Synthesis and Properties of Thermoplastic Expandable Microspheres: The Relation Between Crosslinking Density and Expandable Property

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ABSTRACT: A set of thermoplastic expandable microspheres was investigated with respect to their crosslinking density and expandable property. The crosslinking efficiencies of dipentaerythritol hexaacrylate in a set of thermoplastic expandable microspheres were measured. As expandable properties, expansion curves were measured by using a thermomechanical analyzer, and they also were shown by measuring the change of thickness of the coated compound consisting of ethylene–vinyl acetate copolymer resin emulsion and $CaCO_3$ with thermoplastic microspheres on paper. In view of the expansion ratio and heat resistance, as crosslinking density, a swelling ratio of about 20–25 is needed to achieve optimum expansion without collapse and rupture of microspheres. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 505–512, 2004

Key words: crosslinking; radical polymerization; blowing agents

INTRODUCTION

The thermoplastic expandable microspheres consist of a drop of liquid hydrocarbon, encapsulated by a gas-proof and polymeric shell. Liquid hydrocarbon used as the blowing agent is contained in a 3- to 7-μm-thick shell. When exposed to heat, the shell softens and the hydrocarbon gasifies, causing the microsphere to expand, therefore, turning into a microballoon. Before expansion, the typical diameter is about 20 μm and the density is 1000 kg/m^3. During expansion, the diameter increases to about 100 μm and the density drops to 20–30 kg/m^3. Further heating causes gradual leakage of internal gas from the thinned shell material, making the polymer tensility greater than the internal pressure before the microballoon begins to shrink.[1–4]

Unexpanded microspheres are used as blowing agent. When unexpanded microspheres are heated up to 80–190°C, the microspheres expand, reaching a volume 50–100 times bigger than before. In the range of microspheres, there are grades available with expansion temperatures in the range 80–145°C. The different thermomechanical behavior of the various grades makes it possible to select an optimal grade for each process and application. This phenomenon is used in printing inks to get three-dimensional patterns on paper, wallpaper, and textiles, etc.[1,2]

The microspheres are prepared by a suspension-type polymerization of droplets of a mixture of monomer and blowing agent. Their manufacturing method was first described by The Dow Chemical Co.'s patent[5] and after that there are many patents.[6–9]

To develop excellent microspheres, selection of gas-proof polymeric composition, simultaneous, balance of softening point and melt viscosity of shell polymer, and molecular structure and boiling point of blowing agent must be important. Further, when exposed to heat, ductility and intensity of shell polymer also must be an important factor.[2] From these points of view, as the monomer having gas barrier properties, acrylonitrile and methacrylonitrile are generally used as a polymerizable monomer.[10–15] Japanese Patent Publication No. Hei 5(1993)-15499 describes the method of producing thermoplastic expandable microspheres wherein a polymer obtained from the component comprising 80–97 wt % of the nitrile containing monomers, 3–20 wt % of the nonnitrile containing monomers, and 0.1–1 wt % of trifunctional crosslinking agent is used to microencapsulate a volatile expanding agent. The thermoplastic expandable microspheres obtained by this method are superior in heat resistance in that it is not formed at a temperature of 140°C or less. On the other hand, Japanese Patent Publication No. Hei 5(1993)-285376 describes the method of producing a thermoplastic expandable microsphere, which is particularly excellent in heat resistance. Application of a monomer that can produce a homopolymer having a high glass transition temperature is ef-

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TABLE I
Effect of VAc Content, and Ratio of AN and MAN on Polymerizations of Thermoplastic Microspheres for 15 h at 60°C[a]

	Monomer				Blowing agent						
Run	AN (mol %)	MAN (mol %)	VAc (mol %)	DPE (mol %)	C_5H_{12} (wt %)	C_6H_{14} (wt %)	Yield[b] (wt %)	Particle size[c] (μm)	T_{start}[d] (°C)	T_{max}[e] (°C)	D_{max}[f] (μm)
1	72.4	27.6	0	0.0174	14.8	5.7	90.0	23.4	147	166	616
2	72.1	27.2	0.66	0.0175	14.8	5.7	90.0	19.2	155	171	591
3	71.1	26.9	2.00	0.0176	14.8	5.7	92.0	19.0	134	163	659
4	78.6	20.7	0.67	0.0177	14.8	5.7	86.0	22.1	No expansion		
5	55.9	43.4	0.69	0.0182	14.8	5.7	88.5	19.3	144	157	266

[a] Initiator; AIBN, [AIBN]/[monomer] = 0.008
[b] Based on total monomer (g).
[c] By laser scattering method.
[d] Temperatuere of expansion start by TMA.
[e] Temperature of expansion peak by TMA.
[f] Dimension change of expansion peak by TMA.

fective. Such monomers include methacrylonitrile, acrylamide, methacrylic acid or salts thereof, isobornyl methacrylate, dicyclopentenyl acrylate, and the like. A monomer that can produce a homopolymer having a high glass transition temperature may be used in the amount of 20 to 50 wt % to prepare the microspheres. If the monomer exceeds 80 wt %, the shell formation, especially evenness of the shell, becomes worse to lessen expandability. If the amount is less than 10 wt %, the heat resistance of the microspheres cannot be improved.

In this study, acrylonitrile (AN) and methacrylonitrile (MAN) as the monomer having gas barrier properties and vinyl acetate (VAc) as the non-nitrile-containing monomers were used for obtaining the polymer having high heat resistance and high expansion start.

Frequently, crosslinking agents serve to increase the melt or flow viscosity of the polymeric composition at temperatures sufficiently high to cause volatilization of the blowing agent and subsequent deformation of the originally formed a sphere into a larger hollow sphere. The level of crosslinking must be controlled and optimized to produce foams with maximum expansion. Therefore, the criteria used for optimized crosslink level were to achieve maximum foam expansion for a given foam formulation. On the field of foaming in extrusion process, it has been known that long chain branching contributes excellent processibility of polyethylene and polypropylene, etc.[16–20] However, on the field of thermoplastic microspheres, reports of this type of study have apparently not been published to date.

The objective of this study was to clarify relation between crosslinking density and expandable property of the thermoplastic expandable microspheres. The contents of optimized crosslinking agents for thermoplastic expandable microspheres were determined.

EXPERIMENTAL

Polymerization procedure of thermoplastic microspheres

A polymerization reactor (22L) equipped with an agitator was charged with 7500 g of deionized water, 2550 g of sodium chloride, and 1300 g of 20 wt % colloidal silica dispersion in water (purchased from Asahidenka Industries Co., Ltd., Osaka, Japan). To this mixture was added 20 g of 36 wt % aqueous solution of polyvinyl pyrrolidone. Twenty grams of a solution containing 10 wt % sodium nitrite was added. The pH of the aqueous solution was adjusted to 3–4 with hydrochloric acid. AN, MAN, and VAc were utilized as the monomer. Additionally, dipentaerythritol hexaacrylate (DPE) was purchased from Kyoeisha Chemical Co. Ltd. (Osaka, Japan) and was utilized as the crosslinking agent. Experiments were carried out by using different mole ratios of [AN]/[MAN]/[VAc]/[DPE]. An oil phase mixture was prepared by utilizing 4000 g of the monomer and containing 20 wt % blowing agents (*n*-pentane/*n*-hexane) and 25 g of 2,2′azobisisobutyronitrile (AIBN) as initiator. The oil phase mixture was added to the water phase with violent agitation supplied by a blade rotating at a speed of about 10,000 rpm. The reactor was immediately sealed and a portion was sampled to determine the particle size. The droplets appeared to have diameters from about 10 to 18 μm. After the initial dispersion, the reaction mixture was maintained at a temperature of about 60°C for a period of 15 h. At the end of this period, the temperature was lowered. The beads were filtered and subsequently dried in an air oven at a temperature of about 40°C. All monomers, solvents, and reagents except for DPE and colloidal silica dispersion were purchased from Wako Pure Chemical Industries Co. Ltd., Tokyo, Japan.

TABLE II
Radical polymerizations of AN, MAN and VAc with crosslinking agent for 15 h at 60°C[a]

	Monomer					Polymer				
Run	AN mol%	MAN mol%	VAc mol%	DPE mol%	Yield[b] (wt%)	PAN[c] mol%	PMAN[c] mol%	PVAc[d] mol%	Swelling ratio[e]	gel level[f]
1	71.10	28.24	0.70	0	92	71.6	27.9	0.48	13.4	12.3
2	71.05	28.24	0.70	0.019	91	—	—	0.46	34.5	64.0
3	71.03	28.24	0.70	0.038	92	—	—	0.49	24.5	72.5
4	71.00	28.23	0.70	0.076	90	—	—	0.48	19.8	78.4
5	71.00	28.20	0.70	0.143	93	—	—	0.48	18.1	72.7
6	71.00	28.23	0.70	0.076	91	—	—	—	—	—
7	71.00	28.23	0.70	0.076	91	—	—	—	—	—

[a] Initiator; AIBN, [AIBN]/[monomer] = 0.008. Blowing Agent; C_5H_{12} = 14.8wt%, C_6H_{14} = 5.7wt%.
[b] Based on total monomer (g).
[c] Determined for NMR.
[d] By G.C.
[e] Procedure C of ASTM D 2765; solvent:DMF.
[f] Procedure A of ASTM D 2765; solvent:DMF.

Determination of composition for the microspheres

The copolymer compositions were determined by proton nuclear magnetic resonance (^{1}H-NMR) and by gas chromatography (GC). ^{1}H-NMR was used to determine a formula for this material. The sample was dissolved in the solvent deuterium dimethylformamide (DMF-d^7) and peaks AN and MAN were identified based on library comparisons. As the sample for determination of composition, the polymer containing no crosslinking agent was used. VAc content was determined by GC by reason that it could not be detected by ^{1}H-NMR. The sample was heat treated (180°C × 20 min) and then dispersed in methanol by ultrasound to remove the remaining VAc monomer. After pyrolytically decomposing with methanol at 200°C for 1 h, VAc content of the sample was examined by Shimazu GC-14A.

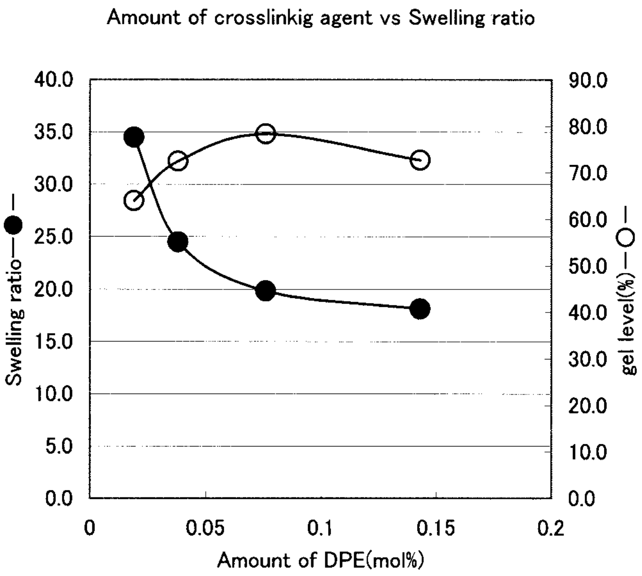

Figure 1 Amount of crosslinking agent versus swelling ratio and gel level.

Morphology determination of expandable microspheres

The samples treated by hot air were analyzed by scanning electron microscopy (SEM; Hitachi 4100 field emission) to study foam cell structures. The images were obtained at 5-kV accelerating voltage and secondary electron imaging. Photomicrographs were obtained at ×50 magnification.

The measuring method of treating by hot air was as follows: Place 1.0 g of each sample into a aluminum foil box (10 × 10 × 5 cm) and then heat in a oven at 180°C for 1 min.

Particle diameter distribution

Particle diameter distribution was measured by means of a particle diameter distribution meter (Horiba LA-910).

Level of crosslinking determination

The amount of crosslinking (gel level and swelling ratio) was determined by *N,N*-dimethylformamide (DMF) extractions. The DMF extraction procedure used conforms to procedures A and C of ASTM D 2765.[21] The crosslinked gels were extracted with 29-g portions of DMF, each for 24 h at room temperature (RT). Then, the gels were dried to a constant weight by vacuum pumping in a dessicator for 24 h.

Determination of the expandable property by using thermomechanical analyzer

As expandable property, expansion curves of the microspheres were measured in a temperature-ramping

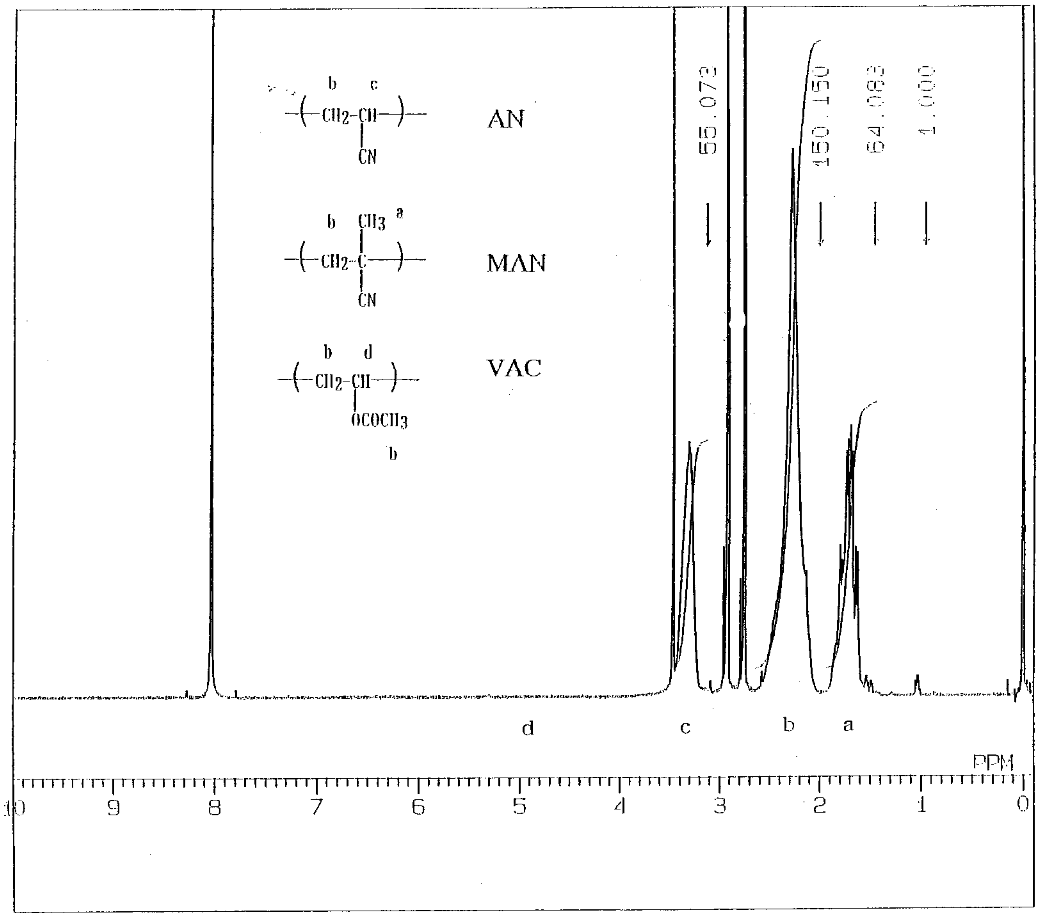

Figure 2 ^{1}H-NMR spectrum of run 1 (Table II).

experiment (5°C/min.) in a thermomechanical analyzer (TMA; TA Instruments). The 24-μm sample was put into a cup and heated at a set speed (5°C/min). When the spheres start to expand, a probe takes up the movement. The temperature at which the expansion starts is called T_{start}, whereas the temperature at which maximum expansion is reached is called $T_{\max}$. The dimension change at which maximum expansion is reached is called $D_{\max}$.

TABLE III
Particle Size and Expandable Property

Run	Particle size[a] (μ m)	T_{start}[b] (°C)	$T_{\max}$[c] (°C)	$D_{\max}$[d] (μ m)
1	20.9	152	155	48
2	19.2	155	171	591
3	20.9	141	165	401
4	21.5	146	168	398
5	20.0	146	163	217
6	17.5	146	165	227
7	25.4	140	166	348

[a] By laser scattering method.
[b] Temperature of expansion start by TMA.
[c] Temperature of expansion peak by TMA.
[d] Dimension change of expansion peak by TMA.

Determination of the expandable property on coating

As expandable property on coating, expansion curves of the microspheres also were measured by changing the

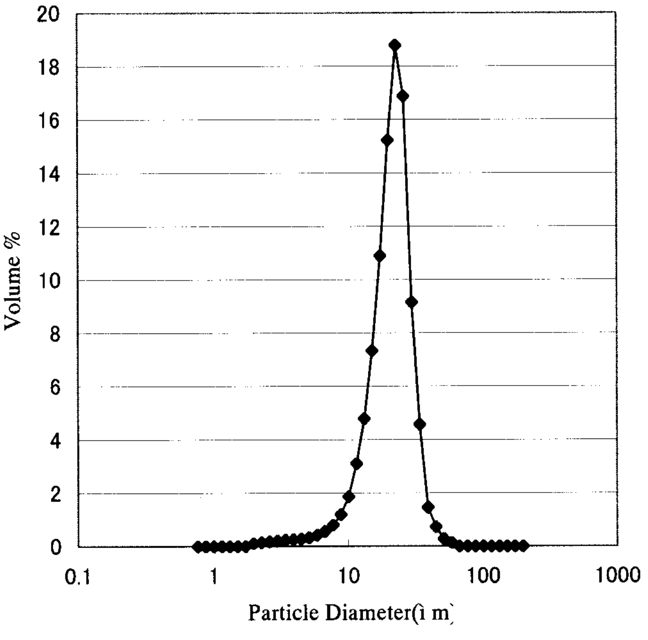

Figure 3 Particle size distribution of run 1 (Table II).

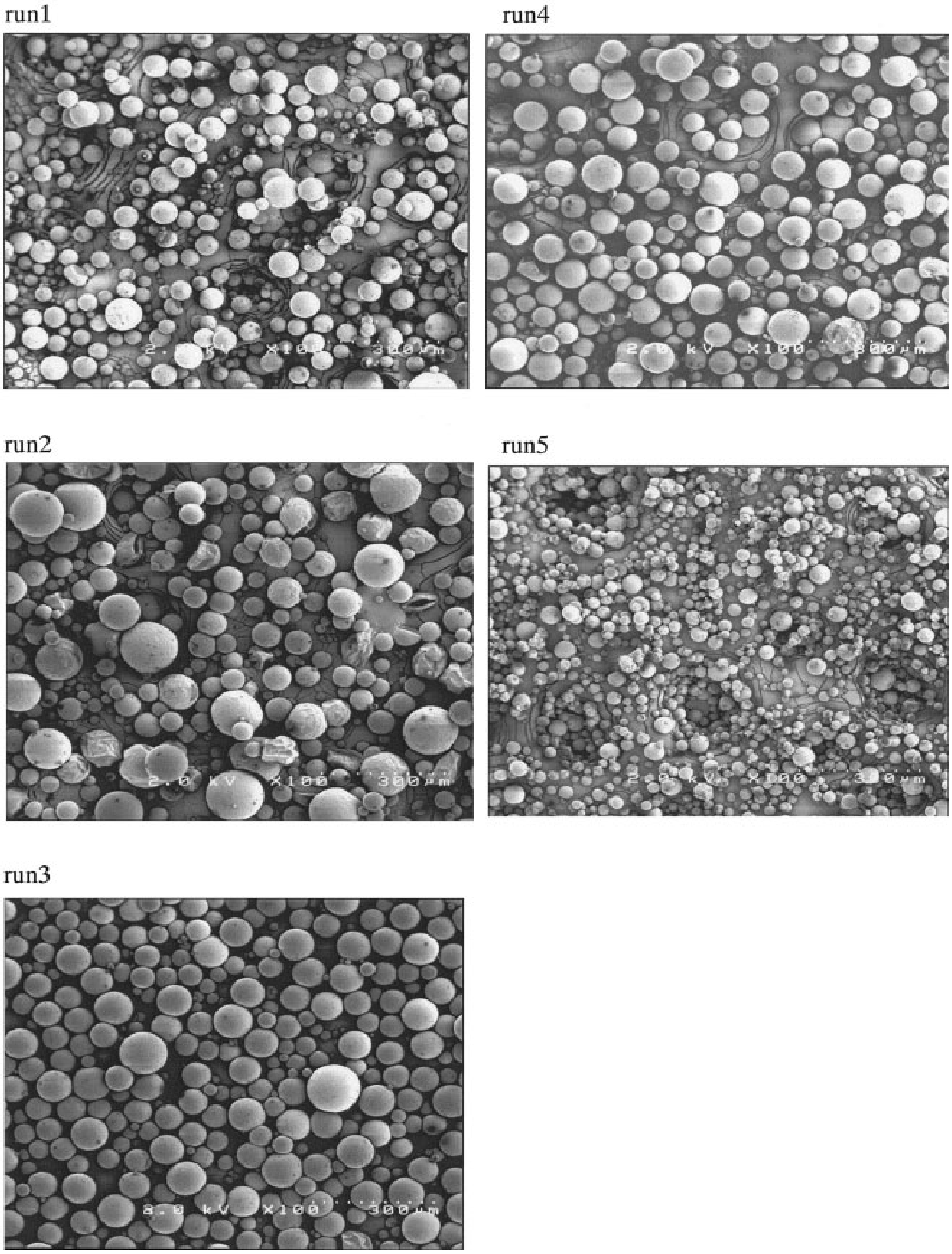

Figure 4 Morphology of expanded microspheres of runs 1–5 (Table II).

thickness of the compound coated on paper by heating. The compound had the composition, in terms of weight %, of EVA/$CaCO_3$/microspheres equaling 55/43.5/1.5. The conditions for coating were as follows.

The compound is coated with a coater at a thickness of 200 μm. After prebaking for 3 min at 90°C, the thickness is measured. After baking for 1min at different temperatures, the thickness is measured. Expansion ratio is calculated by following formula: Expansion Ratio = Thickness of expanded film/Thickness of unexpanded film. Also, the surfaces of the coating were observed with a SEM to study matt properties.

RESULTS AND DISCUSSION

Syntheses of the microspheres

Relation between composition ratio of AN, MAN, and VAc, and expandable property was investigated and are listed in Table I. The effects of the VAc content

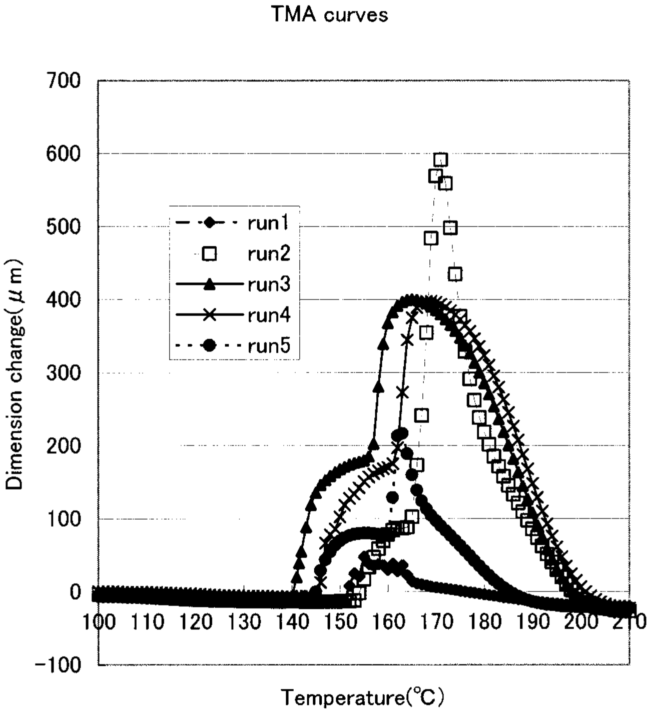

Figure 5 The relation between swelling ratio and expandable property.

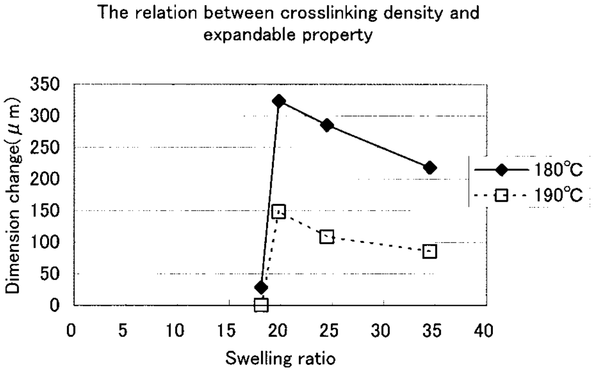

Figure 6 The relation between swelling ratio and expandable property.

were shown in runs 1–3. The addition of VAc of 0.66 mol % had the optimum T_{start} and T_{max} in view of having high heat resistance and high expansion start. Next, the effects of AN/MAN mole ratio were shown in runs 2, 4, and 5. AN/MAN mole ratio of runs 2, 4, and 5 each showed 2.7, 3.8, and 1.3. It is clear from these results that run 2 has the optimum AN/MAN mole ratio. At the present stage, however, we cannot propose any definite scheme that can explain the reason the proportion of AN, MAN, and VAc has an effect on expandable properties. We still need further study in view of gas permeability, ductility, and intensity, etc. of shell polymer. Either way, from the above results, in view of T_{start}, T_{max}, and D_{max}, the components of monomer of AN, MAN, and VAc used were 72.1, 27.2, and 0.66 mol %, respectively.

The relation between crosslinking density and expandable property was studied. DPE as crosslinking agent was used. Table II and Figure 1 showed the effect of the crosslinking agent content. The polymer containing no crosslinking agent exhibited a swelling ratio of about 13.4 and a crosslinking gel level of about 12.3%. The addition of 0.019 mol % of DPE increased swelling ratio to 34.5 and increased polymer gel level to 64.0%. On the other hand, a further increase in addition of DPE decreased swelling ratio from 34.5 to 18.1. Polymer gel level showed the maximum of 78.4%.

In this study, for the main experimental work, only the content of crosslinking agent is changed. All other factors are, as close as possible, held constant. ^{1}H-NMR was also used to determine the copolymer compositions containing no crosslinking agent. The spectrum is shown in Figure 2. We determined the mole ratio of PAN/PMAN is 72/28, as listed in Table II. These results were almost identical to the mole ratio of AN and MAN monomer feed before polymerization, although the peaks at 4.9 ppm due to methylene of PVAc were not detected. The VAc content examined with GC was 0.72 wt %, indicating that VAc monomer did not completely convert to polymer.

As one influence on the expandable property, particle size of thermoplastic microspheres is important. Runs 4, 6, and 7 of Table III show the effect of average particle diameter on expandable property. The value of D_{max} of microspheres, shown in run 6 of Table III, decreases with too small an average particle diameter. The value of T_{start} of microspheres, shown in run 7 of Table III, decreases with too large an average particle diameter. Japanese Patent Publication No. 2000-191817 describes the effect of particle size on expandable property. The coarse particles are easy to foam at a low temperature to impair sharp forming. The coarse particles also involve an expansion ratio that

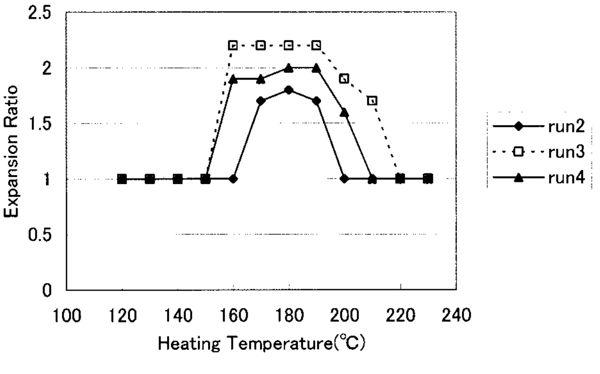

Figure 7 Expansion ratio of runs 2, 3, and 4 (Table II) on coatings.

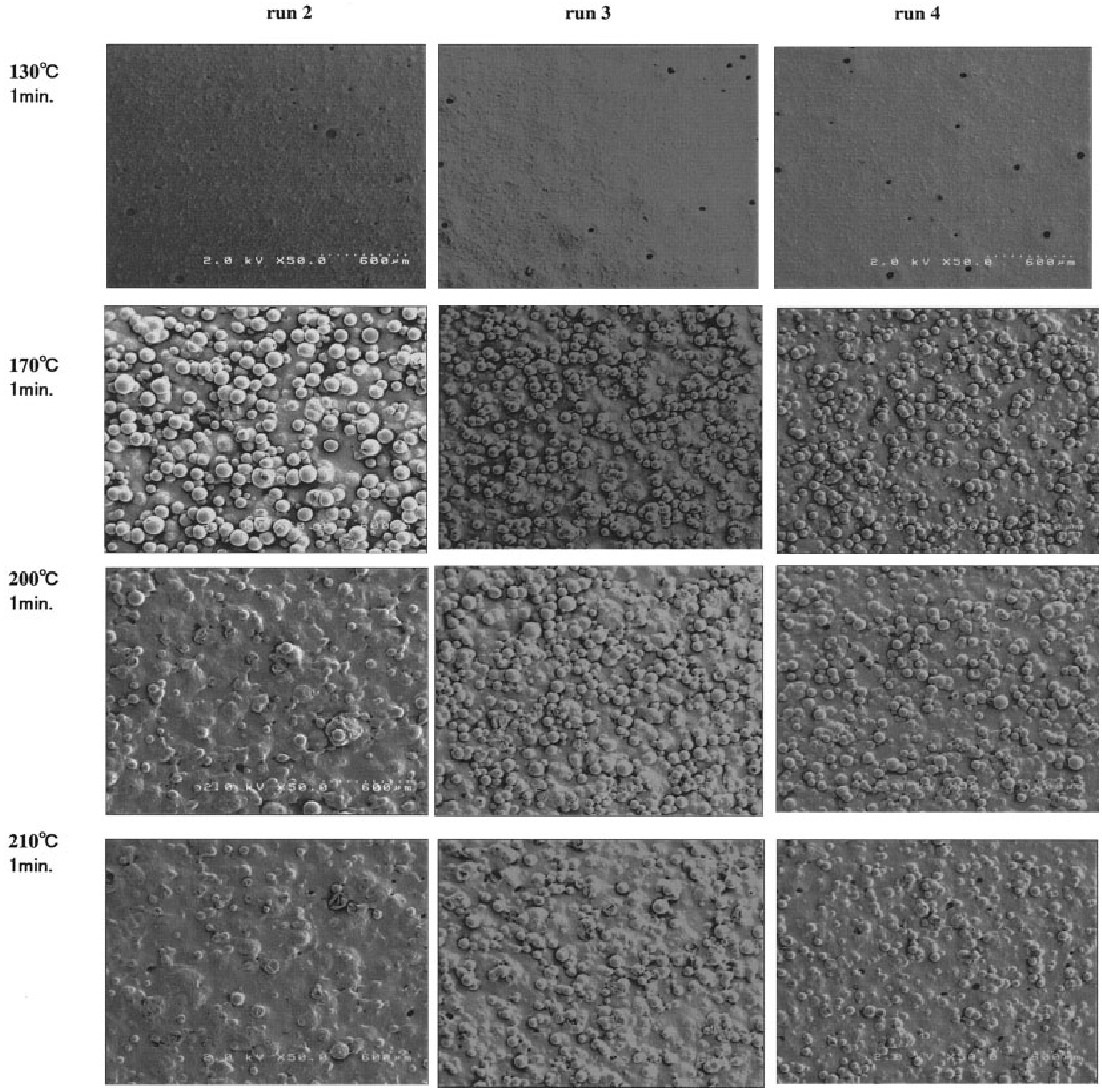

Figure 8 SEM images on the surface of coating of runs 2, 3, and 4 (Table II).

cannot be raised because the blowing agent is easy to escape. The minute particles involve a problem that an expansion ratio cannot be raised because the content of the blowing agent therein is low.[9] Therefore, in an attempt to study the effect of crosslinking density on expandable property, it is important that average particle diameters on each microspheres are approximately the same size. Average particle diameter obtained from a series of experiments is shown in runs 1–5 of Table III. Typical particle diameter distribution (run 1) is shown in Figure 3. The average particle diameters were in the range of 19.2–21.5 μm, suggesting these average particle diameters obtained cannot influence expandable property.

The relationship between expandable property and effectiveness of charge of crosslinking agent

Morphology of microballoon

The effect of expandable property on the content of crosslinking agent was investigated. The comparisons of morphology of microballoon obtained by heating at 180°C for 1 min were performed by using SEM. As is evident from Figure 4, the comparisons of morphology clearly indicated that the microbloon dimensions in runs 3 and 4 containing 0.038 and 0.076 mol % of DPE, respectively, were more uniform in shape and size than those in runs 1, 2, and 5 containing 0, 0.019, and 0.143 mol %.

Thermomechanical properties

As to the effect of expandable property on the content of crosslinking agent, comparisons of expansion curves obtained by using TMA were performed. Comparisons of expansion curves are shown in Figure 5. The values of T_{start}, T_{max}, and D_{max} are shown in Table III. As shown in Figure 5 and Table III, run 2 had the highest value of D_{max}, but showed a sharp expansion at T_{max}, followed by a sharp constriction, although runs 3 and 4 were shown to constrict gradually after T_{max} and had more heat resistance than others. On the process of various applications, microspheres having broader expansion temperature range are required. It is assumed that runs 3 and 4 had the optimum expandable property.

Crosslinking plays a very critical role during foam expansion. An optimally crosslinked polymer can expand, without collapse and rupture of microspheres. Excessive crosslinking restricts foam expansion, whereas insufficient crosslinking results in microballoon collapse and rupture. As shown in Figure 6, the polymer that exhibited a swelling ratio of about 20 has the optimum expansion at 180 and 190°C.

On using printing ink to get three-dimensional patterns and matt on wallpaper, it is required to have heat resistance without collapse of microballoon at about 200°C. We assumed from the experiment described above that crosslinking agents in runs 3 and 4 had the optimum amount. To confirm these, coating on expandable property on the coating was studied.

Expandable property on the coating

Expandable property on the coating was studied and samples of runs 2, 3, and 4 in Table II were used.

Figure 7 shows a plot of expansion ratio measured by changing of thickness of compound coated on at each temperature for 1 min. SEM images on the surface of coating are shown in Figure 8. As shown in Figure 7, run 3 had the highest expansion ratio and was excellent in heat resistance over 200°C. As shown in Figure 8, runs 3 and 4 had a high residual degree of particles on the surface of coating at 200 and 210°C, particularly 1 min, namely good matt.

In view of the expansion ratio and heat resistance, a swelling ratio of about 20–25 was needed to achieve optimum expansion.

CONCLUSION

(1) In expandable microspheres with a blowing agent enclosed in the shell of a polymer, it is necessary to optimize composition of shell polymer and particle size for obtaining a uniform microballoon having a high heat resistance.

(2) The crosslinking efficiencies of dipentaerythritol hexaacrylate in a set of thermoplastic microspheres were measured. In view of expansion ratio and heat resistance, as crosslinking density, a swelling ratio of about 20–25 is needed to achieve optimum expansion without collapse and rupture of microspheres.

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