The Modification of Porous Polymer Beads; Use Packing Material in Gas Chromatography

Yuzi TAKAYAMA

Materials Science, Toyohashi University of Technology, Tempaku-cho, Toyohashi, Aichi 440

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A new method of the surface modification of a porous polymer has been developed and applied to packing materials for gas chromatography. The porous polymer was coated with a α,β-unsaturated polyester solid polymer, which had a high acid value and which was cross-linked on the porous polymer by polymerization. By using this in gas chromatography, formic acid peaks are completely separated from acetic acid and water peaks without any apparent tailing. This polyester layer was not extractable and could stably be used at 230 °C or higher. If the diallyl phthalate polymer is used instead of the α,β-unsaturated polyester, propionic acid and acrylic acid, which are very diffecult to separate, were resolved. The present method may be applicable to some components of composite materials.

It is well known that the quality of the packing material in gas chromatography depends sensitively upon its surface properties. Hence, the material, such as diatomaceous earth and porous polymer,[1] is treated with acids[2] or silylating agents[3] to modify its surface properties. Studies of the surface modification are very important not only in the field of gas chromatography but also in other regions, for instance, that of composite materials. In the present work, as a first step, studies were made of the modification of the surface properties of the porous copolymer of styrene divinylbenzene. Also its quality as a packing material in gas chromatography was studied.

Usually, surface acidity and polarity are introduced by adding the proper monomer raw materials of the polymer. This method, however, is very cumbersome, since the stability of the suspension polymerization sensitively depends upon the conditions of the liquid. Surface properties may also be modified by coating the surface low-molecular weight substances. However, such a coating material easily evaporates in gas chromatography and dissolves into the mobile phase in liquid chromatography or into the organic matrix of composite materials.

With these facts in mind, we used curable substances to coat the surface of the porous polymer beads and so modified their surface properties. By choosing the proper curable substances, we controlled the number of acid points and also obtained a neutral and polar surface. The beads thus obtained were highly suitable as the packing material for gas chromatography. The present method may be applied to the pretreatment of polymers for composite materials.

Experimental

Diaion HP 30 (manufactured by the Nippon Rensui Co., a subsidiary of Mitsubishi Chemical Industry) consists of nonpolar porous polymer beads, nominally made of styrene and divinylbenzene. It is supplied in a wet state. The wet polymer was air-dried at room temperature and further heated to a constant weight in nitrogen flow at 140 °C. About 210—220 g of dry polymer, in spherical form (30—50 mesh), were obtained from 1000 ml of the wet polymer. The apparent density of the dried polymer was 0.275 g/cm^3.

About 33 g of the α,β-unsaturated polyester solid polymer, Espol TVF-5704-0 (supplied by the Mitsubishi Gas Chemical Co.) were dissolved in 400 ml of benzene. This solution was then poured onto 150 g of the dried Diaion HP 30 in a flask of a rotary evaporator. Then, a 100-ml portion of a benzene solution containing 1 ml of *t*-butyl perbenzoate (TBPB) was added to this mixture. The benzene was evaporated to dryness under reduced pressure. This dried polymer was packed in a glass pipe (1 m length; 34 mm inside diameter) and heat-treated in about a 100 ml/min nitrogen flow at 140 °C for 5 h. Thus the polymer was modified by the polyester (PMP). In this process, care must be taken of the following point; beads sticking on the wall have unfavourable properties and must be discarded.

Results and Discussion

Gas Chromatography for Free Fatty Acid (FFA). PMP was packed in 1 m×3 mm i.d. stainless steel column and tested by means of a Shimadzu Model-3BT TCD gas chromatograph with a mixture of C_1-, C_2-acids and water, their peaks being efficiently separated by PMP without any serious tails. For comparison, dried Diaion HP 30 was tested in a similar way. Except for water, it gave peaks with long tails as is shown in Fig. 1(b).

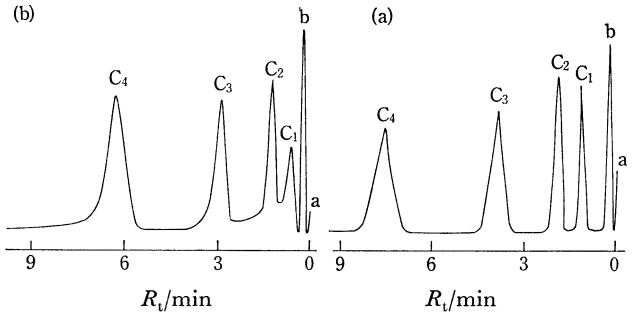

Fig. 1. Gas chromatograms of free fatty acids on (a) Diaion HP 30 modified by TVF 22.5% (see Table 2, Expt. No. 1) and (b) Diaion HP 30 unmodified. All packed in 1 m×3 mm i. d. stainless steel columns. Other conditions: (a) He flow-rate, 15 ml/min; column temperature, 150 °C; isothermal; sample load, 0.5 μl; recorder span, 4 mV. (b) He flow-rate, 16 ml/min; column temperature, 170 °C; isothermal; sample load, 2 μl; recorder span, 16 mV.
Peaks: a, air; b, water; C_1, formic acid; C_2, acetic acid; C_3, propionic acid; C_4, butyric acid.

Usually, an added tailing reducer reduces the retention volume, but this is not the case with Samples Nos. 1 and 2 rows in Table 2. The reason for this is that the TVF added in these present case is not a usual tailing reducer, but essentially changes the surface properties, that is, it increases the affinity to FFA and decreases the radius of the surface pores. The latter change may result in the decrease of the retention time of molecules with larger diameters such as C_4-acid.

Usable Maximum Temperature. The packed column with PMP was kept at 230 °C in a nitrogen flow for 24 h. After this treatment, the PMP was tested as has been described above. As a result, about a 5% shortening of the retention time was observed for all peaks, but there was no change in the peak shapes. Since a similar shortening was also observed in dried Diaion HP 30, the effect may be attributed to the shrinkage of Diaion HP 30. Furthermore, after the above test, the PMP could be taken out of the column smoothly, *i.e.* without any sticking to the column wall or to each other. Its color changed to a light yellowish brown from its original white yellow color. It may be concluded from these experimental results that the usable maximum temperature of PMP was about 230 °C.

Superiority of the α,β-Unsaturated Polyester Solid Polymer. It may be said, from our experience with diatomaceous earth, that the character of a packing material is primarily determined by the liquid phase on it. With this fact in mind, the porous polymer was similarly covered with acidic substances of a lower molecular weight, and its properties as a support were investigated. The favourable acid must satisfy the conditions that it does not destroy the base polymer and not be volatile, even at 240 °C. A small amount of added H_3PO_4 changed the color of Diaion HP 30 homologeneously to gray from the original white-yellow. Sebacic, stearic, and isophthalic acids did not change the color of the base polymer, but began to evaporate at temperatures below 200 °C. Thus, it is presumed that this shortcoming may be overcome by the use of polymer acids.

As for the α,β-unsaturated polyester, a method has been established for controlling the amount of carboxylic acid in it. We can obtain, by polymerizing this polyester on the beads, a film with a large number of acid points and a higher molecular weight; the film is stable even at 230 °C or so. For the present purpose, however, the polyester used must be as pure as possible. The commercially available, in the form of a liquid, contains 40—50% of the styrene monomer, and its acid values range between 5 and 16. If one uses such an impure polyester, the film obtained is inferior in its character, that is, it is thermally unstable and gives a peaks with some tailing. Hence, it is highly advisable to use a so-called solid (crystal) polymer with a high acid value. Solid polymers, TVF-5704-0 and Espol MG-1012, were chosen as modifiers in the present work. The specifications of these materials are given in Table 1.

Effect of the Polyester Concentration. The dependence of the packing character upon the polyester concentration was studied. Furthermore, the effect of coexisting diallyl isophthalate (DAIP) was studied, since this increases the degree of cross-linkage and the

Table 1. Specifications of α,β-unsaturated polyester solid polymers[a)]

Item	Espol TVF-5704-0	Espol MG-1012
Acid value	29.8	21.4
Softing point (°C)	99	96

a) Both solid polymers were supplied by the Mitsubishi Gas Chemical Co.

Table 2. Percentages of α,β-unsaturated polyester and DAIP on diaion HP 30

Expt. No.	Modifier: TVF %	Modifier: MG-1012 %	Modifier: DAIP %	DAIP in modifier %	Digests of result[a)]: V'/V'_{c_1}[b)] C_1	C_2	C_4[c)]	$N_{eff/m}$	Overlap percentages between C_1 and C_2 peaks[d)]	Note
1	22.5				0.281	0.480	1.97	714	0	peaks, sharp and well separated
2					0.170[e)]	0.392	2.32	710	see Fig. 1(b)	C_1 peaks, very long tail
3		44.5		0	0.329	0.520	1.85	462	4.92	peaks, rather broad; C_1, C_2 peak separation, good
4		22.5		0				650	7.10	C_1 peak, short tail; C_1, C_2 peak separation imperfect
5		17.8	26.7	60	0.357[e)]	0.547	1.88	470	15.8	C_1 tail, rather long; C_1, C_2 peak separation considerably poor
6		9.0	13.5	60				677	21.3	C_1 tail, much more long; C_1, C_2 peak separation, poor
7			44.5	100	0.457[e)]	0.589	1.84	626	36.1	C_1 peak was observed as a shoulder on the C_2 peak, having a considerable tail
8	44.5							434	0	peaks, rather broad; C_1, C_2 peak separation good

a) Each run was tested in a 50cm × 3 mm i. d. stainless steel column at 150 °C, and each sample load was 0.5—1 μl. b) V': corrected retention volume. c) C_1: formic acid, C_2: acetic acid, C_3: propionic acid, C_4 : butyric acid. d) $\frac{\text{Peak-height from the valley between two overlaping peaks}}{\text{Height of } C_2 \text{ peak}}$. e) Tailing peak.

solvent stability of the polymerized polyester, *i.e.*, the modifier film, but decreases its acid value. With a decrease in the acid value of the modifier film, the peak tailing became remarkable and the separation of the peaks assigned to C_1- and C_2-acids became difficult. The peak-width was almost independent of the polyester concentration on the base polymer in the region of below about 25%, but became slightly broader with an increase in the concentration above this limit.

In connection with the above facts, the character of DAIP films of 44.5 and 66.8% (by weight) of the base polymer gave a sharp peak with a long tailing for C_1 acid, but sharp pekas for C_2–C_3 acids; the latter is shown in Fig. 2. In this case, there was no unfavourable effect, *i.e.*, broadening, caused by higher concentrations of DAIP.

These results are summarized in Table 2.

This difference between the concentration effects of DAIP and the polyesters may be attributed to that between their dispersive states on the base polymer. As for the polyester film before polymerization, films on beads stick to each other, and some beads become bare when they are prepared in a rotary evaporator; thus, the heterogeneous dispersion state is realized. This model is partly supported by the fact that the unfavourable concentration effect was not observed if the film was prepared in a beaker without any mechanical stirring. Also such phenomena were not observed with DAIP.

The degree of cross-linkage of the polyester on base beads was estimated by the following method. The PMP was put into a Soxhlet extractor and treated with benzene, and then the weight of extract was measured. The bare beads (Diaion HP 30) were similarly treated, but their weight loss was negligible. Hence, only partial TVF and TBPB were extracted from the coated beads. Since TBPB is easily extracted completely, one can estimate the amount of TVF extracted if the initial content of TBPB is known. The experimental results showed that only 6% of the TVF present was extracted. This means that the TVF film is highly cross-linked and stable.

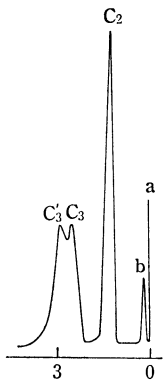

Fig. 2. Profile of propionic acid and acrylic acid on Diaion HP 30 modified by DAIP 44.5% (see Table 2, Expt. No. 7). Packed in a 50 cm × 3 mm i. d. stainless steel column. He flow-rate, 16 ml/min; column temperature, 140 °C; isothermal; sample load, 0.1 μl; recorder span, 2 mV. Peaks: C_3, propionic; C_3', acrylic acid; a and others; see Fig. 1.

Separation of Propionic Acid and Acrylic Acid. As can seen from Fig. 2, the peaks ascribed to propionic (C_3) and acrylic (C_3') acid were separated. This chromatogram was obtained with a short column 50 cm in length, much better separation can be expected with a column of the usual length. This separation may be attributed to the effect of polar groups in the DAIP molecule.

Conclusion

It has been established that α,β-unsaturated polyesters are good modifiers of prorous polymer beads, and that the higher the acid value, the better a modifier for the separation of FFA. In the present work, the best results were obtained with 25% TVF on the base beads. However, this value may depend upon the surface area of the base beads. The Diaion HP 30 used in the present work has a BET area of 200 m^2/g. The optimum concentration increases with the increase in the surface area.

The conventional modifiers presently used are apt to evaporate or be extracted in gas chromatography and liquid chromatography respectively. These unfavourable effects can be avoided by the use of the present techniques.

In the present work, we were mainly interested in the separation of FFA with an acidic modifier, not in the separation of amines. The latter may, however, be successfully done by basically modified packing, which can be obtained by an extension of the present techniques.

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