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EFFECT OF CHANGING MASS RATIO OF STYRENE/BUTYL ACRYLATE ON THE BEHAVIOR OF NANO ORGANO-SILICA IN POLY (STYRENE-*CO*-BUTYL ACRYLATE) EMULSION CORE-SHELL

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ABSTRACT

Poly (styrene-co-butyl acrylate) as shell and nano organo-silica as core were prepared by *in situ* seed emulsion polymerization. The influence of changing mass ratio, butyl acrylate (BuA), and styrene (St) on the prepared emulsion were studied. The ratio of the monomers St/BA were 60/40, 70/30, 40/60 and 30/70 at constant dose of nano organo-silica 3% (based on total monomer content). The prepared nano polymers were characterized using thermal analyses, HRTEM, FESEM, FTIR and UV-Visible. Results have shown that monomer ratio has a significant influence on glass transition temperature (T_g). Thermo gravimetric analysis showed that the systems with higher BuA fraction have better thermal stability than systems with higher (St) fraction.

Keywords: styrene, butyl acrylate, nano organo-silica, core-shell, mass ratio.

INTRODUCTION

Addition of filler to polymers affects matrix structure and hence affects final material properties. Organic/inorganic nano-composites, because of their attractive mechanical, thermal, optical, electrical, and magnetic properties, are used for different purpose in electronics, paints and coatings, adhesive industry, medicine, etc. These unique properties are achieved because of the effect of nano-sized filler and are greatly influenced by dispersion of the filler in polymer matrix (Lucˇicˊ Blagojevic,ˊS. *et al*., 2012). There are several ways of nano-composite preparation: mixing in solution, mixing in the melt and *in situ* polymerization of polymer and/or inorganic phases. Results of previous research (Saricˊ, M. *et al*., 2006; Dong-ming, Q. *et al*., 2008; Zhao, Y.H. *et al*., 2006; Kashiwagi, T. *et al*., 2003; Aidan, N. *et al*., 2014; Daniel, B. and Wolfgang, B., 2015) showed that with *in situ* polymerization, in relation to the other preparation processes, best distribution and dispersion of the filler in polymer matrix was achieved.

Organic/inorganic systems with various particle morphologies can be prepared with different procedures of *in situ* emulsion polymerization. In recent years, particular interest is directed in the development of processes to gain core-shell morphology (Liu, H. *et al*., 2008; Corcos, F. *et al*., 1999; Matyjaszewski, K., 2002; Borgueat-Lami, E., 2007) where silica is a core and polymer is a shell. It is assumed that with such morphology the best distribution of the inorganic component in emulsions and films prepared from emulsions can be achieved. To achieve the core-shell morphology it is necessary to bring on the filler surface function groups that are reactive in the polymerization process; monomer (Mizutani, T. *et al*.,

2006; Mizutani, T. *et al*., 2006; Dashtizadeha, A. *et al*., 2011) and initiator (Luna-Xavier, J.L. *et al*., 2001; Qi, D.M. *et al*., 2006; Luna-Xavier, J.L. *et al*., 2002; Qi, D. *et al*., 2008) with the use of nonionic emulsifiers or to modify the surface of the filler, e.g., with silanes (Mostafa, Y. *et al*., 2013; Wen, X. *et al*., 2008; Bourgeat-Lami, E. *et al*., 2006; Bourgeat-Lami, E. and Lang, J., 1998). Function groups (Borgueat-Lami, E., 2007) can be chemically bounded or physically adsorbed onto the filler surface and can be introduced before or during polymerization procedure.

Encapsulation of silica nano-filler with polymer, i.e. encapsulation efficiency depends on (Wen, X. *et al*., 2008): (a) nature of inorganic particle (silane grafting density), concentration and size of silica nano-filler, (b) use of high hydrophilic monomers and (c) nature and concentration of monomer, initiator, and emulsifier in polymerization. Depending on the above factors various morphologies such as core-shell, daisy like, petal like, raspberry like, and multilayered morphology were obtained (Bourgeat-Lami, E., 2004).

In this paper, nano-organo-silica was prepared by sol-gel technique and *in situ* encapsulated with poly(styrene-*co*-butyl acrylate) emulsion with different monomer ratio [butyl acrylate (BuA) and styrene (St)] in presence of nonionic emulsifier to obtain good dispersability of nano-silica in polymer matrix. Thermal, optical, and morphological properties of nano-composite films were studied.

MATERIALS AND METHODS

Materials

Triethoxyvinylsilane (VTES), ethanol (analytical reagent) and ammonium hydroxides (NH$_4$OH, 35%) were purchased from Sigma-Aldrich. Styrene (St), *n*-butyl acrylate (BuA), acrylic acid (AA) (99%), potassium per-oxydisulfate (KPS), nonyl phenol polyethylene glycol ether (NP-30), sodium acetate anhydrous, sodium dodecyl-benzene-sulfonate (SDBS) and sodium dodecyl sulfate (SDS) were supplied by Across Chemical. All ingredients were used as received without further purification. Doubly distilled water was used throughout the experiments.

In situ preparation of nano-composite emulsions

Mono-dispersed nano-organo-silica spheres were prepared by sol–gel technique in an aqueous solution as reported in literature (Jie, L. *et al*., 2013). The emulsion polymerization was carried out in a 500 mL four neck flask equipped with an inlet for nitrogen gas, reflux condenser, thermocouple and mechanical stirrer through two steps.

a. Seed stage of poly (St/BuA)/nano-organo-silica (core)

Nano-organo-silica (3g) was dispersed in 33g water, (NP-300; as well as 10% of pre-emulsified mixture of monomers containing: (BuA), (St), (SDS) via gentle stirring at ambient temperature for 15 min followed by sonication (Hielscher, UP200S) for 20 min in an ice water bath at 10-15ºC. The mixture was added into three neck glass reactor containing buffer solution with stirring (80rpm). Calculated amount of (KPS) solution (0.5 g dissolved in 10 g H$_2$O) was added into the reactor at (80ºC) and left for 30 min to complete the core stage.

b. Semi-continuous stage of poly (St/BuA) (shell)

The remaining pre-emulsified mixture containing 3g acrylic acid was added using a dual syringe pump within 180 min to obtain poly (St/BuA)/nano-organo-silica emulsions as shown in Table-1.

Table-1. Formulation of the nano-composite emulsion polymers.

Sample \ Ingredients	A	B	C	D
Styrene (g)	60	70	40	30
Butyl acrylate (g)	40	30	60	70
Nano oragno-silica(g)	3	3	3	3

Characterization

Emulsion properties

Solid content was determined as recorded in ASTM D2369. The coagulum was obtained gravimetrically (Faai, Z. *et al*., 2004). Viscosity of the latex was determined according to ASTM D 2196-99 using digital viscometer (Brookfield viscometer DV-I Prime). Water absorption ratio was determined according to ASTM D570-8.

Spectroscopy characterization

Fourier transforms infrared (FTIR) spectra of nano-emulsion films were obtained in the range 4000–500cm^{-1} at ambient temperature using Thermo Nicolet Avatar 370.

Optical properties

Transmittance spectra of the films in the wavelength range 200-800nm were obtained using a UV-visible spectrophotometer (Perkin Elmer Lambda 35) at scanning speed of 300 nm min^{-1}.

Thermal properties

The thermal stabilities of the films were evaluated by (TGA), using a TA Instruments Q500 equipment thermo-gravimetric analyzer. Samples were heated at nitrogen purge flow 50 ml/min^{-1} at 25-500ºC at a heating rate of 10ºC min^{-1}. The glass transition of the films was further studied by Differential scanning calorimetry (DSC) in a TA Instruments Q2000. The thermal history of the samples was erased by heating from -20 to 100ºC at heating rate 10ºC min^{-1} and nitrogen purge flow of 50 ml min^{-1}.

Morphology

High Resolution Transmission electron microscopy (HR-TEM) was used to investigate the morphology of structural hybrid emulsion latex particles with FEI TECHNAI G20Stwin transmission electron microscope at an acceleration voltage of 200kV. A Quanta 250 field emission SEM was used to evaluate the cross section of the nano-composite latex.

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RESULT AND DISCUSSIONS

Solid content, coagulum content and viscosity

It is clear from Table-2 that the solid content of emulsion samples containing high concentration of (St) is more than emulsion samples containing high concentration of (BuA). On the other hand, the coagulum and viscosity of emulsions of high content of (St) were lower than high content of (BuA) samples. This is may be due to with an increase in the hydrophilicity of the latex by incorporation of more butyl acrylate content, which have lower reactivity ratio and higher molar mass than styrene content leads to facilitate carboxyl ionization (Hussain, A.I. and Nasr, H. E., 2010), this resulting in higher particle swelling (increase in viscosity) and hence leads to a decrease in the solid content and an increase in the coagulum content.

Table-2. Solid content, coagulum content and viscosity.

Sample / Test	A	B	C	D
Solid content %	51.7	52.0	49.9	48.4
Coagulum content %	2.1	1.3	3.9	4.3
Viscosity (CPs)	980	860	2000	5500

FTIR spectra of nano-composite films

The spectra of poly(St/BuA)/nano-organo-silica for different mass ratio of monomers are shown in Figure-1, exhibited a number of characteristic spectral bands, at 3027 cm^{-1} (stretching of C–H aromatic bonds), 1600 cm^{-1} (C=C stretching, aromatic), 1493 and 1453 cm^{-1} (C−H bending, backbone). 761 and 700 cm^{-1} (C−H bending, aromatic) correspond to the phenyl group; the peaks at 2960 and 2872cm^{-1} can be attributed to the methyl and methylene groups, the strong absorption bands at 1731 and 1162cm^{-1} correspond to carbonyl (C=O) and asymmetric C–O–C stretching vibrations (Mahdavian, A.R. *et al*., 2007; Chang, G. *et al.,* 2013). The C-H aliphatic and carbonyl groups of the butyl acrylate residues for C and D becomes more intense than A, B samples. The figure clearly displays typical absorption bands of Si–O–Si of the silica which appears at 1100 and 470 cm^{-1} (Zhou, X. *et al*., 2013).
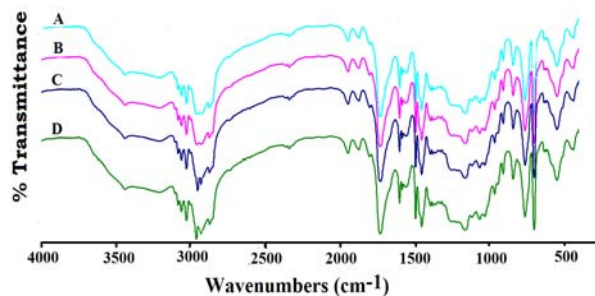
worth to mention that the incorporation of butyl acrylate co-monomer is essential for both film formation and film transparency, nano-composite particles with relatively low BuA content (<50 wt %) samples A and B produced cracked, opaque films after casting, whereas higher BuA contents samples C and D led to good-quality resilient films with much greater optical clarity and less absorbance (Lee, A. *et al*., 2011). In case of increment of styrene percent leads to more absorbance and reduction in transmittance, this reduced transmittance is simply due to the strong UV absorption by the aromatic chromophore in the styrene repeat units (Lee, A. *et al*., 2011).
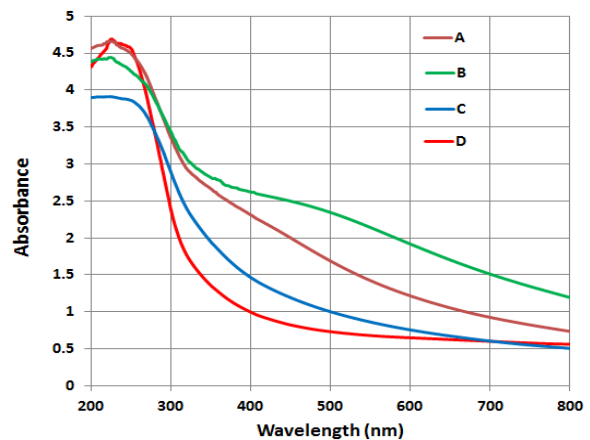

Figure-2. Absorbance spectra of nano-composite films.

Figure-1. FTIR spectra of nano-composite films.

Optical properties of nano-composite films

The optical properties of nano-composite films were greatly affected by mass ratio of styrene and butyl acrylate content and clearly displayed in Figure-2. It is

Thermal stability of nano-composite films

To determine the influence of different monomer ratio of poly (St/BuA) with 3% of nano-silica on thermal stability, TGA analysis was carried out. TGA curves and data for systems are presented in Figure-3 and Table-3.

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Thermal degradation of prepared nano-composites shows degradation in three steps. First peak (T_{max}) around 125ºC is attributed to the formation of a monomer by rupture of ''defect'' bonds of the ''head to head'' type (Ferriol, M. *et al*., 2003) and removal of physically adsorbed water. The second peak with T_{max} around 225ºC refers to the formation of a monomer from a macro-radical formed after the rupture of a *ß*-bond at the end unit containing an unsaturated bond (Buhin, Z. *et al*., 2013). The third peak (T_{max}) around 405ºC corresponds to the degradation of regular polymer backbones (Ferriol, M. *et al*., 2003). It is also visible that the (T_{95}) and residue percent at 500ºC increased by increasing butyl acrylate fractions. The systems with higher content of butyl acrylate fractions is more stable than systems with styrene fractions in the presence of nano-silica, this is due to the blocking action of butyl acrylate sequences (Leskovac, M. *et al.,* 1999). This behavior is similar to poly (methyl methacrylate-*co*-butyl acrylate)/pyrogenic silica system (Buhin, Z. *et al.,* 2013).

Table-3. Thermal stability data derived from TGA curves of mass ratio.

Sample	T_5 (ºC)	T_{50} (ºC)	T_{95} (ºC)	Temp at the largest Decomp rate, ºC	Mass fraction of total weight loss (%) at 500ºC	Residue (%) at 500ºC
A	238.67	403.04	432.13	408.54	96.06	3.8
B	234.17	402.07	433.65	407.11	95.82	4.1
C	217.4	398.31	467.34	404.30	95.69	4.3
D	233.28	395.46	498.3	401.84	94.47	5.4
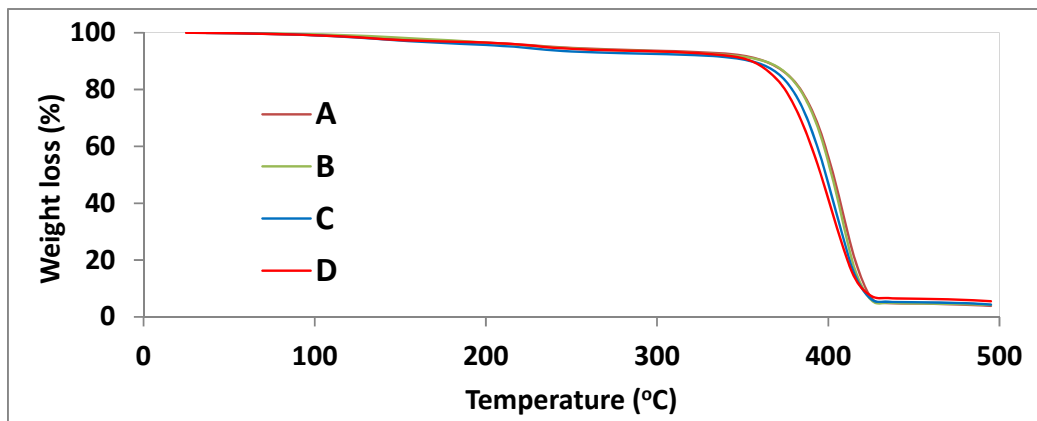
(a)
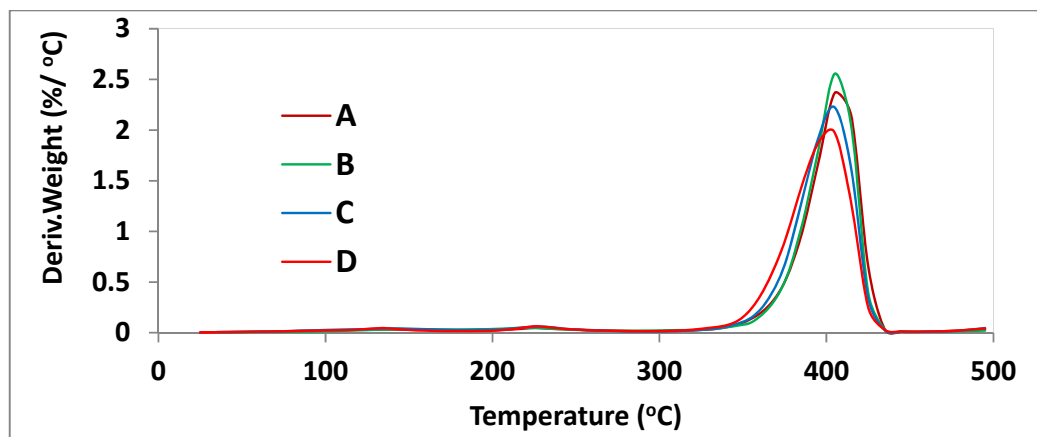
(b)

Figure-3. TGA thermograph of (a) weight loss and (b) DTG.

Glass transition of nano-composite films

Influence of a different butyl acrylate and styrene ratio in copolymer in the presence of 3% nano-silica on glass transition temperature (T_g) by the DSC analysis are shown in Figure-4. It is clear that increasing the hard monomer (St) in the matrix leads to an increase in the glass transition. On the other hand, a dramatic reduction in glass transition was recorded by increasing the soft monomer (BuA).
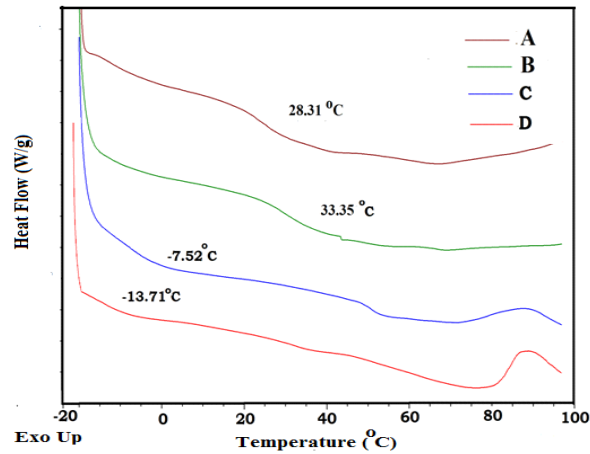

Figure-4. DSC thermograms of nano-composite films.

Morphological analysis

The kinds of monomers have a great effect on the morphology of the emulsion particles. If the monomers are more hydrophilic, they can move closer to water phase while the hydrophobic monomerstend to react far away from water phase (Ma, J. *et al.,* 2013). Consequently, Hydrophilic/hydrophobic nature of the polymer has affected the dispersion of nano-silica inside the matrix. SEM images of mass ratio effect are shown in Figure-5. It is clear that BuA-rich sample Figure-5(b), exhibits more surface roughness and agglomeration of nano-silica in the range of (2µm) than St-rich Figure-5(a).

Representative TEM images are shown in Figure-6 for St-rich nano-composite particles Figure-6(a), which remain well-defined after drying dilute aqueous dispersions at ambient temperature. Moreover, the particle surface of nano-silica is clearly coated with polymer. As more BuA co-monomer is introduced Figure-6(b), the nano-composite particles begin to coalesce on the TEM grid. This is expected, as the lower copolymer glass transition (T_g) promotes film formation during drying (Lee, A. *et al.,* 2011). The investigated properties of monomer ratio effect indicated that the nano-silica has better dispersion and less roughness surface in St-rich than BuA-rich samples.
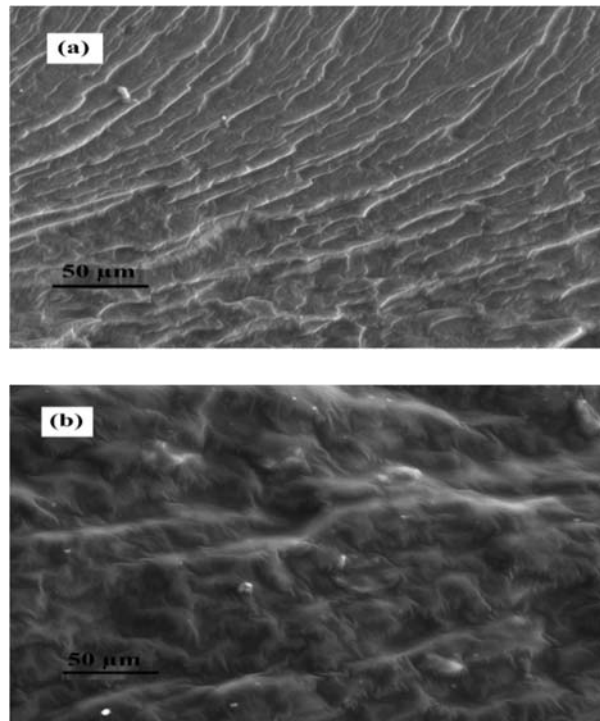

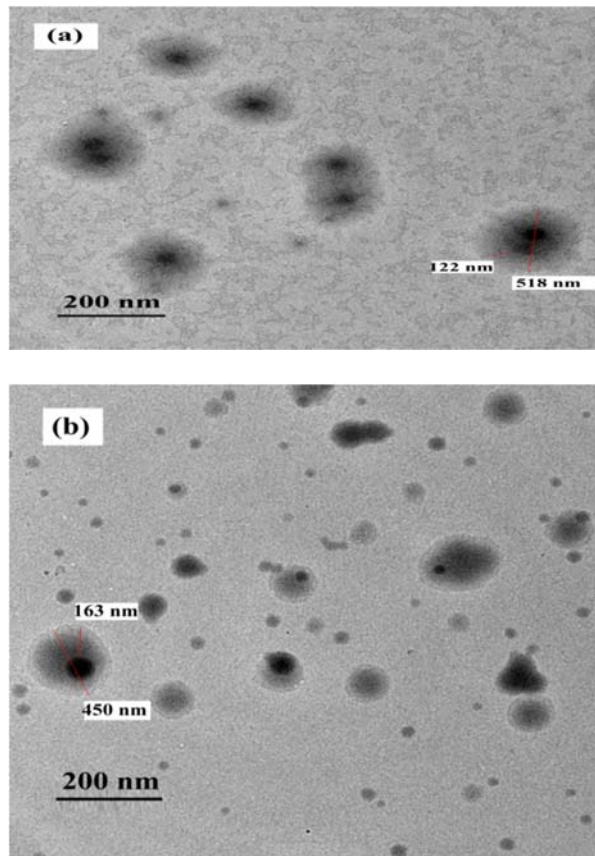**Figure-5.** FESEM of (a) sample A and (b) sample C.

Figure-6. TEM of (a) sample A and (b) sample C.

CONCLUSIONS

The effect of monomer ratio on emulsion morphology as well as on thermal and optical properties of the poly (styrene-co-butyl acrylate)/nano-silica films at constant nao-silica content were investigated. Results of DSC analysis showed that monomer ratio has significant influence on copolymer glass transition temperature. BuA-rich nano-composite films showed more thermal stability than St-rich films. Absorbance spectra of St-rich films are higher than BuA-rich films. The dispersion of nano-silica in St-rich matrix was better than BuA-rich sample.

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