Comparing these calculated values with the measured data, good agreement is found, though the latter values are smaller by about 70×10^{-6} . A possible reason for the measurements being smaller than the calculated values is that the actual thermal expansion coefficient at younger age is slightly different from the analytical value. Another possible reason is some experimental errors.

On the basis of the considerations above, the reasons for setting shrinkage fall into two large categories, that is polymerization during setting of liquid resin, and lowering of temperature after the maximum temperature is reached. The shrinkage mechanisms due to these reasons are summarized as follows.

a) Shrinkage due to polymerization :

Liquid resin before setting, which is a low molecular substance, becomes a high molecular substance through polymerization, where three dimensional carbon-to-carbon combinations are generated, resulting in a higher density of molecules forming the substance. This creates a decrease in volume, namely, shrinkage.

b) Shrinkage due to temperature decrease :

Heat generated by a setting reaction brings up the inner temperature to a certain level, but beyond such level, the inner temperature slopes down to the ambient level. Along with this temperature lowering, there occurs a shrinkage corresponding to the thermal expansion coefficient.

The strain behavior at the constant ambient temperature of 20° C is classified in the three states (a) to (c) illustrated in Fig. 2. The portion (a) is considered as expansion attributable to heat produced by polymerization. In the total shrinkage ((a) + (b) + (c)), almost all the shrinkage of (a) + (b) can be supposed to be caused by polymerization, while the shrinkage of (c) to be almost thoroughly attributable to temperature decrease. Therefore, 75 % of the total shrinkage is by setting and 25 % by temperature decrease.

Study on the methods for reducing the shrinkage

Confinement of setting shrinkage can be achieved by use of steel bars or fibers. When reinforced with steel bars, setting shrinkage is confined by the reinforcement, which generates tensile stress inside PC, reducing its tensile strength. Besides, the greater the steel ratio, the smaller the cracking load (2). In contrast, fibers reinforce PC itself, so its tensile strength may be improved. In addition, since fibers are oriented in a three dimensional manner, setting shrinkage in every direction can be confined. It is therefore more effective to add fibers. The effect of fiber dosage may vary with bonding strength between fibers and matrix, as well as modulus of elasticity of the fibers. We studied the cases with two kinds of fibers, namely, steel and vinylon.

For reducing the amount of shrinkage itself, either shrinkage due to polymerization or shrinkage due to temperature decrease, it is most effective to diminish the amount of liquid resin. The authors, focusing upon the filler which is one component of PC, have been studying the influence exerted upon the performance of PC by the particle size, shape and surface properties of fillers. The study demonstrated that the liquid resin amount can be reduced if an appropriate filler is used (6,7). Then, we investigated two cases of fillers effective for reducing the liquid resin amount, that is, filler with modified surface and spherical particle filler. Additionally, we studied the case of reducing the liquid

736 Kawamura, Kuromoto and Iwai

resin amount using a surface-active agent widely used for dispersing pigment particles in paint.

The measurements of strain and inner temperature in Tests II are shown in Figs. 6 and 7. The properties of the different mixtures in their fresh state are shown in Table 6, while the strength test results at 28 days in Table 7. When implementing Tests II, for improving the abrasion resistance by increasing the compressive strength, the composition of liquid resin was changed a little, and the content of PMMA was made slightly smaller than that in Tests I.

The properties of the fresh mixtures are summarized below.

- a) Since, with fibers mixed, the slump becomes smaller although the amount of liquid resin is the same, the consistency is lower.
- b) When alumina A-ST is used, no slump decrease is observed, though the liquid resin amount is smaller by 1.0% in weight. But the viscosity becomes slightly greater. When alumina B is used, the slump is smaller, because the liquid resin amount is smaller by 1.5% in weight, presenting a reduced consistency.
- c) When a dispersing agent is used, although the liquid resin amount diminishes by 1.5% in weight, the slump becomes significantly larger. In this case, no material segregation was observed, but the viscosity was considerably greater.

Comparing the measurement results of Mixture 1 with the graph in Fig. 2, we know that the tendency at the transition from expansion to shrinkage is slightly different, that is to say, it takes little more time to reach the maximum expansion, and almost the same tendency is found for the inner temperature, though it takes little more time to reach the maximum expansion. The time span for reaching to the maximum strain can be explained by the longer time to reach the maximum temperature. It may be due to a lower temperature at the mixing completion, by about 2° C. The difference in setting shrinkage may be caused by the fact that the content of PMMA in the liquid resin is different from Tests I to Tests II. The powder of thermoplastic polymer, such as PMMA, solved in the liquid resin must have behaved like a shrinkage reduction additive in PC. The content of PMMA has also influenced on the compressive strength and the static modulus of elasticity at 28 days; they are larger by 27 MPa and 8GPa respectively in Tests II. Since the content of PMMA is greater in the liquid resin in Tests I, the specimens have a larger plasticity.

Now look at the measurements of the Mixture 2 and 3. There is no significant variation due to the difference in kind of fiber. Comparison with the measurements of the Mixture 1 demonstrates almost the same tendency of inner temperature, including the maximum temperature level. As for the magnitude of strain, both expansion and shrinkage are smaller. This means decrease of shrinkage amount by 17 to 21%. By the measurement results of the Mixtures 4 and 5, we know that change in filler properties causes a significant change in the inner temperature and strain behavior. With alumina A-ST, comparison with the measurements of the Mixture 1 shows that it takes longer time by about 5 minutes for the inner temperature to reach the maximum, and the maximum temperature is 5° lower. Through comparison of the strain behavior, it is known that the expansion presents no distinct peak, and gets smaller in general, and the shrinkage

too is smaller. This means decrease of shrinkage amount by about 60%. Such strain behavior is found in the case using alumina A-ST, with 7.5% in weight of specific liquid resin (7). This type of behavior is intrinsic to the case with filler surface modified with silane. When alumina B is used, comparing with the measurements of the Mixture 1, the time for the inner temperature to reach the maximum is about 20 minutes longer, and the maximum temperature is lower by 5°C. Consequently, the time up to the maximum expansion is about 15 minutes longer, but almost no difference is found in expansion strain behavior. On the other hand, the shrinkage is smaller, which is translated by about 35% smaller shrinkage amount. The graph for the Mixture 6 comparing with the results of the Mixture 1 shows 5°C lower maximum of inner temperature, and both expansion and shrinkage are smaller. Accordingly, the shrinkage amount is about 15% smaller.

In the cases with fibers mixed, because the mixture proportion is not changed, the inner temperature of PC is approximately equal to that without fibers; thus, the shrinkage amount of PC itself is not changed; but, both expansion and shrinkage diminish, regardless of the kind of fiber, due to confinement effect. The reduction rate of shrinkage is about 17% with steel fibers, while 21 % with vinylon fibers. So there is no remarkable difference due to the kind of fibers at the mixture ratio of steel fibers Vf=0.38%, that of vinylon fibers Vf=0.75%. By comparing the fiber mixture ratio with the reduction rate of shrinkage, we recognize the larger confinement effect of steel fibers. This can be explained by the hook shaped steel fibers which increase the adhesion with PC. This fact can be confirmed by the tendency to strength decrease. With vinylon fibers compared with steel fibers, the strength of adhesion with the matrix is somewhat lower. Besides, strength test demonstrate that no significant improvement can be expected by adding fibers. Nevertheless, it can be said that both kinds of fibers are significantly effective in reducing the shrinkage. It should be noted however further study is necessary to determine the optimum kind of fibers and mixture ratio.

The measurements of inner temperature till 9 hours of the Mixtures 3 to 6 are shown in Fig. 8 with the previous measurements of the Mixture 1. As known from the figure, the less is the specific liquid resin amount, the longer is the time for reaching the maximum temperature and the lower is the maximum temperature level. When the liquid resin amount is reduced and the reduction amount is replaced with filler of the same volume, the filler amount increases, which results in larger heat capacity. The time for reaching the maximum temperature is therefore longer. The fact that, with alumina B, the time for reaching the maximum temperature becomes much longer may be due to larger heat capacity and greater surface of contact between liquid resin and filler because of its larger specific surface area. The relationship between specific liquid resin content and maximum temperature can be expressed by the following formula, resorting to the least square mean method using the measured data given in Fig. 7.

T=3.54R + 14.2

where T is the maximum temperature in $\,^{\circ}$ C, R is the specific liquid resin content in wt%.

The correlation coefficient of this equation is 0.977. Thus the maximum temperature is in proportion to the specific liquid resin. This means the specific liquid resin content is in proportion to the shrinkage due to temperature decrease.

738 Kawamura, Kuromoto and Iwai

Supposing the thermal expansion coefficient is almost the same, at the constant ambient temperature of 20° C, the strain is reduced by about 3% with alumina A-ST, while by about 5% with alumina B and dispersion agent.

If the reduction rate of shrinkage accompanying temperature decrease can be determined as mentioned above, then, with a known shrinkage rate, we can obtain the reduction rate caused by polymerization. The value of reduction rate by polymerization is approximately 57%, 30%, 10% respectively for the Mixtures 4, 5, 6. Hence modification of filler properties is more effective in reducing the polymerization shrinkage, than use of dispersion agent. This demonstrates that the polymerization shrinkage amount is not simply proportional to the liquid resin content, but it considerably varies with the formation state of matrix of liquid resin and filler. With modified surface, filler particles are uniformly dispersed in the high molecular matrix, generating interaction in the interface between filler and liquid resin (7). With spherical particles, the measured static modulus of elasticity is greater. Judging from this, because of the spherical shape, filler particles are packed more densely in the high molecular matrix. Consequently, filler particles confine the volume change, resulting in smaller shrinkage.

The strength decreases in the mixtures with a smaller content of liquid resin regardless of the kind of alumina mixed. With alumina B, the decrease rate of compressive strength is about 5%, that of split tensile strength and flexural strength about 11%. With the other two types of alumina, the reduction of compressive strength is about 15%, that of split tensile strength about 25%, that of Thus the strength decreasing tendency is flexural strength about 32%. considerably greater that with alumina B. There is a possibility of a little decrease of strength caused by reduction of liquid resin amount, but these results mean that the reduction rate of strength is not simply proportional to the reduction rate of liquid resin content. The strength reduction is greater in all cases when tensile stress is produced. It suggests that setting shrinkage is confined by filler particles, which generates tensile stress inside PC, reducing its tensile strength. The tensile strength test results of paste composed of liquid resin and filler alone show that, compared with the same mixture proportion with alumina A, the strength reduction is about 5% with alumina A-ST, about 15% in the case of dispersion agent added with a proportion of 0.5 weight % of filler, and about 23% in the case of dispersion agent added with a proportion of 1.0 weight % of filler. This means that, when dispersion agent is used, the strength of matrix itself decreases, so the use of dispersion agent is not advantageous from the viewpoint of strength characteristics. When alumina A-ST is used, though the strength of matrix itself does not considerably decrease, the strength of concrete is significantly reduced. Judged from the properties in fresh state such as increased viscosity due to increase of filler amount, the most probable reason for strength reduction is that air entrapped at the time of mixing and specimen preparation remains inside the concrete.

CONCLUSION

This paper discussed the mechanism of setting shrinkage and possible methods for reducing it, for achieving the goal of applying MMA-PC to actual structures. The knowledge obtained through this investigation is summarized below.

a) The setting shrinkage is classified into two large categories : shrinkage due to polymerization during setting of liquid resin, and shrinkage due to

temperature decrease after the maximum temperature is reached.

- b) The maximum temperature is in proportion to the liquid resin content. Consequently, the magnitude of shrinkage caused by temperature decrease is proportional to the liquid resin content. By reducing the liquid resin content, it is possible to diminish the shrinkage due to temperature.
- c) The shrinkage due to polymerization is not simply proportional to the liquid resin content, but significantly varies with the matrix forming state of liquid resin with filler. Compared with use of dispersion agent, more effective shrinkage reduction is achieved by modifying the filler properties to confine the volume change generated by polymerization.
- d) By confining shrinkage with fibers, it is possible to reduce the shrinkage without diminishing the liquid resin content.

The results above explain clearly the mechanism of setting shrinkage of MMA-PC. For application to actual structures, it is essential however to know sufficiently the relationship between magnitude of shrinkage and stress generated. Because the setting shrinkage of MMA-PC occurs in a relatively short span of time, it is vital to select a suitable test method. The authors will implement further study on the basis of the results of investigation reported in this paper.

REFERENCES

- Fowler, D.W. "Applications of Polymer Concrete"; Proceedings of the 8th International Congress on Polymers in Concrete, Oostende, Belgium, 1995, pp.13-19. (Editors: D. Van Gemert and K.U. Leuven)
- 2. Koyanagi, W. "Resin Concrete"; Concrete Journal, Vol.31, No.4, April 1993, pp.5-13.
- 3. Kawamura, A., Kuromoto, M., Ishizeki, Y. and Iwai, T. "Properties of Polymer Concrete Using Methyl Methacrylate"; Kumagai Technical Research Report, No.56, November 1997, pp.79-88.
- 4. Kushner, R.G., Fowler, D.W. and Wheat, D.L. "Mechanical and Durability Properties of a High Molecular Weight Methacrylate Polymer Concrete"; ACI Special Publication SP-99, 1987, pp.113-134. (Editor: D.W. Fowler)
- Moriyoshi, A., Omata, F., Kawakami, M., Tokushige, H. and Ohama, Y. "Stresses and Strains of Resin Mortar During Setting"; Proceedings of The Second East Asia Symposium on Polymers in Concrete, Koriyama, Japan, 1997, pp.353-362. (Editors: Y. Ohama, M. Kawakami and K. Fukuzawa)
- 6. Kuromoto, M., Kawamura, A., Asai, S. and Sumita, M. "Characterization of Fillers Applied to MMA Polymer Concrete"; Proceedings of the Japan Concrete Institute, Vol.18, No.1, 1996, pp.489-494.
- Kuromoto, M., Kawamura, A., Iwai, T., Sumita, M. and Asai, S. "Characteerization of Polymer-Filler Interaction in MMA Polymer Concrete"; Proceedings of The Second East Asia Symposium on Polymers in Concrete, Koriyama, Japan, 1997, pp.57-66.

Case	Temperature
1	$20 \ ^{\circ}C \rightarrow 20 \ ^{\circ}C \rightarrow 5 \ ^{\circ}C \rightarrow 20 \ ^{\circ}C$
2	20 °C \rightarrow Max. temperature due to polymerization \rightarrow 20 °C \rightarrow 5 °C \rightarrow 20 °C
3	$20 \ ^{\circ}C \rightarrow 5 \ ^{\circ}C \rightarrow 20 \ ^{\circ}C$

TABLE 1-AMBIENT TEMPERATURE CONDITIONS

Kind of Alumina	Specific gravity	Mean grain size	BET surface area
A	3.95	3.7 µ m	1.4 m²/g
A-ST	3.95	$3.7~\mu$ m	
В	3.95	10.0 µ m	2.0 m²/g

TABLE 3-PHYSICAL PROPERTIES OF FIBERS

	Diameter	Nominal length	Specific gravity	Tensile strength	Young's modulus
Steel fiber	0.8 mm	60 mm	7.85	980 MPa	200 GPa
Vinylon fiber	0.66 mm	30 mm	1.3	880 MPa	29.4 Gpa

Mixture	Kind of	R/F ¹⁾	s/a	Unit resin			Unit con	tent(kg/m³)		
	Alumina	(%)	(%)	content ²⁾ (wt%)	Liquid resin	Filler	Fine aggregate	Coarse aggregate	Fiber	Dispersion agent
1	А	53.5	48.7	7.5	183	342	903	998		
2	А	53.5	48.7	7.5	183	342	903	998	30.0 ³⁾	
3	А	53.5	48.7	7.5	183	342	903	998	9.75 ⁴⁾	
4	A-ST	37.9	48.7	6.5	162	428	903	998		
5	В	31.9	48.7	6.0	151	473	903	998		
6	А	31.2	48.7	6.0	147.5	473	903	998		3.55

TABLE 4-MIXTURE PROPORTIONS OF MMA-PC

Notes : 1) R/F = Liquid resin/Filler (weight percentage)

2) Unit resin content = Percentage of liquid components (liquid resin + dispersion agent) in the mixture

3) Steel fiber 4) Vinylon fiber

742 Kawamura, Kuromoto and Iwai

Ambient temperature	Compressive strength	Static modulus of elasticit
Case 1	66.5 MPa	26.0 GPa
Case 2	68.7 MPa	25.7 GPa
Case 3	65.7 MPa	26.1 GPa

TABLE 5-COMPRESSIVE STRENGTH AND STATIC MODULUS OF ELASTICITY AT 28 DAYS

TABLE 6—PROPERTIES OF THE FRESH MIXTURES

Mixture	R/F^{1}	Unit resin content ²⁾	Slump	Temperature at mixing finis
1	53.5 %	7.5 wt%	20.5 cm	20.5 ℃
2	53.5 %	7.5 wt%	17.0 cm	21.5 ℃
3	53.5 %	7.5 wt%	16.0 cm	20.5 °C
4	37.9 %	6.5 wt%	20.5 cm	20.5 °C
5	31.9 %	6.0 wt%	16.5 cm	20.5 °C
6	31.2 %	6.0 wt%	25.0 cm	19.0 ℃

Notes : 1) R/F = Liquid resin/Filler (weight percentage)

2)Unit resin content = Percentage of liquid components(liquid resin + dispersion agent) in the mixture

TABLE 7-RESULTS OF T	IE STRENGTH TEST	S AT 28 DAYS
----------------------	------------------	--------------

Mixture	Compressive	Static modulus	Split tensile strength	Flexural strengt
	strength	of elasticity		
1	93.8 MPa	34.6 GPa	11.8 MPa	23.3 MPa
2	94.1 MPa	34.1 GPa	11.5 MPa	21.2 MPa
3	91.0 MPa	34.4 GPa	10.3 MPa	21.6 MPa
4	79.7 MPa	31.2 GPa	8.7 MPa	15.5 MPa
5	88.7 MPa	35.9 GPa	10.4 MPa	21.0 MPa
6	82.8 MPa	38.3 GPa	9.1 MPa	15.9 MPa







Fig. 4-Measurement results of strain and inner temperature (case3)



Fig. 5—Variation of strain with time normalized by the strain at the time of the maximum temperature