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Microvoids in unsaturated polyester resins containing poly(vinyl acetate) and composites with calcium carbonate and glass fibers

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Abstract

When thermoplastics is added as a low-profile additive (LPA) to an unsaturated polyester (UP) resin, microvoids are introduced and compensate for the high volume shrinkage of the resin. The characteristics and mechanisms involved in the microvoid formation of a low-shrinkage UP resin system with poly(vinyl acetate) (PVAc) as LPA were investigated in this work. Both PVAc and styrene were found to play vital roles in controlling the microvoid formation. The voids were developed from an isolated type to an interconnected type by increasing PVAc content to reach a co-continuous phase structure of UP resin and PVAc, and their sizes were significantly enlarged by increasing styrene content. The microvoid formation was also affected by the curing conditions and compositions. It was enhanced by high curing temperature, but substantially restrained by an applied external pressure. When a filler was introduced to the PVAc-containing resin or when the resin was cured with *t*-butyl perbenzoate (TBPB), the number of voids increased. A foaming process, i.e. the surplus-styrene nucleation and expansion in the PVAc phase during the curing process, is considered to be the major mechanism for the microvoid formation. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Unsaturated polyester resin; Low profile additive; Microvoid

1. Introduction

The high-volume shrinkage of unsaturated polyester (UP) resin can be substantially reduced by adding some thermoplastics as an anti-shrinkage agent (low profile additive, LPA). This approach has solved the molding problems in UP resin applications, including poor surface appearance, warpage of molded parts, internal cracks and notable depression on the surface opposite thick sections [1]. It was found that many thermoplastics such as poly(vinyl acetate) (PVAc), poly(methyl methylacrylate) (PMMA), polystyrene (PS), polyethylene and polycaprolactones can act as LPA, [1–3]. However, the performance of these additives are quite different depending, to a large extent, on the chemical structure of these plastics. PVAc, PMMA and PS are considered to be most effective and are therefore widely used in industries.

The shrinkage mechanism has been investigated for decades. Bartkus and Kroekel proposed that free monomers tend to boil and exert adequate pressure to counteract the shrinkage of UP resin leaving foam-like occlusions in the cured resin [4]. Pattison et al. suggested that a strain relief through microcracks happens in LPA domains and at UP/LPA interfaces, which compensates the shrinkage [5,6]. Atkins attributed the shrinkage compensation of UP resin to the thermal expansion of LPA, which depended on the coefficient of thermal expansion in addition to the dissolution of styrene in PVAc plasticizing the polymer and reducing its T_g of LPA [1]. Although the mechanism has not been fully understood, it is generally accepted that the shrinkage compensation is due to the stress-related microvoid formation in the LPA phase and interfacial regions between LPA and UP resin [7–10].

A phase separation between LPA and UP resin during the curing process is a necessary condition for stress cracking because it provides a LPA phase and its interface with UP. The separation is believed to occur at the very beginning of the curing process and is related to the chemical structure, molecular weight and dipole moment data of LPAs [1,10]. Microvoid formation occurs after the phase separation and develops markedly at a vinyl conversion of about 50% [8,10]. The volume fraction of microvoids increases with increasing LPA content. The more the microvoids are formed, the better the shrinkage compensation can be achieved.

A large number of microvoids in a cured system is good for shrinkage control but could be disastrous for mechanical

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properties. Polymeric foam, which is characterized by negative shrinkage (i.e. expansion) and very poor mechanical properties, is an extreme example of such an effect. A substantial reduction in mechanical properties, in fact, was found when PVAc content in a low-profile resin was elevated to some critical levels [11–14]. This indicates that the shrinkage reduction should be balanced with the retention of mechanical properties in LPA applications. How to achieve this goal, however, depends greatly on manufacturing processes. For example, a high content of LPA is required to obtain the balance for compression molding, [1] but much lower LPA content is needed for pultrusion processes for reasonable mechanical properties. An understanding of microvoid formation is, therefore, very fundamental for the application of LPA. In this work, the characteristics and mechanisms of microvoid formation in an UP resin containing PVAc and its composites with $CaCO_3$ and glass fibers were investigated.

2. Experimental

2.1. Materials

The commercial UP resin, supplied by Alpha/Owens-Corning, was a copolymerization product of 40 mol% maleic anhydride (MA), 10 mol% orthophthalic acid (PA), and 50 mol% propylene glycol (PG), measured by a ^{1}H NMR spectrometer. The resin contained 70 wt.% solid unsaturated polymer (UP) and 30 wt.% styrene monomer measured by a combined precipitation/evaporation method.

The low-profile additive was LP90 (supplied by Union Carbide), a 60/40 mixture of styrene with PVAc. Methyl ethyl ketone peroxide (MEKP, half-life time $t_{1/2} = 10$ h at about 140°C) by Adrich, *t*-butyl perbenzoate (TBPB, $t_{1/2} = 10$ h at 101°C, $E_d = 134$ kJ/mol, mw = 194) by Akzo, di-(4-*t*-butyl-cyclohexyl) peroxydicarbonate (P16N, $t_{1/2} = 10$ h at 43°C, $E_d = 124$ kJ/mol, mw = 398) by Akzo were used as radical initiators. In most cases, 1.2 wt.% of MEKP based on the received resin was used in the experiments. However, a binary initiator system of P16N/TBPB = 3/4 with a total amount of 1.2 wt.% on the resin was used to prepare the mixture for fabricating glass fiber-reinforced composites. TBPB was also used for comparison with MEKP. The calcium carbonate ($CaCO_3$) fillers were a product of Steep Rock Resources Inc. with an average particle size of 7 μm.

Mixing of all the ingredients was carried out at room temperature with a stirrer speed at about 400 rpm. The mixtures with various compositions were poured into aluminum dishes, degassed and then cured in an oven at a constant temperature of 70–80°C or 120–140°C for 40 m. For composite preparation, a mixture containing $CaCO_3$ was pasted onto glass mats which were then wrapped with aluminum foil and placed in an open mold heated to 70°C. An external pressure was used to expel extra resin mixture and keep the mold closed. After 6 m, the partially reacted samples were then further cured at an elevated temperature of 120–140°C with or without the pressure for 30 m. A post-cure treatment at 120–140°C for 40 m was applied for all the samples prior to analytical measurements.

2.2. Measurements

Morphology studies with a scanning electronic microscope (Philips SEM-515), were carried out on the Au/Pd coated fractured surfaces of the samples. Selected samples were etched with methyl ethyl ketone for 30 m to dissolve PVAc at the fractured surface for further phase investigation.

The reaction of resin mixture was isothermally traced by a DuPont 910 differential scanning calorimeter (DSC) by placing the mixture in a hermetically sealed aluminum pan. The glass transition temperatures of the cured samples were also measured with the DSC at a heating rate of 10°C/min.

The densities of cured samples were determined by weighing the samples, which were carefully ground, polished and then dried, in air and in distilled water, respectively. Water adsorption of the samples was measured as the weight gain of the dried samples after they were immersed in distilled water at 25°C for 30 h. Void content of the cured samples were determined using the measured density data according to the following equations [15]:

$$V_v = (D_{ct} - D_{ce})/D_{ct} \tag{1}$$

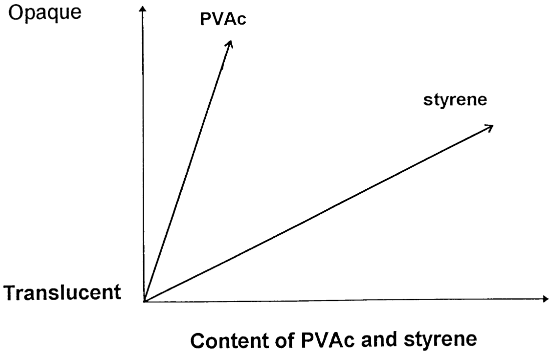
$$D_{ct} = 1/\sum_{i=1}^{n} (W_i/D_i) \tag{2}$$

where V_v is the volume content of voids, D_{ce} the measured density of the sample with multiple phases, D_{ct} the theoretical density calculated by the weight content (W_i) and density (D_i) of *i* phase, and *n* is the total number of phases in the sample. For a sample consisting of UP, styrene and PVAc, for instance, the density of the UP/styrene copolymer cured under the same conditions and the density of PVAc were used for the calculation. PVAc was obtained by evaporating styrene from the PVAc/styrene solution of LP90. Since PVAc does not participate in the chemical reactions of the UP resin [8–10,12], it is treated as an independent component.

Flexural properties of the glass mat-reinforced composites were measured with a Lloyd Instrument. Four-point bending with a support span of 30 mm and a loading span of 20 mm was applied. The standard deviation was kept less than 15.6 MPa for strength and less than 0.53 GPa for the modulus.

Table 1
Effects of PVAc and styrene on microvoids in UP resin

UP/St./PVAc	Sample appearance	Density (g/cm^3)	Void content (vol%)	Water adsorption (wt.%, 30 h/25°C)
100/55.7/8.6	Translucent	1.243	0.56	0.87
100/58.3/10.3	Translucent/ opaque	1.231	0.81	1.18
100/64.3/14.3	Opaque	1.125	8.41	6.02
100/70/8.6	Opaque	1.210	1.31	0.89
100/84.6/8.6	Opaque	1.112	6.79	1.87



3. Results

3.1. Effects of PVAc and styrene on microvoid formation

Fig. 1 shows the fractured surfaces of the cured PVAc-containing UP resins under SEM. The samples without PVAc but with the same amount of styrene as those containing PVAc were also analyzed for comparison purposes. The compositions of the resin mixtures are expressed as parts relative to 100 parts of solid UP. Microvoids, as can be seen in the figure, were not generated simply by raising the styrene level, but were induced when a small amount of PVAc was added into the resin. Apparently, PVAc plays a vital role in the development of microvoids. A co-continuous phase between UP resin and PVAc was achieved when the PVAc level was raised to 14.3 parts (Fig. 1(d)). Meanwhile, styrene showed a co-effect with PVAc on the microvoids and enlarged the microvoid size when its content was greatly increased, e.g. from 55.7 parts (Fig. 1(b)) to 84.6 parts (Fig. 1(f)). A further increase in styrene level to over 100 parts resulted in an expansion-like split of the sample when cured at 120–140°C.

Table 1 summarizes the microvoid content and other void-related characteristic parameters of the cured samples. The void content increased with increasing PVAc level and/or styrene level. It is of interest to note that the co-continuous structure achieved by increasing PVAc (third line of Table 1) is characterized by both high void content and high water adsorption. Meanwhile, the high-void samples (the bottom line) achieved by raising styrene content adsorbed much less water. It suggests that the microvoids in the samples with co-continuous UP resin/PVAc phases are somehow interconnected.

With increasing PVAc and/or styrene content, the sample appearance changed from translucent to opaque, reflecting the change in the size and density of the microvoids. Note that the samples composed of two distinguished parts, i.e. translucent and opaque parts, were obtained between the compositions corresponding to completely translucent samples and opaque ones. When PVAc or styrene level was raised to the region, the percentage of opaque part in the samples increased. The transition of translucent-to-opaque is more sensitive to PVAc than to styrene. Using SEM, it was observed that the microvoids in the opaque part of such samples were larger than those in the translucent part. An inhomogeneous morphology in a PVAc-containing UP resin was also reported by Bucknall when PVAc was at 4% [12]. It is difficult to explain this segregation phenomenon from the reported UP-styrene-PVAc phase behavior [8,16]. Further investigations are needed.

3.2. Effects of curing temperature and initiator on microvoid formation

Microvoid formation depends greatly on curing temperature. As shown in Fig. 2(a), a small number of fine voids were formed when a mixture of UP/St/PVAc = 100/64.3/14.3 was cured at 22–25°C by MEKP/cobalt dusyn. In this case, PVAc is more likely to be dispersed within the inter-particle region of the UP resin as very fine domains were revealed by etching the surface (Fig. 2(b)). The T_g value of the PVAc phase in the sample was measured by DSC to be 45–48°C and was identical to that of virgin PVAc. It indicates that the phase separation between the UP resin and PVAc was complete in the sample. The sample was translucent, low porous and low-water adsorptive (as seen in Table 2). The water adsorption was, in fact, similar to that of the sample containing the same level of UP and styrene but without PVAc.

When the resin was cured by the same amount of MEKP at 70–80°C, much more and larger microvoids were formed in the materials (Fig. 2(c) and Table 2). By etching the surface, it was observed that the corresponding morphology was co-continuous with PVAc mostly coated on the particle surfaces of the UP resin. However, the void size and volume content were much lower than those cured at 120–140°C (Fig. 1(d) and Table 2).

It was also found that the initiator type had a significant effect on the microvoid formation. As shown in Fig. 2(d) and Table 2, for the same resin compositions, *t*-butyl perbenzonate (TBPB) resulted in a very porous structure when the resin was cured at 70–80°C. Some big voids over 1 μm were clearly seen in the fractured surface. The corresponding water adsorption was also much higher than that of the resin cured by MEKP at the same temperature or even higher temperatures. No significant effect, however, was observed by changing the initiator content. At a fixed temperature, the microvoid content increased only slightly with the increase of initiator content.

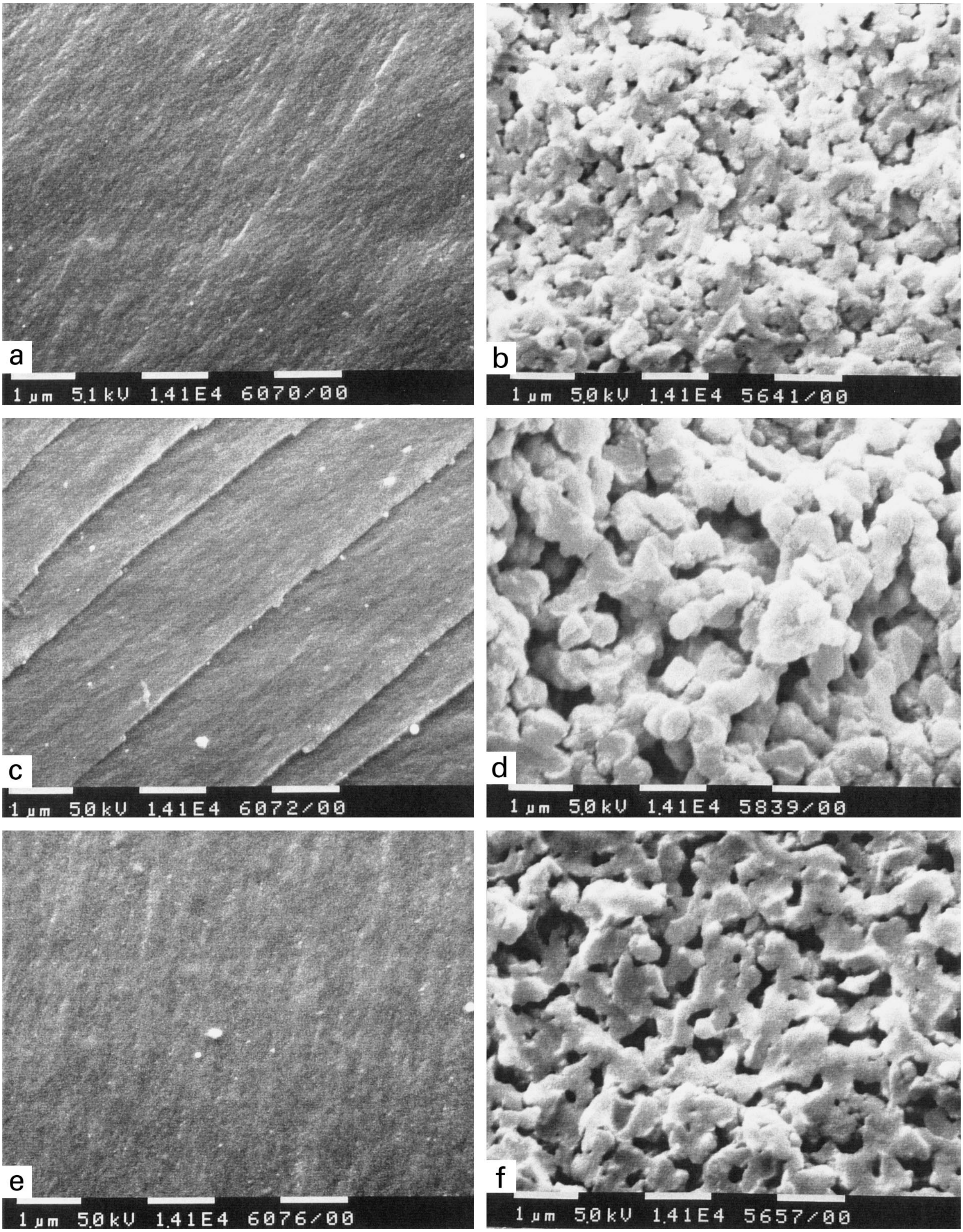


Fig. 1. SEM micrographs of the fractured surfaces of PVAc-containing UP resins: the effects of PVAc and styrene on the microvoid formation. These resins were cured by 1.2 wt.% MEKP at 120–140°C. UP/St/PVAc: (a) 100/55.7/0; (b) 100/55.7/8.6; (c) 100/64.3/0; (d) 100/64.3/14.3; (e) 100/84.6/0; (d) 100/84.6/8.6.

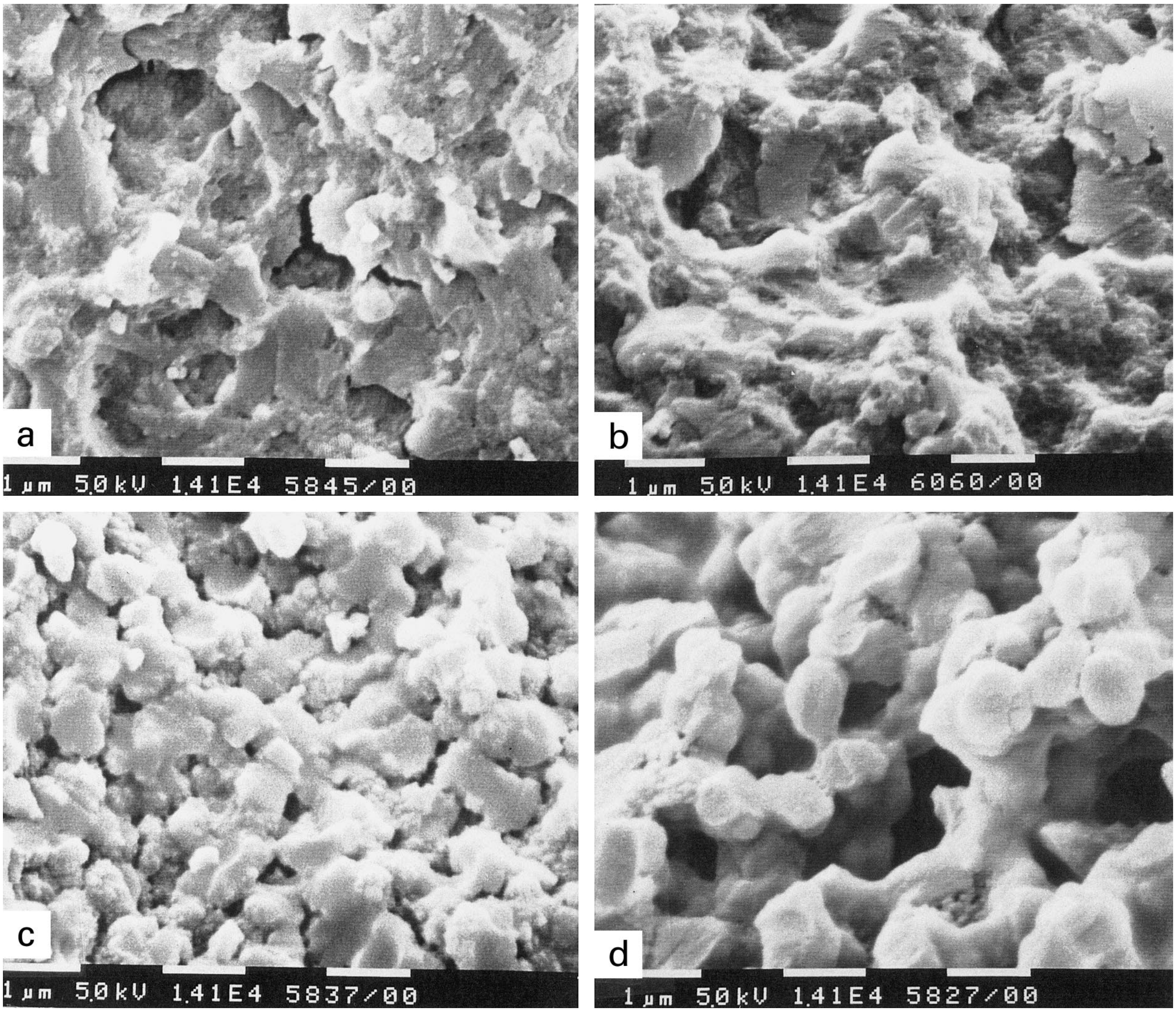


Fig. 2. SEM micrographs of the fractured surfaces of PVAc-containing UP resins: the effects of temperature and initiator type on the microvoid formation. UP/St/PVAc: 100/64.3/14.3. This resin was cured by: (a) and (b) 1.2 wt.% MEKP/cobalt dusyn at 22–25°C; (c) 1.2 wt.% MEKP at 70–80°C; and (d) 1.2 wt.% TBPB at 70–80°C. Sample (b) was etched with methyl ethyl ketone (MEK).

Table 2
Effects of curing temperature and initiator on microvoids in UP resin containing PVAc (UP/St./PVAc = 100/64.3/14.3)

Curing temperature (°C)	Initiator		Sample appearance	Density (g/cm^3)	Void content (vol%)	Water adsorption (wt.%, 30 h/25°C)
	Type	Concentration (wt.%)				
22–25	MEKP/Cobalt[a]	1.2	Translucent	1.219	0.81	0.46
70–80	MEKP	0.6	Opaque	1.157	5.86	4.65
70–80	MEKP	1.2	Opaque	1.156	5.94	4.79
70–80	MEKP	2.4	Opaque	1.151	6.34	5.01
70–80	TBPB	0.6	Opaque	1.072	12.77	8.77
70–80	TBPB	2.4	Opaque	1.048	14.73	9.40
120–140	MEKP	0.6	Opaque	1.130	8.06	6.05
120–140	MEKP	1.2	Opaque	1.125	8.46	6.02

[a] 10% cobalt dusyn on MEKP.

3.3. Effect of fillers on microvoid formation

The filler ($CaCO_3$) was found in favor of microvoid formation. As shown in Fig. 3, for the same base of UP/St/PVAc = 100/55.7/8.6, the microvoid size was enlarged when the filler was added into the resin mixture (compared to Fig. 1(b)). The sample appearance changed from translucent to opaque, corresponding to the increase in

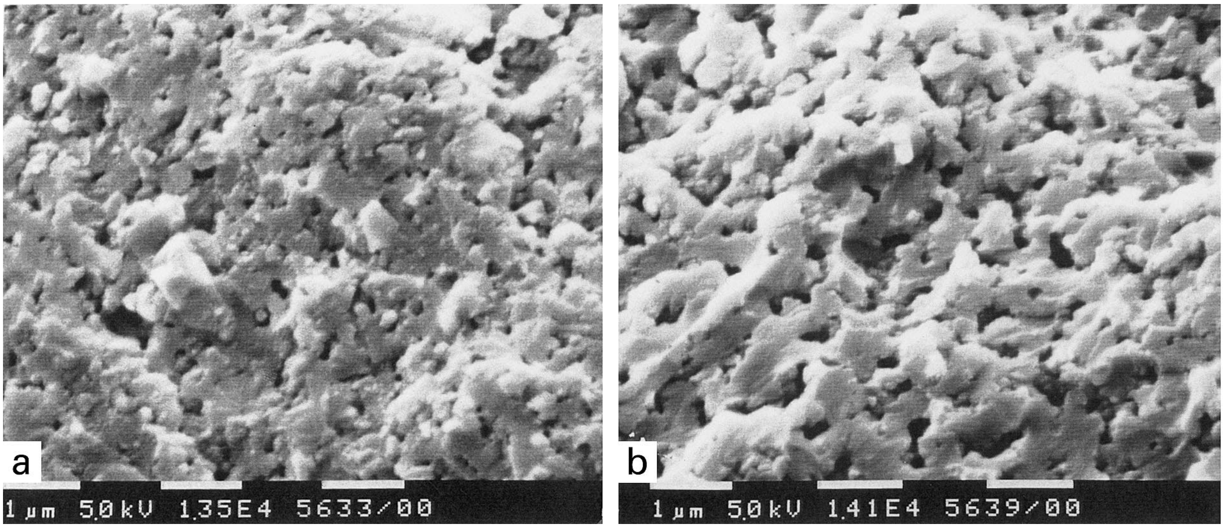


Fig. 3. SEM micrographs of the fractured surfaces of PVAc-containing UP resins: the effects of the filler ($CaCO_3$) on the microvoid formation. UP/St/PVAc: 100/55.7/8.6. The resin was cured by 1.2 wt.% MEKP at 120–140°C. The $CaCO_3$ contents were: (a) 14.3 wt.%; and (b) 29.0 wt.%.

void content and water adsorption (as presented in Table 3). However, no filler effect was observed if PVAc content was reduced to 7.1 parts even if the filler content was increased to 45 wt.% in the total mixture. It means that the fillers can only affect the microvoid formation when the PVAc content is elevated to a certain critical level.

3.4. Effect of external pressure on microvoid formation

Microvoid formation is very sensitive to external pressure applied during the curing process. Fig. 4 illustrates the effect of applied external pressure on the sample appearance for a mixture of UP/St/PVAc/filler = 100/64.3/14.3/35.7. This composition corresponds to a co-continuous structure if the resin is cured at 70–140°C. It was also used for matrix and glass mat reinforcements with 17 wt.% of the final composites as measured by a decomposing method. Samples cured under pressure appeared translucent. Samples cured totally without pressure or cured partially with pressure followed by successive curing under pressure appeared opaque or partially opaque. It indicates that the external pressure restrained the microvoid formation in the composite matrix. Since the glass mats used were very hard, and the composite samples obtained by pressure-free curing were too loose for reasonable measurements, further comparisons of composite morphology and properties were made between full-pressure cured samples (translucent) and partial-pressure cured samples (translucent in the central part with 70–80% in total thickness and opaque skin layer with 20–30% total thickness).

Table 3
Effects of calcium carbonate on microvoids in UP resin containing PVAc (UP/St./PVAc = 100/55.7/68.6)[a]

$CaCO_3$ content (wt.%)	Sample appearance	Density (g/cm^3)	Void content (vol%)	Water adsorption (wt.%, 30 h/25°C)
14.3	Translucent	1.342	0.86	0.86
24.1	Translucent/ opaque	1.413	1.68	0.92
29.0	Opaque	1.451	1.89	1.33

[a] Cured with 1.2 wt.% MEKP at 120–140°C.

Fig. 5 shows the SEM graphs of full-pressure cured samples and the opaque parts of partial-pressure cured samples. Analysis was carried out on the polished cross sections because it was difficult to directly observe the matrix in a fracture surface due to the influence of glass fibers. Although it was possible for the thin films produced in polishing to overlap the microvoids, a significant difference was still observable between the two samples (compare Fig. 5(a) with (c)). After surface etching with methyl ethyl ketone (a good solvent of PVAc), the difference became more visible (Fig. 5(b) with (d)). The UP resin particles in the full-pressure cured samples were well bounded with small in-between voids. The particles in the opaque part of partial-pressure cured samples, however, were separated by microvoids of large sizes so that very rough surfaces were produced.

Table 4 presents the physical and mechanical properties of the above composites. The fiber contents in the two samples were the same (17 wt.%), but the density, water adsorption, flexural strength and flexural modulus of the full-pressure cured samples were higher than those of their of partial-pressure cured counterparts. The reduction in porosity by external pressure resulted in denser materials with improved mechanical properties. However, the pressure effect was not found when mixtures containing low PVAc contents were used to fabricate the composites. The pressure can constrain the void formation only for high-void producible mixtures.

Table 4
Effects of pressure on the properties of UP resin composites containing PVAc

UP/St/PVAc/$CaCO_3$	Sample preparation (glass mat as reinforcement)	Sample appearance	Density (g/m^3)	Water adsorption (wt.%, 25°C for 30 h)	Flexural strength (MPa)	Flexural modulus (GPa)
100/72.4/14.3/35.7	Cured under pressure[a]	Transculent	1.406	0.86	143.6	8.55
	Partially cured under pressure and continuously cured without pressure[b]	Transculent/opaque	1.379	3.18	121.7	7.27
100/66.4/7.1/77.1	Cured under pressure[a]	Transculent	1.532	0.98	144.7	9.48
	Partially cured under pressure and continuously cured without pressure[b]	Transculent	1.532	1.04	148.0	10.41

[a] As indicated in Section 2.
[b] As indicated in Fig. 4.

4. Discussion

4.1. Characteristics of microvoids

The curing process of UP resin, i.e. the copolymerization of UP with styrene, is a free-radical chain-growth crosslinking with inhomogeneous characteristics. Basically, there are four stages involved in the process: induction, microgel formation, transition and macrogelation [17–19]. The cured resins consist of interconnected microgel particles [20]. As one of the most effective low shrinkage additives (LPA), PVAc enhances the intramolecular reactions of UP and the microgel formation during curing [21]. More importantly, PVAc can act as a segregating agent for the

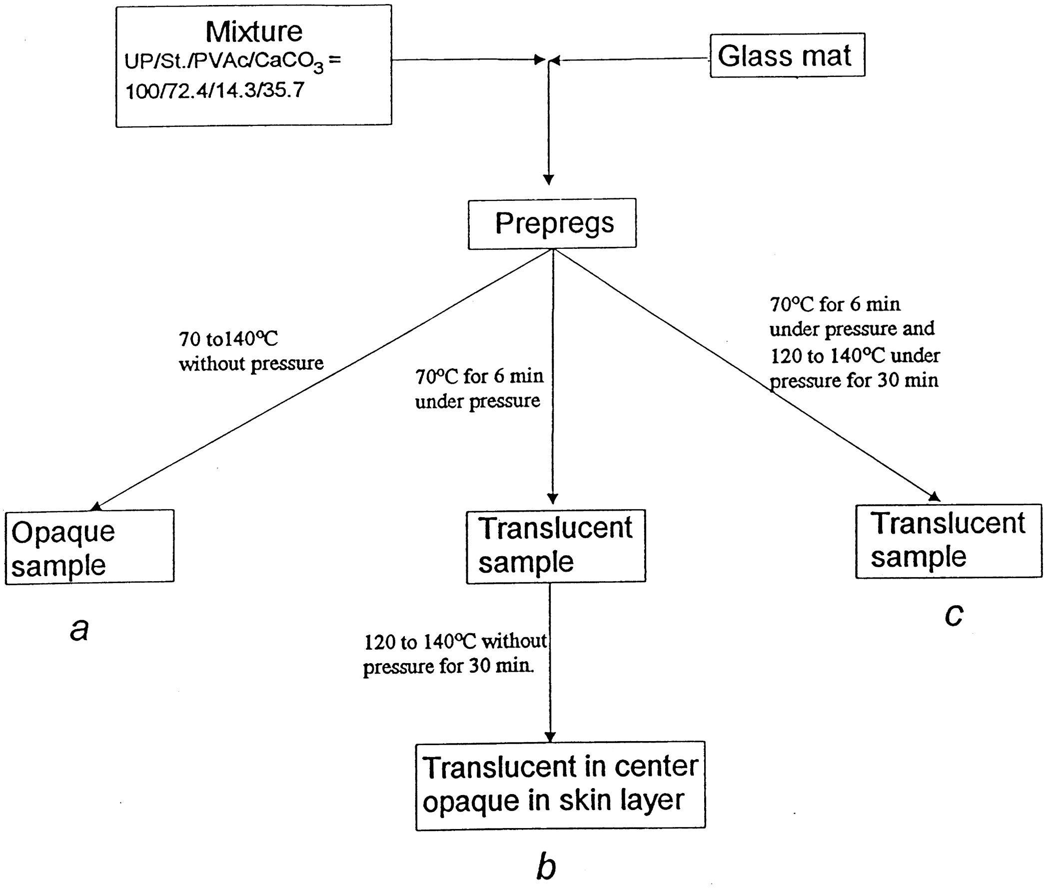


Fig. 4. Illustration of the external pressure effect on sample appearance. UP/St/PVAc/$CaCO_3$: 100/72.4/14.3/35.7. (a) Pressure-free curing. (b) Partial-pressure curing. (c) Full-pressure curing.

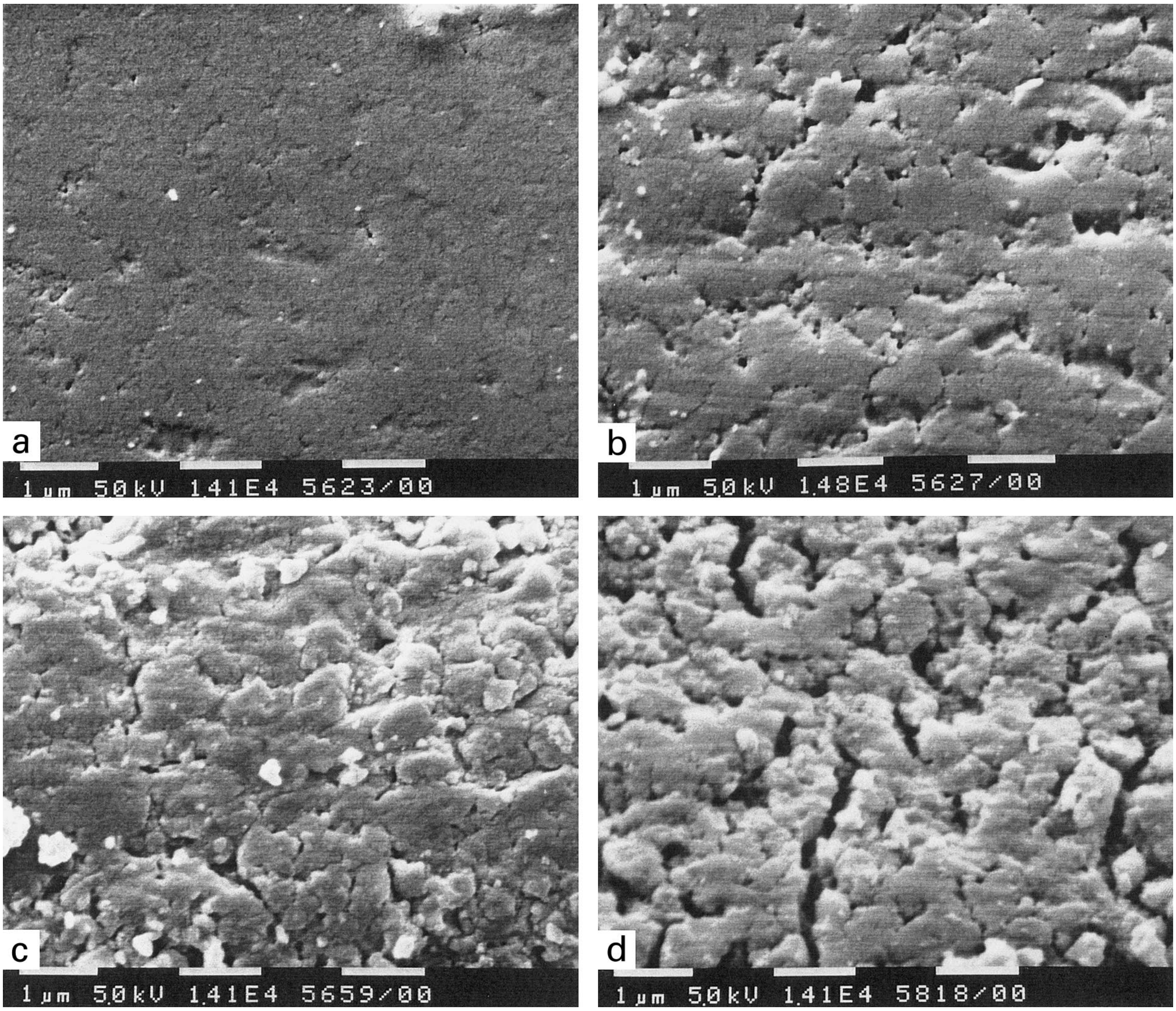


Fig. 5. SEM micrographs of the polished surface of PVAc-containing UP resin composites. UP/St/PVAc/$CaCO_3$: 100/72.4/14.3/35.7. (a) and (b) cured under pressure; (c) and (d) partially cured with pressure and successively cured free of pressure as indicated in Fig. 4. Samples (b) and (d) were etched with MEK.

microgels [9,10]. When the microgel phase migrates from the PVAc-containing mixture, a layer of PVAc coats the microgel particles and prevents the particles from merging. As a result, partially interconnected UP resin particles are formed. PVAc, as revealed by the etching method, resides mostly in the open surfaces of the particles (Fig. 2(b)).

Fig. 6 presents a simple model, which can be used to illustrate the microvoid formation on the basis of the microgel-formation mechanism. The microvoids are classified as isolated (Fig. 6(b)) and interconnected (Fig. 6(c)) types based on the morphology analysis discussed earlier. Isolated microvoids are formed with low PVAc contents. An increase in styrene enlarges the voids. Interconnected microvoids, on the contrary, are formed when the PVAc content is high enough to generate a co-continuous structure between UP resin and PVAc. The connection of microvoids may deteriorate the materials mechanically. The literature recommended the low-shrinkage co-continuous void structure for commercial applications [11,12]. However, such a structure is not considered ideal for pressure-free or low-pressure processing. In case no external pressure is applied, a good balance between shrinkage reduction and mechanical property retention is suggested to be achieved by generating bigger but isolated microvoids, i.e. expanding the voids in Fig. 6(b).

For both types of microvoids, their profiles are related to curing conditions. Increasing the curing temperature makes the microvoid profiles smoother. It is interesting to note that very smooth profiles were observed for the microvoids generated using TBPB as an initiator (see Fig. 2(d)). The reasons for this are not clear and it requires further investigations.

When an external pressure is applied during the curing process, both size and shape of the microvoids are substantially altered. As shown in Fig. 5, the microvoids in the full-pressure cured samples are much smaller and less interconnected than those in the partial pressure-cured samples.

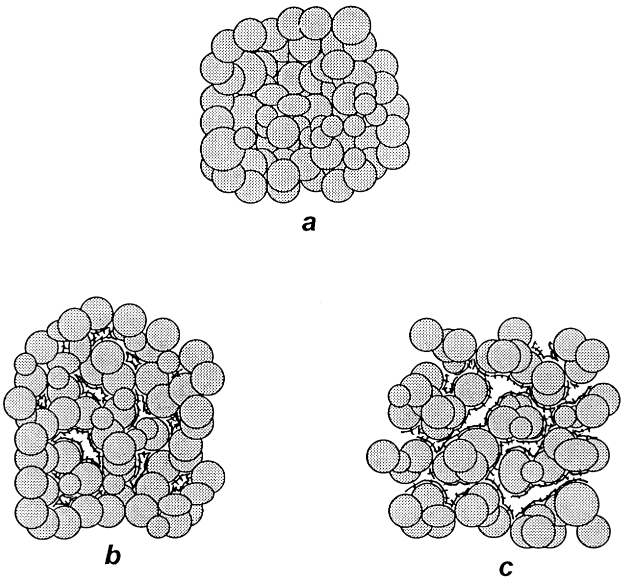


Fig. 6. Illustration of the morphology of cured PVAc-containing UP resin. (a) UP resin. (b) Low PVAc-containning UP resin. (c) High PVAc-containning UP resin. Shaded circles represent microgel particles and (+ + + +) the PVAc phase.

Note that the resin mixture for fabricating the composites can result in a co-continuous structure. For the partial-pressure cured samples, it is believed that the microvoids were developed after the pressure was released (as indicated in Fig. 4(b)) because the samples changed from translucent to opaque appearance after the pressure was released and the resin was further cured. But the observation that the microvoids preferred to develop in the skin part is difficult to explain. One possible reason is that there existed a substantial residual stress in the samples after they were partially cured under external pressure, and such stress still restrained the microvoid formation in the central part after the external pressure was released.

4.2. Mechanism of microvoid formation

Several mechanisms were proposed to explain the microvoid formation. Among them, the strain relief by cracking in the LPA phase and at the interface between the UP resin and LPA has been accepted by most researchers [5–10]. In this work, however, cracking is not considered the principal mechanism of microvoid formation. It is known that the total volume shrinkage of UP resin is about 7%, [10,21] which corresponds to a linear shrinkage of 2.4% in the system. This small strain is far below the elongation of rubbery PVAc and too small to cause cracking [22]. In addition, the reaction in the UP resin takes at least minutes to complete which is slower than the typical intrinsic relaxation response of rubbery polymers to a mechanical strain.

Bartkus and Kroekel suggested that surplus styrene is left in the PVAc-rich phase after microgel particles are phased out of the mixture [4]. The styrene molecules either: (1) diffuse out of the phase to react with microgel particles (termed as diffusion reaction); or (2) remain in the PVAc-rich phase; or (3) phase out to form a styrene phase within PVAc. The diffusion reaction does not consume all the styrene because residual styrene can always be detected in the cured UP resin containing LPA [8]. Between the rest of the two possibilities, the phase separation is more likely to occur, considering the effect of reaction heat. Each microgel particle is acting as a microheater, which heats the neighboring styrene-containing PVAc phase. Such heat may cause the phase separation of styrene with PVAc followed by the bubble nucleation and expansion of styrene in PVAc. This mechanism is similar to polymer foaming: saturate or mix the polymer with a blowing agent and then heat the mixture to nucleate and expand bubbles [23]. In the UP resin-PVAc system, the heat is supplied by the curing reaction itself.

LPA forms a layer of skin covering the bubble to keep styrene pressure and, more importantly, to prevent the contact and thereby reaction of styrene with surrounding reactive microgel particles. The expansion of styrene within PVAc compensates the shrinkage of microgel particles. The shrinkage eventually stops and the bubbles become microvoids in the resin.

On the basis of this foaming mechanism, the revealed effects of styrene, curing temperature and external pressure on the microvoid formation can be readily explained. When styrene content is increased, more styrene is trapped in PVAc and phased out, boosting expansion and thus enlarging microvoids. The nucleation and expansion of styrene are enhanced by increasing curing temperature but are restrained by applying an external pressure during the curing process. Therefore, more and bigger microvoids can be obtained at higher temperatures and the microvoid content can be dramatically reduced when external pressure is applied.

The enhanced microvoid formation by the $CaCO_3$ filler can be attributed to an assisting effect of the filler on the bubble nucleation. Small particles usually provide sites for the bubble nucleation in a polymer matrix and are widely used as nucleating agents in the foaming processes. $CaCO_3$ is believed to play a similar role in the present system. Meanwhile, the more porous structure caused by initiating the reaction with TBPB might be related to its released carbon dioxide which can act as an additional blowing agent.

4.3. LPA applications

Substantial external pressure is usually applied for compression molding, injection molding or transfer molding, and can substantially restrain the microvoid formation. Therefore, a high content of LPA must be used in sheet molding (SMC) and bulk molding compounds (BMC) to trap more styrene and to nucleate more bubbles so that the final microvoid content can fully compensate the shrinkage of UP resin. This is the reason why the LPA content in a commercial formulation [1] is higher than the reported critical content for the co-continuous structure development [11,12].

In a pultrusion process, however, the situation is different. It was reported that there is an initial pressure in the pultrusion die when styrene is heated to expand. When the pultrusion profile begins to shrink, however, it experiences a pressure-free curing process [24]. It means that the microvoid formation, which develops markedly at a monomer conversion of about 50% [8], occurs in the pressure-free part of the die. In addition, relatively high temperatures, which enhance the microvoid formation as revealed earlier, are usually applied to keep high reaction rates in the die for a high-speed production. Very weak materials with interconnected microvoids may be thus produced by the pultrusion process even when a relatively low content of LPA, compared with SMC and BMC processes, is applied to the resin system.

A principle for the application of LPA can be summarized from the above analysis. The LPA content should be adjusted according to the type of process. High LPA contents should be used for the manufacturing processes with external pressure such as SMC and BMC, but low contents for the pressure-free processes such as pultrusion. More precisely, the critical LPA content, which corresponds to a co-continuous structure under the pressure-free condition, is suggested as the parameter for applying LPA. The LPA content can be above this critical value for the processes with external pressure, but it must be kept below this value for the pressure-free processes to retain profile mechanical properties.

5. Conclusions

Microvoids were formed in the UP resin curing when PVAc was added. The void formation was to a large extent controlled by PVAc and styrene. Isolated microvoids developed into interconnected ones with the increasing PVAc content and were significantly enlarged by adding a large amount of styrene. Curing temperature, initiator, filler content and external pressure also affected the formation of microvoids. High curing temperature and high filler loading enhanced the microvoid formation, while the external pressure substantially restrained the microvoid formation. In addition, when the initiator methyl ethyl ketone peroxide (MEKP) was replaced by *t*-butyl perbenzoate (TBPB), more voids were formed in the resin. It was suggested that the microvoid formation did not arise from the strain-relief cracking but from the nucleation and expansion of surplus styrene in the PVAc-rich phase. The microvoid formation was explained as a foaming process in which styrene was phased out of PVAc, nucleated and expanded by the reaction heat.

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