

Observation for Mechanical Property Variations of Single Polymer Particles

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ABSTRACT: Monodisperse polymer particles were prepared via conventional microsuspension polymerization or one-step seeded polymerization, using 1,6-hexanedioldiacrylate or its mixture with ethylene glycol dimethacrylate (EGDMA) as crosslinking monomer and poly(methyl methacrylate) synthesized by soap-free polymerization as seed particles. For the study, the effects of the ratio of the absorbed monomer or monomer mixture to the seed polymer particles (swelling ratio), the ratio of EGDMA in absorbed monomer mixture, the dosage of initiator, polymer particle structure, and the electroless Ni plating on the mechanical properties of

polymer particles, such as recovery rate, K -values, breaking strength, and breaking displacement were investigated using micro compression test. It was observed that monomer swelling ratio influenced only on breaking strength, whereas EGDMA ratio in monomer mixture, dosage of initiator, polymer structure and electroless Ni plating did on both K -values and breaking strength. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 585–592, 2007

Key words: polymer particle; swelling ratio; particle structure; electroless plating; mechanical property

INTRODUCTION

In recent years, the hot issues in electronic packaging industry are making products smaller/lighter and developing the environmentally friendly processes. From this viewpoint, the development of anisotropic conductive film (ACF) technology is consistent with the recent trends of electronic packaging industry because it can replace traditional soldering or under-fill encapsulation process, which may cause environmental problems and high cost. Thus it is being widely used for packaging technology in flat panel display, such as tape carrier package,¹ chip on glass,² or chip on film,^{3–4} and is extending its application field to flip chip packaging.^{5–10}

ACFs are adhesive films with anisotropic conductivity induced by dispersing conductive particles into polymer matrices, such as thermoplastics and thermosetting resins, as shown in Figure 1. Mostly metal coated inorganic or organic particles are used as these conductive particles, and they usually have double layer structure, which consists of Ni inner layer for electrical conductivity and Au outer layer for protecting inner layer from the oxidation and increasing the reliability of electrical performance.^{11–13} However, polymer particles with elasticity are mostly

used as core materials in these days because contact area between bonding electrodes and conductive particles increases with thermal compression as shown in Figure 1, and this gives rise to better connection reliability. Therefore systematic investigation of mechanical properties of single polymer particles is very important for the development of ACF technology, but little systematic investigation has been reported in the literature except for several patents.^{14–16}

In this study, using five mechanical properties (recovery rate, K -values, breaking strength, and breaking displacement), which were introduced in patents,^{14–16} we investigated the effects of (1) the ratio of the absorbed monomer or monomer mixture to the seed polymer particles (swelling ratio), (2) the ratio of ethylene glycol dimethacrylate (EGDMA) in absorbed monomer mixture, (3) the amount of initiator, (4) polymer particle structure, and (5) electroless Ni plating on the variations of earlier five mechanical properties of monodisperse poly[MMA-HDDA (or EGDMA)] and poly(1,6-hexanedioldiacrylate) (HDDA) particles synthesized via one-step seeded polymerization or suspension polymerization, using micro compression test (MCT).

EXPERIMENTAL

Materials

For the preparation of poly(methyl methacrylate) (PMMA) seed polymer via soap-free polymerization,

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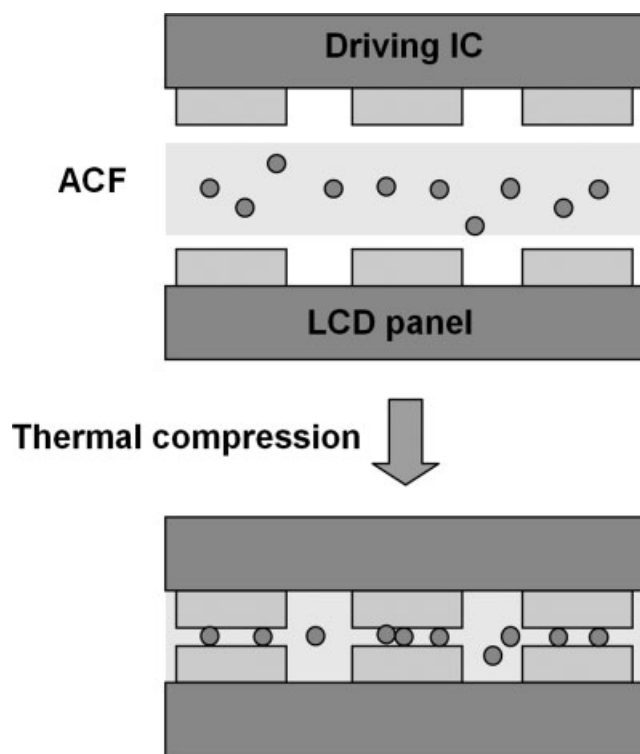


Figure 1 Schematic of the ACF bonding process.

MMA (99%, Junsei, Tokyo, Japan) was purified using an inhibitor removal column (Aldrich, Milwaukee, WI) and stored at -5°C prior to use. KPS (potassium persulfate, Junsei) was used as initiator without further purification and 1-Octanethiol (Aldrich) was used as chain transfer agent.

HDDA and EGMMA were purchased from Aldrich and used as crosslinking monomer without further purification for the seeded polymerization. BPO (benzoylperoxide, Morecambo, England) was used as initiator. PVA (polyvinylalcohol, Aldrich, $M_w = 85,000\text{--}146,000$) was used as dispersant for seeded and suspension polymerization. SLS (sodiumlaurylsulfate, Aldrich) was used as emulsifying agent for emulsification of monomer mixture.

For the electroless Ni plating, Nickel(II) sulfate (Acros) was used as Ni source and sodium hypophosphite (Aldrich) was used as reducing agent. Lead(II) nitrate (Aldrich) was used for the stability of plating bath and glycine was used as complexing agent.

Polymerizations

The polymerization procedure for the preparation of PMMA seed particles via soap free polymerization is as follows. First, the chemicals summarized in Table I were put into a 1000-mL-round flask equipped with a mechanical stirrer and reflux condenser under

TABLE I
Standard Recipe for the Preparation of Seed Polymer Particles by Soap Free Polymerization

Chemicals	Amount (g)
MMA	40
1-Octanethiol	0.5
KPS	0.3
Water	690

a well controlled temperature. The chemicals were stirred gently with nitrogen purging for 1 h to remove dissolved oxygen. Then, the temperature of the reactor was increased to 70°C and a predetermined amount of initiator was added to the reactor, and the polymerization reaction was continued 8 h. The reactor was cooled down and the seed particles were separated using centrifugation, washed with deionized water 3 times and dried in a vacuum oven. The characteristics of seed particles thus prepared are summarized in Table II. For the seeded polymerization, the chemicals summarized in Table III were added to a 50-mL vial and emulsified using ultrasonic homogenizer. A predetermined amount of seed particles was added to earlier monomer emulsion and this vial was placed in a shaking incubator at room temperature for 24 h for monomer absorption.

After the monomer absorption, a predetermined amount of PVA solution was added and polymerization was performed in a shaking bath under temperature control for 24 h. After the polymerization, the same separation and cleaning procedures employed for the seed polymerization were used to collect the poly(MMA-HDDA) particles.

For the preparation of poly(HDDA) particles, conventional microsuspension polymerization and multi-step wet sieving method with electroformed sieves (Precision Eforming LLC, Cortland, NY) were adopted as follows. The chemicals summarized in Table IV were added to a 1000-mL stainless steel vessel and emulsified at a stirring speed of 20,000 rpm with the homomixer during 10 min. After this, the emulsion was transferred to a 1000 mL temperature controlled (70°C) dual jacket reactor equipped with mechanical stirrer and reflex condenser. The stirring speed was set at 200 rpm and the polymer-

TABLE II
Physical Properties of PMMA Seed Particles

Diameter (μm)	C_v	M_w
0.85	5.2	18,000

$$C_v (\%) = \sigma/D_n \times 100.$$

σ standard deviation of diameter; D_n , number average diameter.

TABLE III
Ingredients for the Synthesis of Polymer Particles by Seeded Polymerization

Chemicals	Amount (g)
HDDA	1
Initiator	0.05
SLS (0.3%) solution	17
PVA (3%) solution	3

ization was continued 8 h. After polymerization, the same separation, and cleaning procedures employed for the seed polymerization were used to collect the poly(HDDA) particles. The detailed procedure of wet sieving is available from the literature.¹⁷

Electroless Ni plating

The theoretical background and general procedures of electroless Ni plating are well known from the literatures.^{18–20} Prior to electroless plating, polymer particles need to be pretreated. The known amount of polymer particles were first sensitized using SnCl₂/HCl acid solution for 5 min under ultrasonic irradiation and rinsed with deionized water twice. As a second step, activation was performed by immersing these particles into PdCl₂/HCl acid solution for 5 min and rinsed. Through activation step, a surface redox reaction occurs, (reduction of Pd²⁺ to Pd and oxidation of Sn²⁺ to Sn⁴⁺). After pretreatment, polymer particles were placed in a plating bath (pH = 5, 60°C) and plated via dropping metal solution and reducing agent solution. The detailed compositions of plating bath and dropping solutions are summarized in Table V.

Characterizations and mechanical property measurements

The analysis of polymer particle size and distribution was performed by using AccuSizerTM 780A (PSS.NICOMP, Santa Barbara, CA), and the surface morphologies of electroless Ni plated particles were observed by a scanning electron microscope (JEM 1200EX, Tokyo, Japan). The mechanical properties such as recovery rate, *K*-values, breaking strength,

TABLE IV
Ingredients for the Synthesis of Polymer Particles by Microsuspension Polymerization

Chemicals	Amount (g)
HDDA	50
PVA	4.5
BPO	0.5
Water	450

TABLE V
Compositions of Electroless Ni Plating Bath and Dropping Solutions

Dispersion solution	
H ₂ O	1000g
PVP (K-30)	0.1g
Dodecyltrimethylammonium bromide	0.1g
lead(II) nitrate	0.001g
Dropping Solution A	
Nickel(II)sulfate	1 mol
Glycine	1 mol
Dropping Solution B	
Sodium hypophosphite	3 mol

and breaking displacement were obtained by calculating the average value of 10 individual particles' MCT (Fisher H100C; Sindelfingen, Germany) measurements. The measurement method for each mechanical property is as follows.

Recovery rate (*R_r*)

As shown in Figures 2 and 3(a), A polymer particle (diameter: *D*, radius: *R*) is placed on the smooth surface sample table and compressed with indenter at the speed of 1 mN/s to maximum load value (5 mN), and after that, the load is decreased at the same speed to standard load value (0.1 mN). The recovery rate represents the degree of particle recoverability after being deformed by compressing, and is defined as the ratio (*L*₂/*L*₁) represented by %, wherein *L*₁ is the displacement from standard load point to maximum load point during compression and *L*₂ is the displacement from the maximum load point to the standard load value during releasing.

$$R_r = [L_2/L_1] \times 100 \quad (1)$$

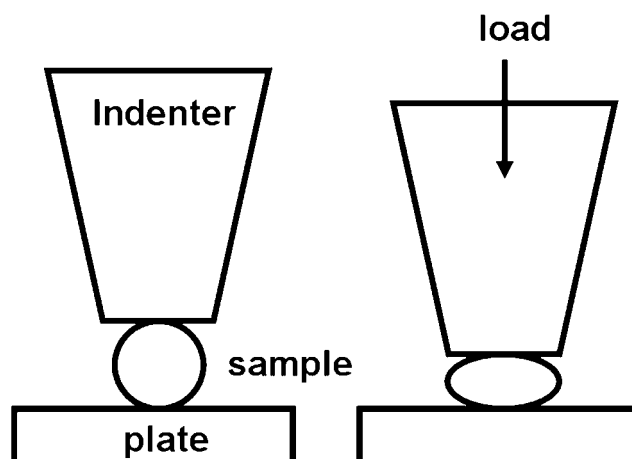


Figure 2 Schematic of the microcompression test.

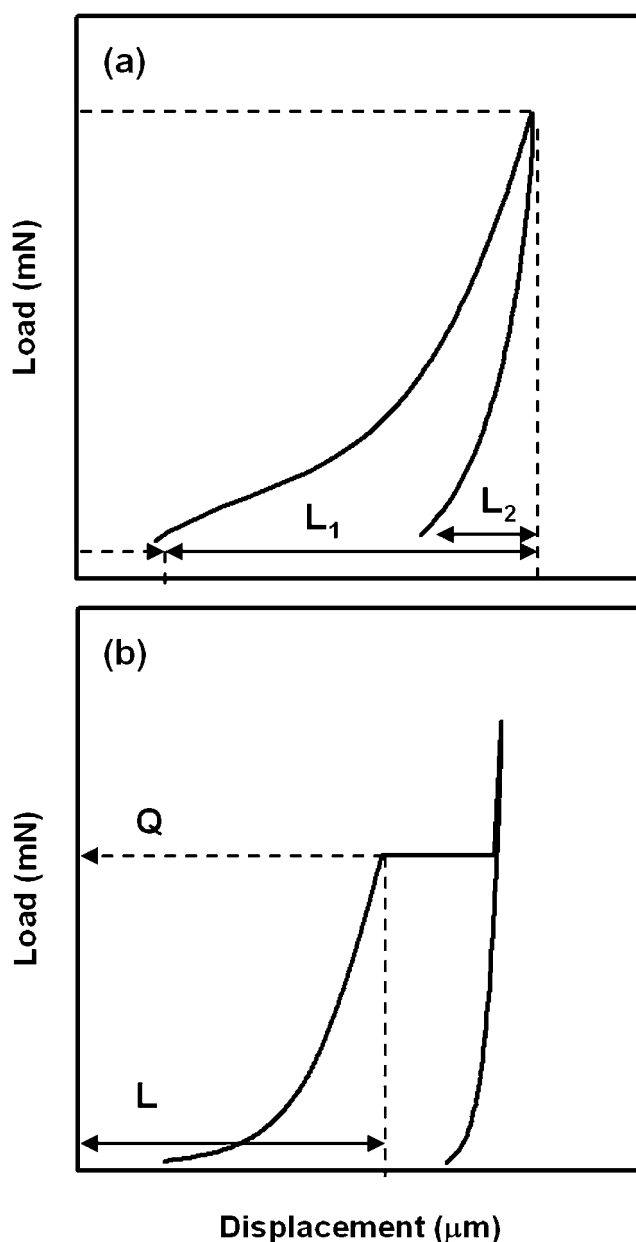


Figure 3 Plots of test force versus compression displacement for monodisperse polymer particle.

K-values (K_{10} and K_{20})

Load value (F) and compression displacement (S) at the point of 10% (or 20%) compression deformation of the particle are measured, while compressing single particle with indenter at the speed of 0.67 mN/s. K -values are defined as follows and represent the degree of particle hardness.

$$K = (3/2^{1/2})FS^{-3/2}R^{-1/2} \quad (2)$$

Breaking strength (S_o)

Breaking strength represents the compression rupture strength of the particle. It is calculated by measuring

load value (Q) at the breaking point, while compressing with indenter at the speed of 0.67 mN/s as shown in Figure 3(b), and defined as follows.

$$S_o = 2.8Q/\pi D^2 \quad (3)$$

Breaking displacement (F_r)

Breaking displacement represents the compression rupture displacement of the particle. It is calculated by measuring compression displacement (L) at the breaking point, while compressing as shown in Figure 3(b), and defined as the ratio (L/D) represented by %, wherein D is the diameter of particle.

$$F_r = (L/D) \times 100 \quad (4)$$

RESULTS AND DISCUSSION

Effect of swelling ratio

Monodisperse crosslinked poly(MMA-HDDA) particles were prepared with the increase of swelling ratio from 50 to 150 to investigate the relationship between swelling ratio and mechanical properties of polymer particles. The analysis of particle size and distribution was performed using AccuSizer as shown in Figure 4. The diameters of synthesized polymer particles were increased with the swelling ratio, but maintained good monodispersity ($C_v < 6.5$). This observation was confirmed by the SEM photographs as shown in Figure 5, and it indicates that the crosslinking monomer (HDDA) was well absorbed into the seed particles irrespective of swelling ratio variation.

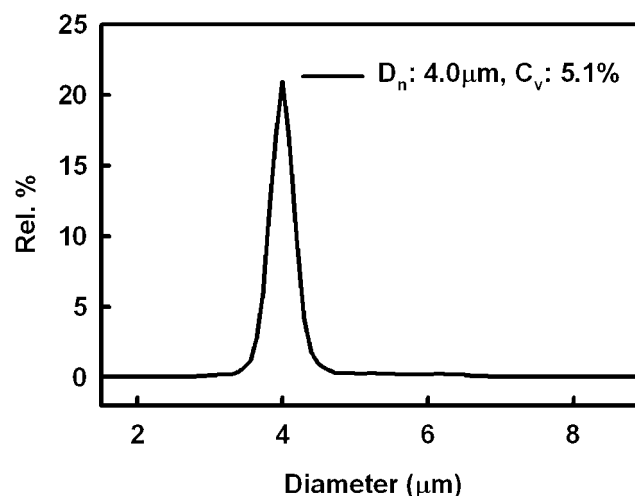


Figure 4 The histogram of poly(MMA-HDDA) particle size distribution ($S/R : 100$).

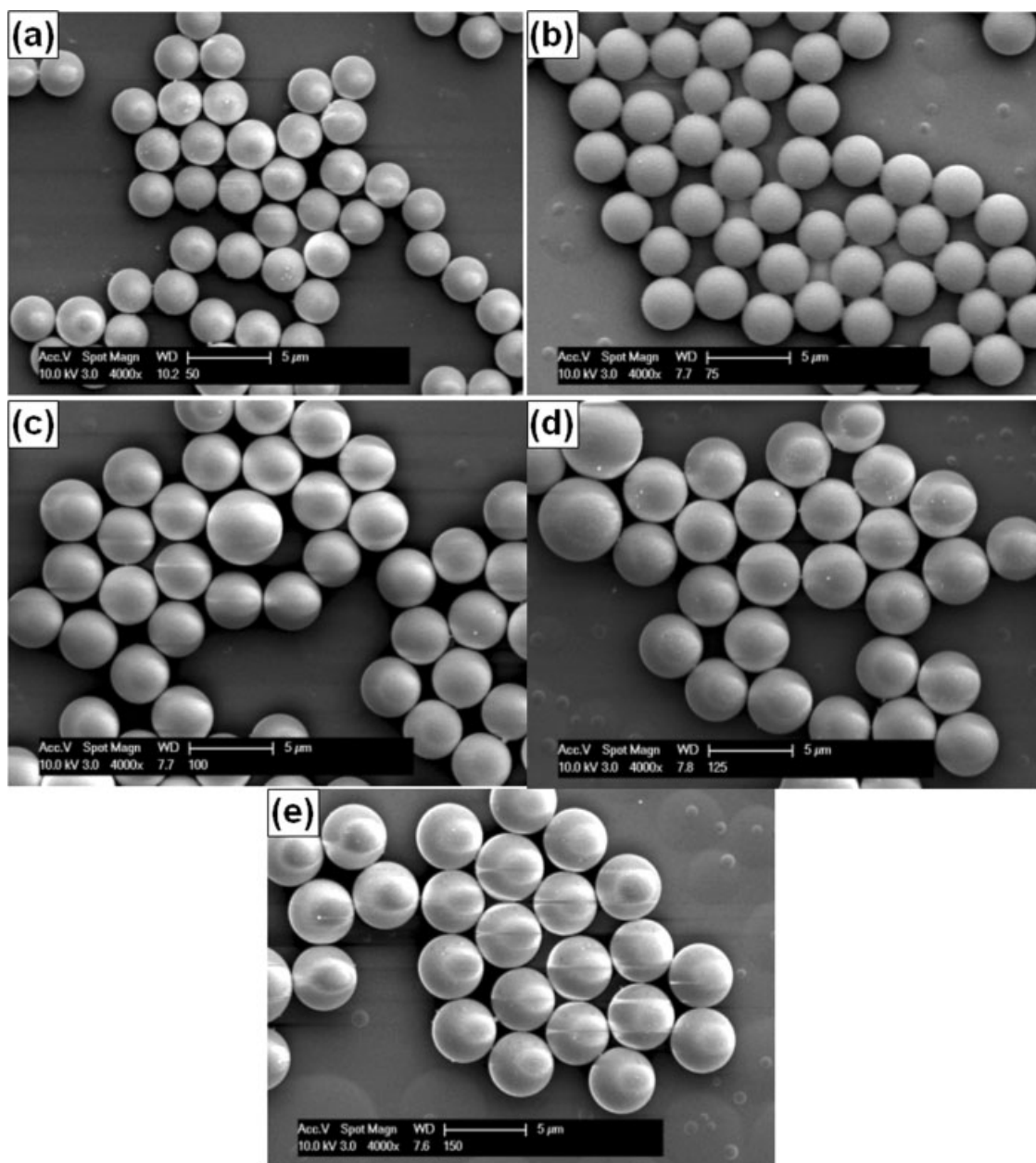


Figure 5 The SEM photographs of the poly(MMA-HDDA) particles with different swelling ratio: (a) 50, (b) 75, (c) 100, (d) 125, and (e) 150 ($\times 4000$ magnification).

Using these polymer particles, the measurements of mechanical properties were performed, and the results were summarized in Table VI. It was observed that recovery rate, K -values and breaking displacement were remained more or less constant, but breaking strength was increased steadily with the increase of swelling ratio. Thus, it seems that only breaking strength is closely related to the variation of swelling ratio, i.e., the ratio of crosslinked domain in the polymer particle. However, further study is necessary because the additional range of swelling ratio and the effect of molecular weight of seed polymer were not investigated at this time.

TABLE VI
Variation of Mechanical Properties of Poly(MMA-HDDA) Particles with Swelling Ratio

S/R	D_n (μm)	R_r (%)	K_{10} (MPa)	K_{20} (MPa)	S_o (MPa)	F_r (%)
50	3.2	63	1430	1098	670	54
75	3.7	63	1518	1271	740	51
100	4.0	64	1554	1257	800	54
125	4.2	61	1531	1228	880	53
150	4.3	56	1436	1206	1000	60

TABLE VII
Variation of Mechanical Properties of Polymer Particles with EGDMA Ratio (S/R : 100)

EGDMA (%)	D_n (μm)	R_r (%)	K_{10} (MPa)	K_{20} (MPa)	S_o (MPa)	F_r (%)
0	4.0	64	1554	1257	800	54
34	3.9	57	2274	1926	780	53
50	4.0	56	2775	2270	700	51
75	3.8	47	3316	2759	600	46

Effect of EGDMA ratio in monomer mixture

From the previous discussion, it was observed that recovery rate, K -values and breaking displacement were more or less independent on the variation of swelling ratio. Thus it would be meaningful job to find out the parameters which are closely related to earlier properties.

For this purpose, the effect of molecular structure changing of crosslinking monomer on the variation of mechanical properties was investigated by mixing some amounts of EGDMA having shorter flexible spacer with HDDA at a fixed swelling ratio ($S/R : 100$). They are summarized in Table VII. It was observed that recovery rate, breaking strength and breaking displacement decreased slowly with the increase of EGDMA ratio, but K -values increased rapidly. It is not much difficult to imagine that increasing the EGDMA ratio in monomer mixture makes polymer particles more brittle, harder or have higher crosslinking density because of short and rigid flexible spacer of EGDMA. We can thus speculate that recovery rate, K -values and breaking displacement are closely related to the characteristics of crosslinked polymer domain such as brittleness, hardness, crosslinking density, etc.

Effect of Initiator dosage

The effect of initiator dosage on the mechanical property variation of poly(MMA-HDDA) particles at a fixed swelling ratio ($S/R : 100$) was also investigated. The results were summarized in Table VIII. It showed that recovery rate and breaking displacement

TABLE VIII
Variation of Mechanical Properties of Polymer Particles with a Dosage of Initiator (S/R : 100)

Initiator (%)	D_n (μm)	R_r (%)	K_{10} (MPa)	K_{20} (MPa)	S_o (MPa)	F_r (%)
0.2	4.2	63	1165	925	890	56
1.0	3.9	63	1528	1288	870	55
2.0	4.0	64	1554	1257	800	54
6.0	4.0	63	1665	1361	660	51

remained more or less constant but breaking strength decreased slowly with the increase of initiator up to 2%, and then decreased fast. However K -values increased steadily with the initiator dosage. As mentioned earlier, these behaviors of mechanical property variation can be observed when polymer particles become harder. Thus, it leads us to speculate that increasing the initiator dosage increases the hardness of the particles. However, we don't have experimental evidence to prove it at this point. We just surmise that increasing the initiator dosage is helpful for obtaining higher crosslinking density, and it increases the hardness of polymer particles. However, the effect of initiator dosage on the mechanical properties was relatively weaker compared with that of EGDMA.

Effect of Polymer Structure

A polymer comprising one or more networks and one or more linear or branched polymer(s) characterized by the penetration on a molecular scale of at least one of the networks by at least some of the linear or branched macromolecules is defined as semi-IPN. Thus, poly(MMA-HDDA) particles synthesized via seeded polymerization have semi-IPN structure. The comparison of mechanical properties of poly(MMA-HDDA) particles with HDDA homopolymer particles having fully crosslinked structure would be also meaningful. For this purpose, we prepared monodisperse HDDA homopolymer particles ($3.8 \mu\text{m}$, $C_v < 8.7$) via conventional micro-suspension polymerization and multi-step wet sieving with precision electroformed sieve, and then performed the measurement of the variations of mechanical properties. They are summarized in Table IX.

When 2% of initiator was used, only breaking strength was distinctively changed (46% increase) when compared with semi-IPN structured particles shown in Table VIII. This observation is well matched with the results of the swelling ratio variation experiments shown in Table VI. And it seems very reasonable because the semi-IPN structured particles with higher swelling ratio may as well have more similar mechanical properties to the fully

TABLE IX
Variation of Mechanical Properties of Polymer Particles Prepared by Microsuspension Polymerization with a Dosage of Initiator

Initiator (%)	D_n (μm)	R_r (%)	K_{10} (MPa)	K_{20} (MPa)	S_o (MPa)	F_r (%)
2.0	3.8	60	1620	1294	1170	49
6.0	3.8	56	2031	1422	1060	47

TABLE X
Variation of Mechanical Properties of Ni Plated Polymer Particles with the Plating Time

Time (min)	Ni plating thickness (nm)	R_r (%)	K_{10} (MPa)	K_{20} (MPa)	S_o (MPa)	F_r (%)
0	0	64	1554	1257	800	54
30	11	58	1668	1300	780	53
60	60	55	1960	1504	750	52
90	101	53	2622	1628	690	51
120	122	50	3294	1680	650	49

crosslinked particles than those with lower swelling ratio. However, with the increase of initiator dosage up to 6%, not only breaking strength (61%) but also K -values (23%) were distinctively increased. At this point, it is not clearly understood why the difference of K -values between two different structures is getting bigger with the increase of initiator dosage. We just surmise that the effect of initiator dosage discussed previously is more distinctive for the fully crosslinked structured polymer particles.

Effect of electroless Ni plating

Polymer particles should be coated with metal to be used as conductive particles for ACF. Thus, not only the mechanical properties of polymer particles but also the mechanical properties of metal coated polymer particles are important. Table X summarizes the variation of mechanical properties of Ni coated polymer particles with plating time and coating thickness, and Figure 6 shows the SEM photographs of the surface morphologies of Ni coated polymer particles. We can observe from Table X that K -values, especially K_{10} was increased rapidly, but recovery rate, breaking strength and breaking displacement were decreased slowly with Ni plating. These behaviors of mechanical property variation are very similar to experimental observations shown in Table VII. It is needless to say that these are because Ni plating increased the hardness of polymer particles. However, when compared with the variation of K -values in Table VII, the increasing rate of K_{10} with plating time is much higher than that of K_{20} . This observation indicates that K_{10} is closely related to the characteristic of outer layer of particles, such as coating material or thickness of coating layer because of small compression displacement, whereas K_{20} is related to the characteristic of polymer particles, such as hardness or crosslinking density because of the relatively big compression displacement.

CONCLUSIONS

In this study we have observed the variation of mechanical properties of monodisperse crosslinked poly(MMA-HDDA) particles with the monomer

swelling ratio, composition of monomer mixture and the dosage of initiator. When HDDA was used as crosslinking monomer, recovery rate, K -values and breaking displacement were remained more or less constant but breaking strength was increased with the swelling ratio. However, with the increasing of EGDMA ratio, recovery rate, breaking strength and breaking displacement were decreased, but K -values were increased because the short and rigid flexible spacer of EGDMA made the polymer particles more brittle or harder. On the other hand, breaking strength was decreased but K -values were increased with the increasing of initiator dosage. Fully cross-linked particles showed similar values of recovery rate and breaking displacement, but did much higher K -values and breaking strength when compared with semi-IPN structured particles. After electroless Ni plating, K -values, especially K_{10} was increased sharply with the increasing of plating time, but recovery rate, breaking strength, and breaking displacement were decreased because of the increased hardness.

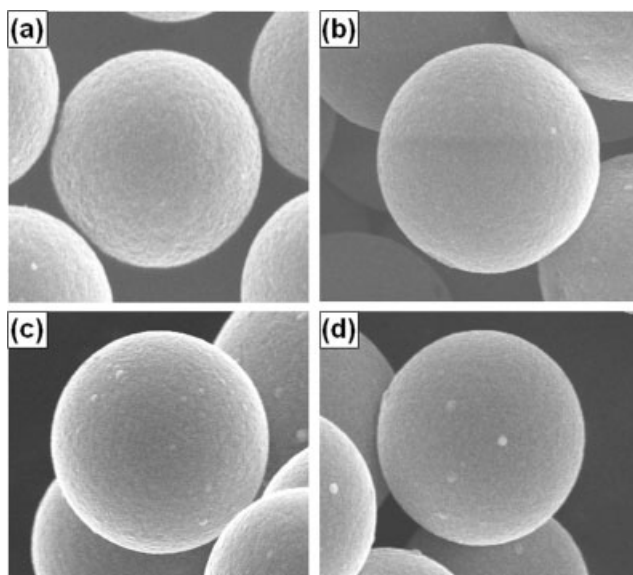


Figure 6 The SEM photographs of the Electroless Ni plated poly(MMA-HDDA) particles with different plating times: (a) 30, (b) 60, (c) 90, (d) 120 min ($\times 15,000$ magnification).

References

1. Watanabe, I.; Fujinawa, T.; Arifuku, M.; Fujii, M.; Gotoh, Y. Proceedings of ninth International Symposium on Advanced Packing Materials, 2004.
2. Joshi, R. *Microelectron J* 1998, 29, 343.
3. Chang, S.; Jou, J.; Hsieh, A.; Chen, T.; Chang, C.; Wang, Y.; Hung, C. *Microelectron Reliab* 2001, 41, 2001.
4. Rizvi, M.; Chan, Y.; Sharif, A. *Solder Surf Mount Technol* 2005, 17, 40.
5. Sarkar, G.; Mridha, S.; Chong, T.; Yuen, W.; Kwan, S. *J Mater Process Technol* 1999, 89–90, 484.
6. Chan, Y.; Luk, D. *Microelectron Reliab* 2002, 42, 1185.
7. Chan, Y.; Luk, D. *Microelectron Reliab* 2002, 42, 1195.
8. Wu, Y.; Alam, M.; Chan, Y.; Wu, B. *Microelectron Reliab* 2004, 44, 295.
9. Seppala, A.; Ristolainen, E. *Microelectron Reliab* 2004, 44, 639.
10. Uddin, M.; Alam, M.; Chan, Y.; Chan, H. *Microelectron Reliab* 2004, 44, 505.
11. Goward, J. M.; Whalley, D. C.; Williams, J. *Microelectron Int* 1995, 37, 55.
12. Whalley, D. C.; Mannan, S. H.; Williams, D. J. *Assem Autom* 1997, 17, 66.
13. Oguibe, C. N.; Mannan, S. H.; Whalley, D. C.; Williams, D. J. *IEEE Trans Compon Packag Manuf Tech A* 1998, 21, 235.
14. Saiuchi, K.; Kohara, H.; Yamada, K.; Kanki, K. U.S. Pat. 5 1996, 486, 941.
15. Saiuchi, K.; Kohara, H.; Yamada, K.; Kanki, K. US Pat 5,615,031 (1997).
16. Park, J. K.; Chung, P. M. Kor. Pat. 10,002,183 (2004).
17. Danjiyou, K. Jap. Pat. P2001-347111A (2001).
18. Iacovangelo, C. D. *Plating Surf Finish* 1995, 77.
19. Hagiwara, K.; Watanabe, J.; Honma, H. *Plating Surf Finish* 1997, 74.
20. Motizuki, I.; Izawa, K.; Watanabe, J.; Honma, H. *Trans IMF* 1997, 77, 41.