because the lower the polymerization temperature, the lower the conversion and the lower the oil-absorption capacity.

Effect of Acrylate Concentration

The effect of acrylate concentration on oil absorbency is depicted in Figure 6. Monomer feed ratios (wt % of styrene/wt % of LA) were 50/50, 60/40, 70/30, 80/20, and 90/10. The acrylate concentration has an effect on three factors: (1) the hydrophobicity, (2) the glass transition temperature, and (3) the crosslinking density of the crosslinked styrene-acrylate copolymer. For all S-LA copolymers, oil absorbency increases as the LA concentration increases, due to the increase of hydrophobicity. This has been verified by FTIR absorbance spectroscopy. Long-chain aliphatic alkyl groups in LA introduce the hydrophobic property to the copolymer. Figure 7 depicts the spectra

of S-LA copolymers with various concentrations of LA. It shows the change of the peak intensity according to the extent of aliphatic alkyl groups. From A to E, in order of increasing acrylate concentration, the intensity of several peaks at the 3000–3100- cm^{-1} region become less intense. These peaks are due to CH stretching of the aromatic ring in styrene. However, the characteristic peaks of aliphatic —CH— stretching at the 2800–3000- cm^{-1} region become more intense. The peaks at 2925 and 2853 cm^{-1} are —CH₂— asymmetric and symmetric stretching peaks. Relatively less intense peaks at 2953 and 2870 cm^{-1} are —CH₃ asymmetric and symmetric stretching peaks, which are almost beyond recognition. The increase of these four peaks represents the introduction of long-chain aliphatic alkyl groups with a certain hydrophobic property.

In addition to the change of hydrophobicity, the glass transition temperature also has influence on the oil absorbency. According to the results of the first part of this series, the glass transition temperature decreased as the acrylate concentration increased and the glass transition temperatures of the crosslinked copolymers were equal to or slightly less than those of linear copolymers. In the case of the crosslinked S-LA copolymers, the

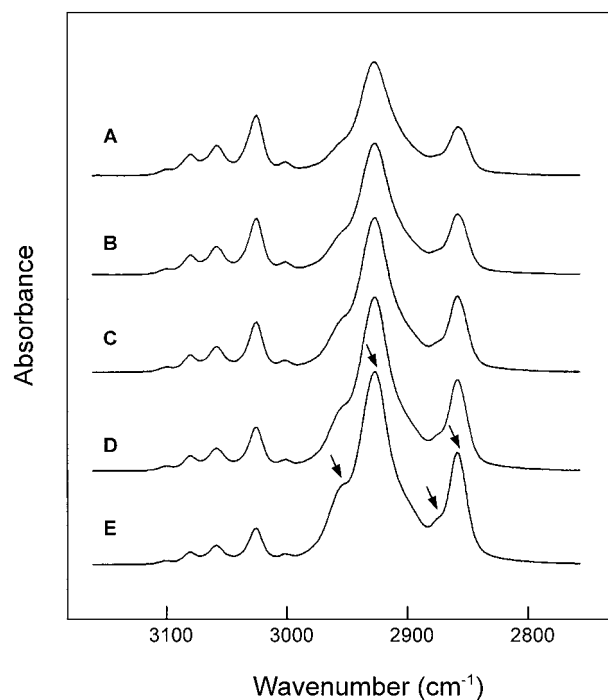


Figure 7 FTIR absorbance spectra of S-LA copolymers: (A) S/LA = 90/10; (B) 80/20; (C) 70/30; (D) 60/40; and (E) 50/50.

glass transition temperatures of S/LA = 70/30, 60/40, and 50/50 were below 30°C, the temperature during the oil-absorption tests. At this time, the polymeric chain relaxation is generated and the soluble materials including linear, branched, and very lightly crosslinked copolymers are dissolved in oil. The dotted line, indicating the weight percent of the remaining polymer, in Figure 6 shows that the soluble materials rapidly decreased at $W_{LA} = 0.3$. However, the oil absorbency increased at $W_{LA} = 0.3$ because the copolymer had an improved flexibility over the glass transition temperature. The flexible copolymer can easily produce the space to absorb oil.

Finally, the crosslinking density is also affected by the S/LA concentration and has influence on the oil absorbency. With increasing the concentration of LA, the crosslinking density decreases because the reactivity of styrene with DVB is higher than that of acrylate with DVB, and as a result, oil absorbency increases. However, a further increase in W_{LA} , the weight fraction of the LA monomer feed, promotes the side reaction of LA, which increases the crosslinking density and results in a relatively slow increase in oil absorbency at $W_{LA} = 0.5$. The self-crosslinking of acrylate was confirmed through solubility tests in the preceding part of this series.¹

Considering the content of the remaining polymer, the behavior stated above can be clearly explained. On the whole, the content of the remaining polymer decreases as the content of LA increases, because the solubility of the polymer increases as the hydrophobicity increases and the fraction of soluble materials also increases due to the decrease in \bar{X}_n by chain transfer of LA. At 0.3 of W_{LA} , the content of the remaining polymer decreases rapidly because of the improved flexibility of the copolymer over the glass transition temperature. Also, then, the slope of the decrease in oil absorbency becomes slow because of the self-crosslinking of LA.

Effect of the Type of Acrylates

Figure 8 shows the effect of a variety of acrylates, including the length of alkyl groups and whether it is acrylate or methacrylate, on the oil absorbency. The oil absorbency in the gel composition $W_{SA} = 0.5$ was excluded in this figure because the SA (solid state) could not be dissolved in styrene any more. The oil absorbency is found to be in the order EHA < LA < LMA < SA. Considering the oil absorbency of EHA, LA, and SA, it can be

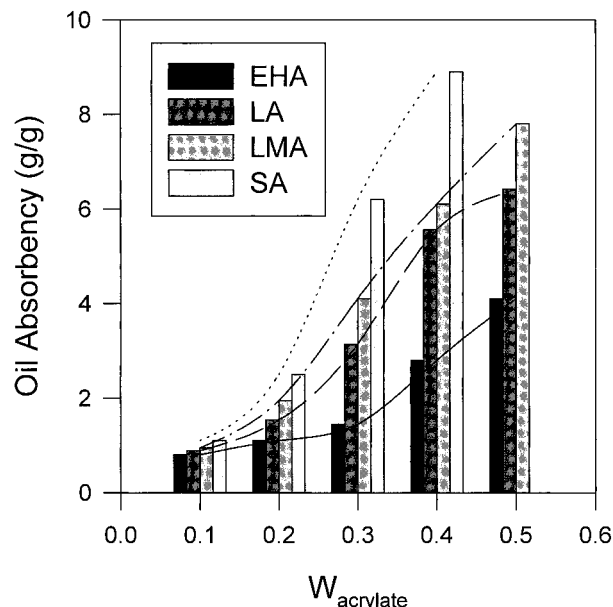


Figure 8 Variation of oil absorbency with different types of acrylates: 0.5 g BPO; 90°C.

concluded that oil absorbency increases with increase of the length of alkyl groups, that is, the number of carbon in alkyl groups: EHA (C_8) < LA (C_{12}) < SA (C_{18}). It can be easily explained by the fact that the longer the aliphatic side group exists, the more hydrophobic property can be introduced to the copolymer. Comparing the oil absorbency of the S-LA copolymer with that of the S-LMA copolymer, the latter is higher than the former because the α -methyl group in LMA gives a hydrophobic property to the copolymer and promotes the oil-absorption capacity.

Effect of Moisture

For common use, it is inevitable that oil absorbents are exposed to not only air but also to water. To investigate the effect of moisture on oil absorption, oil absorbencies of the dry sample and the air-equilibrated sample were measured. The results are shown in Table I. The dried samples show slightly more oil absorption than those equilibrated with air. Water vapor, which is present in the air, absorbed into the material and formed a barrier to oil penetration. However, the difference is small enough to be ignored. The styrene and acrylate monomer unit is hydrophobic so that the extent of water absorption is small, as shown in Table I.

Table I Effects of Moisture on Oil Absorbency

Samples (S/LA)	Oil Absorbency (g/g)		Wt % of Water Absorbed
	Dry Sample	Air-equilibrated Sample	
50/50	6.42	6.24	1.9%
60/40	5.56	5.40	2.2%
70/30	3.14	2.89	2.4%
80/20	1.54	1.43	1.2%
90/10	0.89	0.90	2.1%

CONCLUSIONS

The effect of various reaction conditions on the oil absorbency of crosslinked styrene-acrylate copolymers was investigated. The following conclusions were drawn from the oil absorption tests:

1. Oil absorbency increased with a decreasing amount of the crosslinking agent (DVB) and reached its maximum when the amount of DVB is 0.5 wt %.
2. The optimal concentration of the initiator (BPO) was 0.5 g (4.13×10^{-2} M).
3. In spite of decreasing oil absorbency with increasing polymerization temperature, the degree of the decrease in oil absorbency is small enough to be ignored due to the increase in the rate of polymerization.
4. Oil absorbency was increased by incorpora-

tion of hydrophobic acrylate units. Too much concentration of acrylate, however, introduced the side reaction of crosslinking and resulted in the slight drop in oil absorbency.

5. The longer alkyl acrylate introduced higher oil absorbency (SA > LA > EHA). Oil absorbency of methacrylate was higher than that of acrylate (LMA > LA).
6. In the presence of moisture in the copolymer, the oil absorbency decreased to a small extent.

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