

Generation of Multicomponent Polymer Particles using Microdroplet Evaporation Technique

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Recently, considerable attention has focused on the generation of nano- and micrometer scale multicomponent polymer particles with specifically tailored mechanical, electrical and optical properties. As only a few polymer-polymer pairs are miscible, the set of multicomponent polymer systems achievable by conventional methods, such as melt blending, is severely limited in property ranges. Therefore, researchers have been evaluating synthesis methods that can arbitrarily blend immiscible solvent pairs, thus expanding the range of properties that are practical. The generation of blended microparticles by evaporating a common solvent from solution droplets containing two dissolved immiscible polymers seems likely to exhibit a high degree of phase uniformity. A second important advantage of this technique is the formation of nano- and microscale particulates with very low impurities, which are not attainable through conventional solution techniques. When the timescale of solvent evaporation is considerably lower than that of polymer diffusion and self-organization, phase separation is inhibited within the atto- to femto-liter volume of the droplet, and homogeneous blends of immiscible polymers can be produced. We have studied multicomponent polymer particles generated from highly monodisperse microdroplets that were produced using a Vibrating Orifice Aerosol Generator (VOAG). Ultra-thin slices of polymer particles were characterized by a Scanning Electron Microscope (SEM), and the degree of uniformity was examined using an Electron Dispersive X-ray Analysis (EDAX).

1. Introduction

Polymer blends find wide range of applications in the field of opto-electronic devices, organic solar cells, membrane sciences and drug delivery (Adachi et. al., 1997, Jukes et. al., 2005). One of the main aspects for these applications is the uniformity of the blend so that the properties obtained are uniform throughout the material. This is often not possible, since, in many cases, the polymers are incompatible with one another and thus separate into distinct phases. Bulk solution based techniques can be used to produce polymer blend particles; for example, polymer blend particles have been produced from miniemulsions dispersed in solutions (Kietzke et. al., 2003). These techniques can reduce the extent of phase separation in many polymer blends, but it is difficult to

achieve uniform blends due to the slow evaporation of solvent from the bulk solution. The microdroplet evaporation technique requires using a solvent that can dissolve both polymers, and establishing evaporation conditions that permit rapid solvent evaporation without boiling. If the solvent evaporation rate from a solution droplet is much faster than the diffusion and self-organization time-scales of the polymers, then the phase separation can be inhibited to yield a homogeneously blended microparticle. Microdroplets evaporate rapidly in a vapor-free gas phase, and the evaporation rate can be significantly enhanced by the judicious choice of solvent and temperature. Using light scattering and diffraction patterns, Barnes et. al. (1999) have shown that a single suspended droplet of a binary polymer solution can be transformed into a homogeneous polymer blend microparticle.

The objective of this study is to examine polymer blend microparticles produced from highly monodisperse microdroplets of binary polymer solutions. We have used a Vibrating Orifice Aerosol Generator (VOAG) to generate highly monodisperse microdroplets from a solution of polystyrene/polyvinyl chloride (PS/PVC). We have examined the characteristics of the final polymer microparticles using a Scanning electron microscope (SEM) and determined the degree of uniformity by mapping the chlorine content of PVC observed in ultra thin slices of the particles that were analyzed using an Electron Dispersive X-ray Analysis (EDAX).

2. Experimental Section

2.1 Solution preparation

Two highly incompatible polymers, polystyrene (PS, $M_w=280,000$) and polyvinyl chloride (PVC, $M_w=75,000$), were examined in this study. These polymers were purchased from Sigma Aldrich, USA. Equal proportions of both the polymers (50:50) were dissolved in a common solvent, tetrahydrofuran (THF), to get a desired total polymer concentration in the solution in the range of 2 to 4 wt%. The solution was slightly warmed to dissolve the components in the solvent to obtain a clear, homogeneous solution.

2.2 Polymer blend particle production

The experimental system consists of a modified vibrating orifice aerosol generator (VOAG) which produces a continuous, linear stream of monodisperse droplets. Devarakonda (1998), Devarakonda et. al. (1998) and Devaraknoda and Ray (2003) have provided a detailed description of the system for generation of monodisperse droplets from a VOAG. Recently, Gao et. al. (2007) have produced monodisperse polymer microspheres by photopolymerization in droplets generated by a VOAG. The operation of the system is based on the fact that a cylindrical jet forms when a liquid is forced through an orifice. The jet breaks into monodisperse droplets if orifice is vibrated at a certain frequency. The droplet size for a liquid stream flowing at a volumetric rate of Q , through the orifice vibrating at a frequency f , is given by,

$$a = \sqrt[3]{\frac{3Q}{4\pi f}} \quad (1)$$

The operating parameters of the VOAG used to produce monodisperse droplets for this study are listed in Table 1.

In this study, just after generation, the droplets were dispersed using nitrogen gas to prevent droplet-droplet collisions and allowed to fall vertically downwards in a cylindrical chamber (diameter= 17.8 cm, length= 2.1 m). Also, dry nitrogen gas was allowed to flow counter-currently past the droplets to ensure complete evaporation of the solvent. Heating tapes were wound round the chamber wall to maintain a desired temperature in the atmosphere surrounding the droplets.

Table 1: Operating parameters of VOAG

orifice size	frequency, f	flow rate, Q
15 μm	150 kHz	0.294 ml/min

2.3 Characterization

The morphology of the solid particles produced from the droplets was studied by a Scanning electron microscope (Hitachi S-3200N). To obtain the distribution of each component inside the particle, samples were placed in Beem capsules, embedded in Spurr's resin, and kept under vacuum for 48 hours. They were then polymerized at 60°C for 48 hrs, and finally, very thin slices were cut using a Reichert-Jung Ultracut E microtome. The thickness of the slices was about 60 nm. The slices were placed on copper grids and examined in the FEI Tecnai Biotwin 12 transmission electron microscope (TEM). An Energy Dispersive X-ray Analysis (EDAX) (coupled with SEM) was performed for mapping the chlorine distribution in a sample. Each of the samples was coated with a thin layer of Gold and Palladium before using it under the SEM.

3. Results and Discussion

Figure 1 shows the SEM micrographs of a few polymer particles that were produced from a solution containing 2 wt% of polymers. The micrographs clearly show that the particles are (i) near 10 μm in dimension, (ii) spheroidal, and (iii) often have indentations. While the initial droplets generated by the VOAG are spherical, the dried particles have varied morphologies. This is due to nonuniform drying conditions inside the chamber. Surface hollows and indentations can be attributed to the rapid drying of the droplets. The solvent evaporates rapidly and forms a surface skin or shell that is below the glass transition of the system. Further solvent loss reduces the volume of the droplet while the surface skin maintains a constant area. Eventually, the shell collapses and forms folded or donut shaped particles. Several groups have reported such phenomena in drying droplets (Vehring 2008, Wang et. al. 2009, Mitchell, 1987). Even though the particles were not spherical, the objective was to study the extent of phase separation or the lack of it thereof. The elemental difference between PS and PVC is the presence of chlorine in PVC. This prompted us to do an EDAX on the thin slices of the blend particles that were prepared using the microtome. Fig 2(a) shows an image of the

cross-section of a slice on which EDAX was performed at three distinct locations. The slice was about 60 nm thick, and its diameter was about 12 μm as observed by TEM (not shown here). Analysis was done over an area of $3 \times 3 \mu\text{m}^2$.

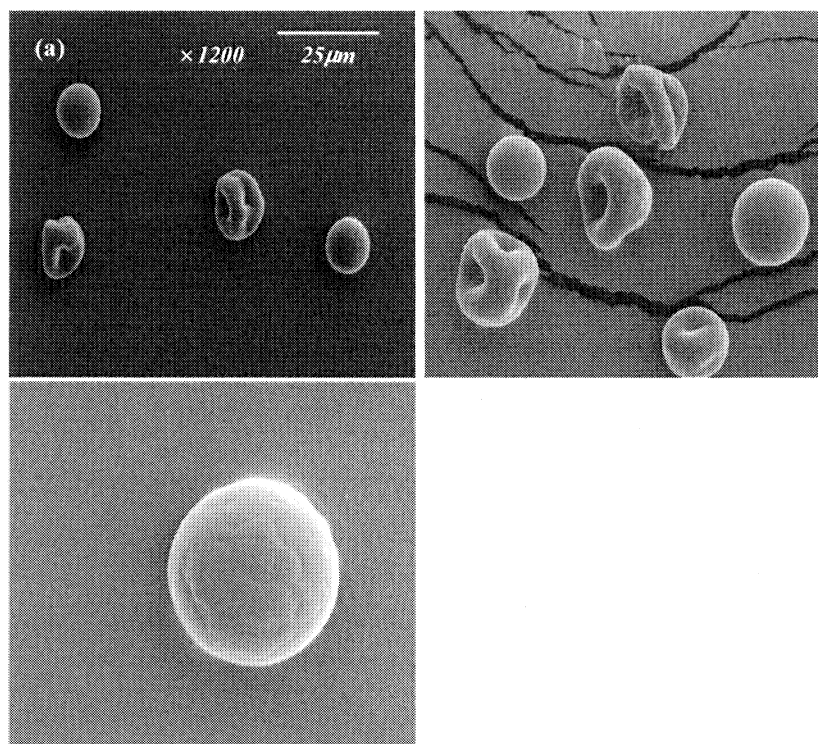


Figure 1: SEM micrographs of the polymer blend microparticles generated using the modified VOAG.

Fig 2 (b), (c) and (d) show the EDAX spectra corresponding to the three points shown in fig 2(a). The EDAX spectra clearly show primary and secondary peaks of chlorine. Also, one can observe additional peaks that comprise of gold, palladium and copper. The chlorine peaks for all the three points are observed to have intensity in the range of 110 to 150 photon counts. This suggests that the distribution of chlorine is more or less uniform throughout the cross-section. Thus, qualitatively, PVC and PS are dispersed uniformly in the particle. Further analysis would require studying more number of points in the cross-section and calculating the average percentage of chlorine in similar kinds of samples to better understand the distribution of PVC and PS in the blended microparticles. We should note that PVC has 55 wt% chlorine, while a 50:50 mixture of PVC and PS by weight contains 29 wt% chlorine. This might be possible to verify by

EDAX. In addition, glass transition measurements should show Tg's for both PVC (78 C) and PS (100 C). As the polymer chains in the blend should be highly strained, we would expect to see departures from the pure component Tg's. Repeated heating/cooling cycles should lead to particles that are phase separated. DSC might be a way to confirm the homogeneity of the blend.

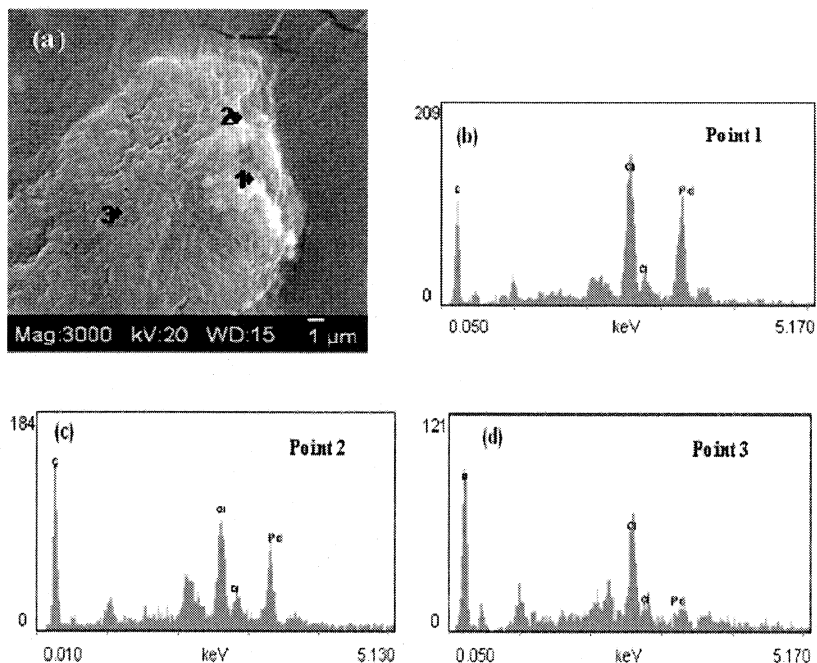


Figure 2: (a) SEM image of the ultra thin section with points on which EDAX was performed, (b), (c) and (d) are the respective EDAX spectra of the 3 points shown in (a)

4. Conclusions

Uniformly blended microparticles of two incompatible polymers were prepared by using the microdroplet evaporation technique. Droplets were generated from a binary polymer solution, using a modified VOAG. Microparticles produced after complete evaporation of the solvent were examined using SEM and EDAX. The results show that uniform polymer blend microparticles can be produced by rapid evaporation of the microdroplets. Future studies would involve examining the factors that control the morphology of the final particles that form after the solvent evaporation, including the effects of droplet size, polymer concentration, solvent volatility, and temperature. A more quantitative measurement and mapping of chlorine in the samples are needed to fully ensure that the particles produced are indeed uniformly blended microparticles.

References

- Adachi A., Hibino S., Koyoma T., and Taniguchi Y., 1997, Sub-micrometer sized organic light emitting diodes with triphenylamine containing-polycarbonate as a guest molecule in a polymer blend, *Japanese Journal of Applied Physics*, 36, L827-L830.
- Barnes M. D., Kung C. Y., Lerner N., Fukui K., Sumpter B. G., and Noid D.W., 1999, Homogeneous polymer blend microparticles with a tunable refractive index, *Optics Letters*, 24, 121-123.
- Devarakonda V., 1998, 1998, Physical and chemical processes in microdroplets, PhD thesis, University of Kentucky.
- Devarakonda V., Ray, A. K., Kaiser, T., and Schweiger G., 1998, Vibrating orifice droplet generator for studying fast processes associated with microdroplets, *Aerosol Science and Technology*, 28, 531-547
- Devarakonda V., and Ray A. K., 2003, Effect of interparticle interactions on evaporation of droplets in a linear array, *Journal of Aerosol Science*, 34, 837-857.
- Gao Z., Grulke E. A., and Ray A. K., 2007, Synthesis of monodisperse polymer microspheres by photopolymerization of microdroplets, *Colloid and Polymer Science*, 285, 847-854
- Jukes P. C., Heriot S. Y., Sharp J. S., and Jones R. A. L., 2005, Time Resolved Light Scattering Studies of Phase separation in thin films of semiconducting Polymer blends during spin coating, *Macromolecules*, 38, 2030-2032.
- Kietzke T., Neher D., Landfester K., Montenegro R., Guntner R., and Scherf U., 2003, Novel approaches to polymer blends based on polymer nanoparticles, *Nature Materials*, 2, 408-412
- Mitchell J. P., Snelling K. W., and Stone R. L., 1987, Improvements to the Vibrating orifice aerosol generator, *Journal of Aerosol Science*, 18, 231-243
- Vehring R., 2008, Pharmaceutical Particle Engineering via Spray drying, *Pharmaceutical Research*, 25, 999-1022
- Wang B., Shum H. C., and Weitz D. A., 2009, Fabrication of toroidal particles by polymer solidification in microfluidics, *European Journal of Chemical Physics and Physical Chemistry*, 10, 641-645.