Deformation and Fracture of Crosslinked Polystyrene Particles

J. Y. He [1,a] , Z. L. Zhang [1,b] and H. Kristiansen [2,c]

[1] NTNU Nanomechanical Lab, Department of Structural Engineering, Norwegian University of Science and Technology (NTNU), 7491, Trondheim, Norway

[2] Conpart AS, 2013, Kjeller, Norway

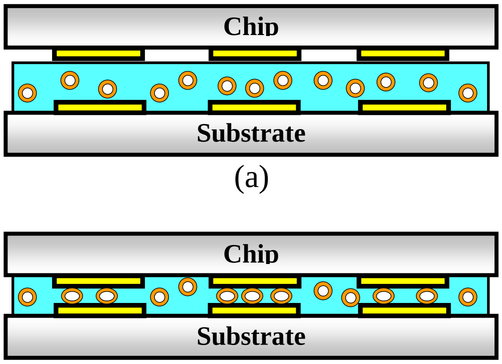
[a] jianying.he@ntnu.no, [b] zhiliang.zhang@ntnu.no, [c] helge@conpart.no

Keywords: polystyrene particle, nanoindentation, crosslink density, loading rate, deformation, fracture.

Abstract. Micron-sized polymer particles, due to their susceptibility to different chemical modification and excellent mechanical properties, have been widely used in chemical analysis and biotechnology, such as additives in coating and paint, ink products, chromatographic support, and electronic packaging technology, etc. In addition to functionalities, mechanical properties of polymer particles under a large deformation are of crucial importance to different applications. However, due to small volume, spherical geometry and large deformation, mechanical characterization of individual micron-sized particles are difficult and challenges the existing experimental methodologies. In this work, micron-sized polystyrene crosslinked with divinylbenzene (PS-co-DVB) particles have been prepared by seeded polymerization based multi-step swelling process, known as Ugelstad method. Three groups of PS-co-DVB particles have identical size and different crosslink density. The SEM observation has proven the perfectly spherical geometry and highly uniform size of particles. The mechanical response of individual particles has been investigated by means of nanoindentation-based flat punch technique. The crosslink density of particles and the loading rate during compression have been taken into account. The results show that particle deformation and fracture experience a ductile-to-brittle transition when crosslink density increases. A faster compression on the strongly crosslinked particles induces more brittle behaviour.

Introduction

Monodisperse polymer particles with a diameter ranging from 0.5 to 10 μm have been widely used in chemical industries and biotechnology [1]. Recently there is a growing interest in such polymer particles with potential application in new electronic packaging technologies, such as Anisotropic Conductive Adhesives (ACA) in Flat Panel Displays (FPDs) [2-4]. Usually the particles used in these applications consist of a polymer core - double metal layer structure in which the polymer core improves contact compliance, Ni inner layer produces electrical conductivity and Au outer layer protects Ni layer from the oxidation and thus increases the reliability of electrical performance at the same time. The design of such metal coated polymer particles in electrical packaging technologies brings a number of advantages in terms of lead-free, reducing package size and high-density interconnections. During the bonding process, the particles are highly deformed to get the large contact area in order to achieve a low resistance connection, as shown in Fig. 1. The electrical characteristics as well as the reliability of the interconnection are mostly determined by the mechanical behaviour of the particles. Thus the mechanical properties of individual particles are very important for the design of electrical assemblies.



(a)

(b)

Fig. 1. Schematic plot of an ACA using metal coated polymer particles (a) before bonding and (b) after bonding.

Due to the complexity of spherical shape and large deformation involved in the particles used in the ACA assembly, mechanical characterization of individual particles is full of challenge. To cope with this problem, the authors have developed a nanoindentation-based flat punch method for measuring the mechanical response of micron-sized polymer particles under compression [5]. The contact load-displacement relationship, size effect and large deformation behaviour of individual polymer particles have been investigated [6-8]. The aim of the present work is to study deformation and fracture of polystyrene-co-divinylbenzene particles with same size but different crosslink density to understand the effect of crosslink density and loading rate on the mechanical behaviour of individual particles.

Experimental

Particles Polystyrene-co-divinylbenzene (PS-co-DVB) particles, due to their good stiffness, adaptability in a wide pH range and susceptibility to chemical modification, have been utilized in numerous applications as well as electronic packaging technology [9]. Using the well-known Ugelstad method with a multi-step swelling process, monodisperse PS-co-DVB particles were prepared [10]. The particles had a network structure characterized by styrene crosslinked with divinylbenzene. The amount of activated divinylbenzene monomer added in the preparation process was used to calculate the crosslink density of final particles which was varied from 2, 21 to 55wt%. The particles were expected to be an amorphous type at room temperature and the size was around 5.1μm in diameter. To obtain individual particles for the mechanical test, a dispersion procedure was developed to drop particle-ethanol suspension onto a silicon chip. The specimen was then left in a clean environment for 12 hours to dry any residual ethanol from the particles.

Inverse nanoindentation test A nanoindentation device (TriboIndenter® Hysitron Inc., MN., USA) with a diamond flat-end punch was employed to compress individual particles, which can be considered as an inverse nanoindentation, schematically shown in Fig. 2. The load control mode was applied in which the normal force followed a pre-defined load function. The contact load and displacement were recorded at real-time and the stress-strain relationships were obtained by normalizing the force and the displacement to the maximum cross-section area and the diameter of undeformed particles, respectively, which can be expressed as [11]:

$$\sigma_C = \frac{P}{\pi r^2} \tag{1}$$

$$\varepsilon_C = \frac{D}{2r} \tag{2}$$

where *P* was the applied force, *D* was the displacement during compression and *r* was the radius of the undeformed particle.

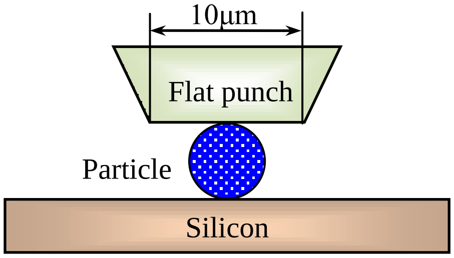


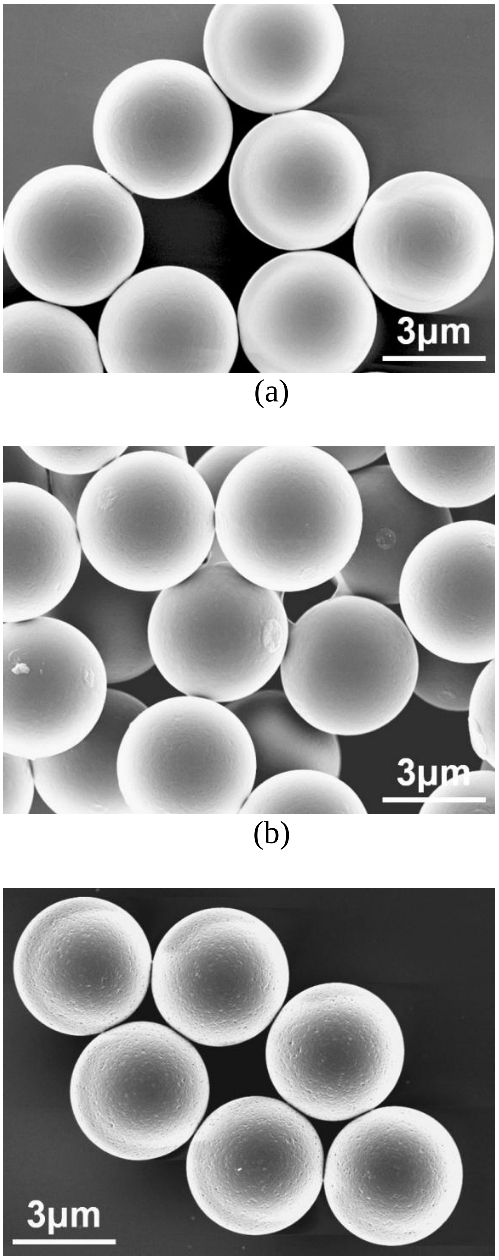
Fig. 2. Schematic plot of the nanoindentation-based flat punch test.

SEM observation The particle morphology was examined using a field emission scanning electron microscope (Zeiss Ultra 55 LE FE-SEM). Prior to SEM, the particles were placed in a clean environment for two weeks in order to recover any residual deformation. To minimize the charge dissipation, the SEM was operated at a relatively low voltage of 2.0kV and a working distance of 2.0mm. All images are taken from the top view, in the direction of compression.

Results and discussion

Particle morphology The characteristic morphologies of three groups of PS-co-DVB particles are displayed in Fig. 3. It can be observed that each group of particles synthesized by Ugelstad method possesses the monodisperse size distribution and the perfect spherical geometry. 2wt% crosslinked particles show a smooth surface. With the increase of crosslink density, the particle surface becomes relatively rough with tiny pores on the surface.

Crosslink effect First the effect of the crosslink density on the mechanical properties of PS-co-DVB particles is investigated. Three groups of particles were compressed to a peak load 20mN with constant loading/unloading rate 2mN/s. On each group of particles, at least 5 compression tests were replicated to examine the repeatability of particle behaviour. It has been found that the loading segments of particles are pretty consistent. This is in contrast to bulk polymer material in which the mechanical properties often show a relatively large scatter due to the variation of microstructure, crosslinking density and anisotropy, etc. The corresponding stress-strain relationships using Eq. (1) and (2) are plotted in Fig. 4 (a). The unloading segments are neglected here since the concern of this study is the loading behaviour of particles. The mechanical behaviour of particles is significantly influenced by the crosslink density. The higher crosslink density causes stiffer particle behaviour. At the small strain level, the crosslinking effect is moderate. This could result from the elasticity of styrene segments between crosslinks in network structure. When reaching a relatively high strain level, the effect of crosslink density becomes prominent. A ductile-to-brittle transition of particle behaviour is implied as the crosslink density increases. The 2wt% crosslinked particle is deformed up to 80% strain. However, the 21wt% and 55wt% crosslinked particles experience a strain burst on loading segment at around 63% and 55% strain level, respectively. The previous study has demonstrated that the strain burst implies destructive failure of the particles [8]. The characteristic SEM images of the 2wt% and 55wt% crosslinked particles are also shown in Fig. 4 (b) and (c). When compressed to 60% deformation, the 2wt% crosslinked particle becomes a "pancake" with a number of surface cracks. A flattened contact area which presents the residual deformation of particles can be clearly observed. However, the 55wt% crosslinked one is crushed when the deformation reaches 55%. The cracks propagate along the meridian direction during the disintegration. The fracture morphology of particles further verifies the ductile-to-brittle transition of particle behaviour with increasing crosslink density.

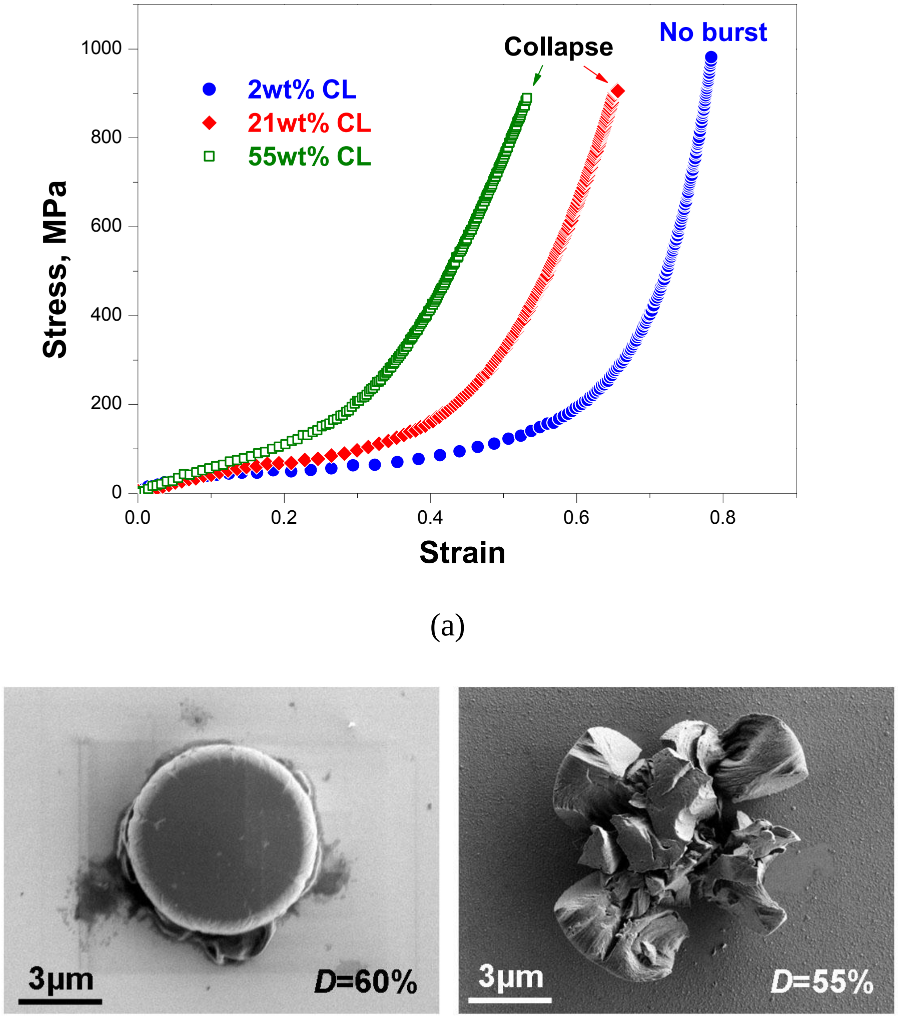


(a)

(b)

(c)

Fig. 3. SEM photograph of undeformed particles. (a)-(c) present particle with crosslink density 2, 21 and 55wt%, respectively. Electron high tension (EHT) = 2.0kV; working distance (WD) = 2.0mm.



(a)

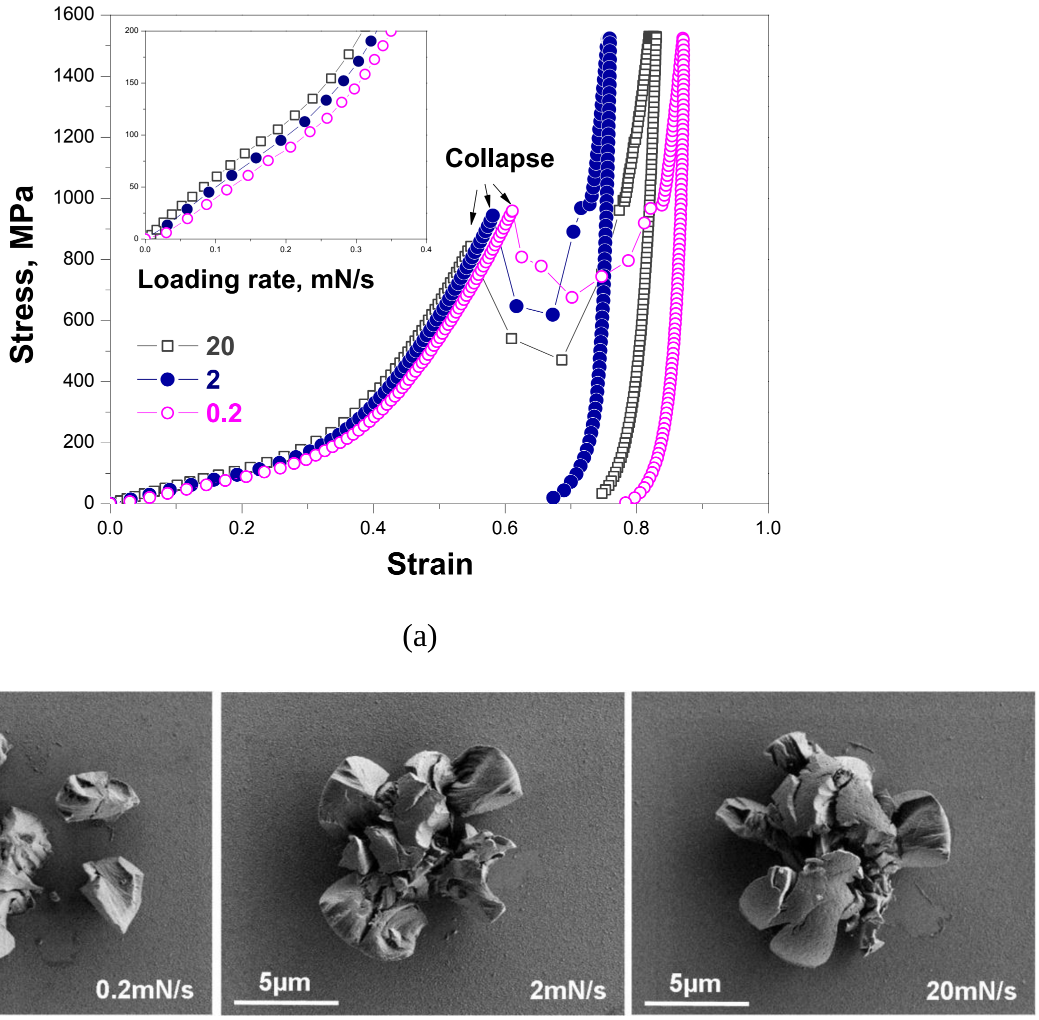
(b)

(c)

Fig. 4. (a) Comparison of the compression stress-strain curves of three particles; (b) the characteristic SEM image of 2wt% crosslinked particle after compression and (c) 55wt% particle after compression.

It is well established that the mechanical properties of polymers are sensitive to the crosslink density [12]. Crosslinking increases the tightness of the polymer network and limits the molecular mobility of chains between the junctions. Thus a higher crosslink density leads to a more viscoelastic behaviour of polymers. The theoretical studies for amorphous crosslinked polymer suggest that the randomly crosslinked networks of molecules undergo a transition from a fluid-like to an amorphous solid state as the crosslinking increases [13,14]. The presented work indicates that it is also applicable to the micron-sized PS-co-DVB particles.

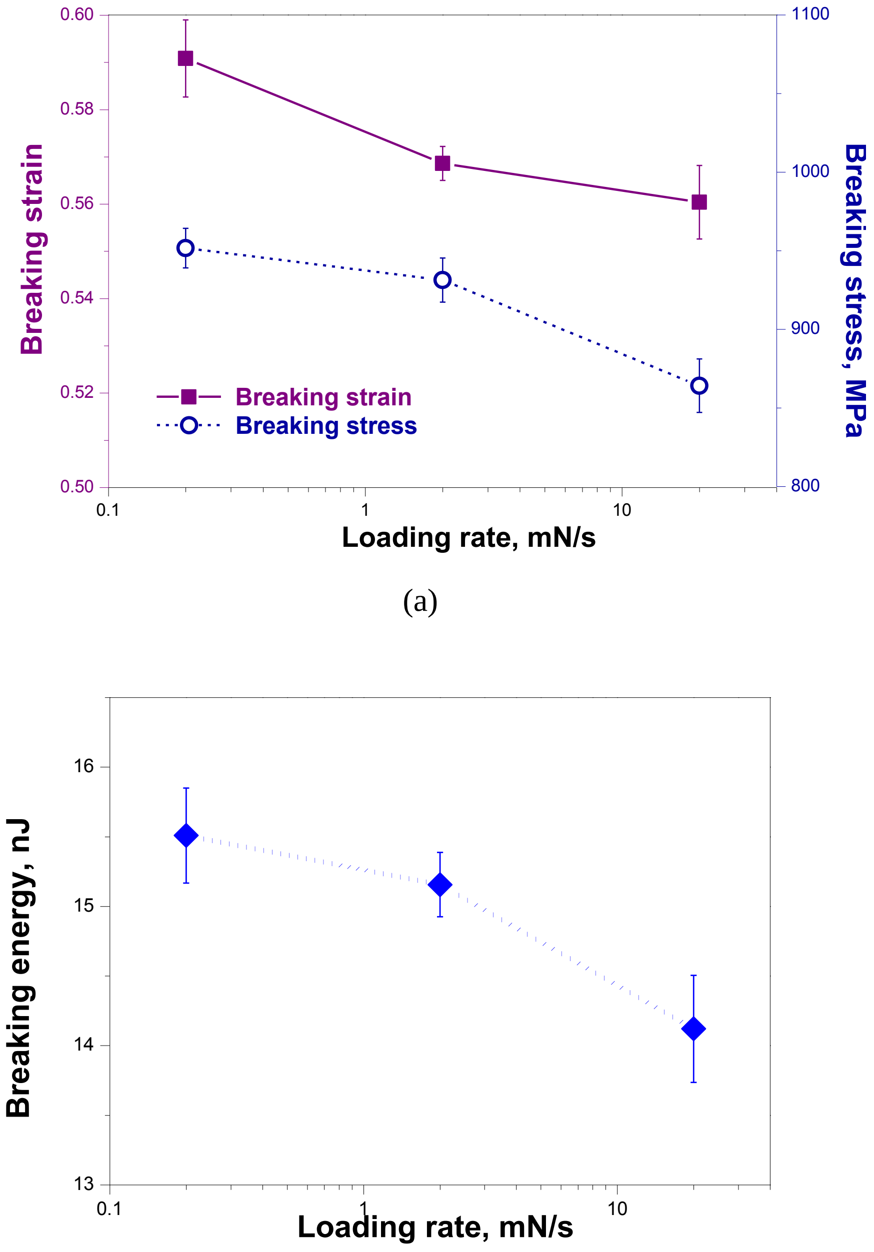
Loading rate effect The rate dependent behaviour is a significant feature of polymer materials. To better understand the rate dependent behaviour of polymer particles, the different loading rate 0.2, 2 and 20mN/s was applied on the 55wt% crosslinked one to a peak load 30mN. The obtained stress-strain relationships are plotted in Fig. 5 (a). It clearly shows a rate dependent behaviour that the faster compression the harder particle behaviour, even in the small deformation scale as shown in the inserted diagram. The corresponding fracture morphology of particles compressed at different loading rate is also shown in Fig. 5 (b). It can be seen that the cracking is always along the meridian direction of particles. The fracture pattern of particles is affected by the loading rate. The smaller loading rate leads to more pieces of fragments. The fracture properties including breaking strain and breaking stress are analyzed, which are directly read from the corresponding values at the burst point on stress-strain curves. The breaking energy is calculated by integral of contact load-displacement curves prior to displacement burst. The influence of varying loading rates on these parameters is shown in Fig. 6. With increase of the loading rate, both breaking strain and breaking stress decrease and also induce decreasing breaking energy. This is in agreement with the fracture morphology of particles.



(a)

(b)

Fig. 5. The loading rate effect on the stress-strain relationship of 55wt% crosslinked particles (a) and corresponding fracture morphology (b).



(a)

(b)

Fig. 6. The loading rate effect on the fracture properties of 55wt% crosslinked particles: (a) breaking strain and breaking stress; and (b) breaking energy.

The mechanical response of highly crosslinked polymer materials is often described with their viscoelasticity, depending on the time and the temperature [15]. The faster compression leads to less time available for the stress redistribution in terms of molecular chain rearrangement and reorientation within particles. It also reduces the probability of local plastic deformation through restricting the elastic shear deformation with the formation of slippage bands. This causes a larger compression modulus, hence a more brittle behaviour of particles and lower fracture energy under faster compression.

Summary

By using a nanoindentation-based flat punch method, the mechanical properties of monodisperse PS-co-DVB particles has been studied to improve the understanding of particle behaviour used in electronic packaging technology. The mechanical response of particles has been found to be very sensitive to the crosslink density and loading rate. As the crosslink density increases, a ductile-to-brittle transition of particle behaviours has been disclosed, which shows that the higher the crosslink density, the stiffer the particle and more brittle the fracture. A viscoelastic response of highly crosslinked particles is illustrated by the dependence of particle behaviour on the loading rate. The bursting parameters, such as breaking strain, breaking stress and breaking energy are linked to the loading rate. The higher loading rate results in the faster fracture due to the reduced time available for the stress redistribution within the particles.

Acknowledgements

This work was financed by The Research Council of Norway, Invitrogen Dynal AS and Conpart AS via NANOMAT KMB Projects MS2MP (Grant No. NANOMAT-187269). The authors would like to thank Dr. Geir Fonnum and Dr. G. Modahl at Invitrogen Dynal AS for the help on particle preparation.

References

[1] M. S. Toprak, B. J. Mckenna, M. Mikhaylova, J. H. Waite and G. D. Stucky: Adv. Mater. Vol. 19 (2007), p. 1362.
[2] J. Liu, A. Tolvgård, J. Malmodin and Z. Lai: IEEE T. Compon. Pack. T. Vol. 22 (1999), p. 186.
[3] W. S. Kwon and K. W. Paik: IEEE T. Compon. Pack. T. Vol. 29 (2006), p. 528.
[4] Y. C. Lin and J. Zhong: J. Mater. Sci. Vol. 43 (2008), p. 3072.
[5] J. Y. He, Z. L. Zhang, and H. Kristiansen: Int. J. Mat. Res. Vol. 98 (2007), p. 389.
[6] J. Y. He, Z. L. Zhang, M. Midttun, G. Fonnum, G. I. Modahl, H. Kristiansen and K. Redford: Polymer Vol. 49 (2008), p. 3993.
[7] J. Y. He, Z. L. Zhang, and H. Kristiansen: J. Appl. Polym. Sci. Vol. 113 (2009), p. 1398.
[8] J. Y. He, Z. L. Zhang, and H. Kristiansen: Mater. Lett. Vol. 63 (2009), p. 1696.
[9] T. Ellingsen, O. Aune, J. Ugelstad and S.Hagen: J. Chromatogr. Vol. 535 (1990), p. 147.
[10] J. Ugelstad, A. Berge, T. Ellingsen, R. Schmid, T. N. Nilsen and P. C. Mork: Prog. Polym. Sci. Vol. 17 (1992), p. 87.
[11] Z. L. Zhang, H. Kristiansen and J. Liu: J. Comput. Mater. Sci. Vol. 39 (2007), p. 305.
[12] D. C. C. Lam and A. C. M. Chong: Mater. Sci. Tech. A Vol. 281 (2000), p. 156.
[13] S. Ulrich, X. Mao, P. M. Goldbart and A. Zippelius: Europhys. Lett. Vol. 76 (2006), p. 677.
[14] S. V. Panyukov and Y. Rabin: Phys. Rep. Vol. 269 (1996), p. 1.
[15] S. T. Choi, S. R. Lee and Y. Y. Earmme: Acta Mater. Vol. 56 (2008), p. 5377.