Asian Journal of Chemistry; Vol. 23, No. 6 (2011), 2609-2613

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Interactive Effects of Copolymers and Nano-Sized Pigments on Coated Recycled Paperboards in Flexographic Print Applications

SINAN SONMEZ

Department of Printing Education, Faculty of Technical Education, Marmara University, Goztepe-34722, Istanbul, Turkey

Corresponding author: E-mail: ssonmez@marmara.edu.tr

(*Received*: 9 August 2010; *Accepted*: 14 February 2011) AJC-9621

The object of this study is to show the effects of two different copolymers with coating pigments on flexography. For this purpose, recycled base paperboard was coated with four coating formulations that contain nano-sized clay and ground calcium carbonate using styrene/*n*-butyl acrylate and acrylic/vinyl acetate copolymers. As a reference, conventional clay and ground calcium carbonate pigments with the same copolymers were also applied. Optical and physical properties of coated recycled paperboards were compared. The coated samples were then printed with a water based flexographic ink using a laboratory K-proofer press. Printability properties were then measured and compared. It was found that the use of styrene/*n*-butyl acrylate copolymer resulted in an increased print density, print gloss, print chroma and a decreased print mottle. However, the use of acrylic/vinyl acetate copolymer increased the PPS porosity and permeability properties of coated recycled paperboards. As a result, print densities of coated recycled paperboards decreased. In addition, the use of acrylic/vinyl acetate copolymer decreased print chroma and increased print mottle. Although the use of nano-sized clay with styrene/*n*-butyl acrylate had no significant effect. The use of nano-sized ground calcium carbonate with styrene/*n*-butyl acrylate copolymer significantly increased print chroma and decreased print mottle.

Key Words: Copolymer, Styrene/*n*-butyl acrylate, Acrylic/vinyl acetate, Pigment, Coating, Printability, Flexography.

INTRODUCTION

In the development and improvement of processes and technology incremental gains in the performance and productivity of component elements is essential. In the printing and image production process, coating formulations including mineral pigments, binders and additives have advanced to provide optimized paper properties, improving both printability and appearance[1].

Many different types of polymer latex make up pigment coatings. Chemical stability and compatibility with common pigments, starch, protein, insolubilizers, lubricants and miscellaneous additives commonly used to make the coating formulations for paper and paperboard[2].

Monomers appropriate to emulsion polymerization prepare latexes. These change the performance in the binding of latexes in the final coated product as well as in the wet-coating formulation[3]. Combining monomers with a range of rigidities is necessary in order to obtain a range of polymer films of variable rigidities. In most cases, a monomer such as vinyl acetate or styrene, which yields hard polymers, is combined with a monomer such as butyl acrylate or butadiene, which yields a soft polymer. The coating structure, optical properties and overall print quality can be significantly affected by the characteristics of the latex binders which are used in the coating formulations.

A coating improves and controls smoothness, ink receptivity and surface structure[4]. A more uniform surface provides much more uniformity of ink transfer[3]. Therefore, the ingredients in the coating formulations have an important part in obtaining good print quality[5]. The objective of this study is to determine the interaction between copolymer types, pigment types and pigment particle size on the surface appearance and flexographic print properties of coated recycled paperboards.

EXPERIMENTAL

Commercial pre-coated recycle paperboard was used as the base substrate for coating. The properties of the coating materials are given as reported by the supplier in Tables 1 and 2.

Methods: For this study, eight different coatings were prepared. The formulations of the coatings applied are given in Table-3. All coatings were prepared at 60 % solids. The pH of the coatings was adjusted to pH 8. After mixing for 0.5 h, the pH, per cent coating solids and viscosity were measured. The viscosities of the coatings were measured with a

TABLE-1
MINERAL PIGMENT PROPERTIES

Pigments	Solid (%)	Brightness (%)	pH
Commercial clay (Imerys, #1 clay)	69	88	7 ± 1
Nano-sized clay (Imerys, XP01-800)	60	88	6
Commercial $CaCO_3$ (Imerys, Hydrocarb 90)	76	94	9 ± 0.5
Nano-sized $CaCO_3$ (Omya, XP01-8100)	60	87	9

Brookfield viscometer (spindle No. 4; 1314 ± 222 cP at 100 rpm). A coating weight (16 ± 1 g) was applied on pre-coated recycled paperboard samples by a blade type, cylindrical laboratory coater (CLC).

All samples were conditioned for 24 h at 50 % relative humidity and 23 ºC (73.4 ºF) before testing. The uncalendered coated recycled paperboard samples were tested for PPS porosity, air permeability, caliper, roughness, gloss, CIE whiteness and brightness. The Parker print porosity was measured using a parker print surf (PPS) tester at 1000 kPa with a soft backing. The thickness of the coated recycled paperboard samples were measured using a TMI Micrometer.

Paper roughness was measured using a PPS ME-90 (1000 kPa, soft backing) based on TAPPI T555-OM-99. Air permeability was calculated from the PPS porosity results[6]. The brightness of coated samples was measured with a Brightimeter Micro S-5 based on TAPPI Standard T452-OM-98 (457 nm light). Paper gloss was measured at 75º using a Novo-Gloss™ Glossmeter based on TAPPI standard T480-OM-99.

Printed-coated recycled paperboards were prepared using a K Motorized Printing Proofer in flexographic mode. The effected screen frequency was 100 Lpi and effect anilox roller screen frequency was 163 Lpi, with cell volume of 10 bcm. The ink used was a performa reflex blue XGL305696 flexographic ink described elsewhere. After the printing, print density, print contrast, dot gain and CIE L*a*b* values were measured with an X-Rite EyeOne IO spectrophotometer. Print mottle[7] was measured using a Verity IA print target analysis program. ImageXpertsoftware was used to measure dot quality[8].

RESULTS AND DISCUSSION

Optical and physical properties: The optical and print properties were measured for 10 samples of each coating formulation and the averages were reported. The use of acrylic/vinyl acetate copolymer in coating formulation decreased slightly the brightness of coated recycled paperboards. The brightness of the coated recycled paperboards with commercial $CaCO_3$ are slightly higher than those of commercial clay. In addition, the use of nano-sized pigments increased the brightness relative to commercial pigments. Nano-sized pigments increased PPS porosity and permeability, thereby giving low print density. However, the use of styrene/*n*-butyl acrylate copolymer in coating formulations demonstrated a decreased effect on PPS porosity and permeability. The parker print surf porosities of the substrates are very important for the determination of the printability. A high degree of ink holdout is associated with low PPS porosity. The use of nano-sized $CaCO_3$ significantly increased PPS porosity and permeability. The lowest PPS porosity and permeability was measured in the coating formulation that contain 100 parts clay, No. 1. While the change of copolymer did not have a positive or negative effect on Hunter Gloss 75º value of coating formulations with commercial clay. The use of acrylic/vinyl acetate copolymer on coating formulations significantly increased the Hunter Gloss 75º value of coating formulation with commercial $CaCO_3$. Moreover, the use of nano-sized pigments with acrylic/vinyl acetate copolymer had a positive effect on the Hunter Gloss 75º value. But, the Hunter Gloss 75º values of the commercial pigments were higher than nano-sized pigments. The parker print surf roughness and thickness values of all samples were all similar (Table-4).

Printability properties: Print density is an important factor in a good quality print due to its determining effect on the contrast between print and substrates[9]. The physical properties of paper, smoothness and porosity, are prime factors for optimal print density. In addition, paper permeability has as much

TABLE-2
COPOLYMERS PROPERTIES

Copolymer	Dry matter (%)	Viscosity (cps)	Density (g/cm^3)	Glass trans. temperature (T_g ºC)	pH
Styrene/n-butyl acrylate copolymer (BASF, Acronal S 728)	50 ± 1	200-700	1.04	23	6.5-7.5
Acrylic/vinyl acetate copolymer (RohmNova, Polyco 3103 NP)	50 ± 1	5-125	1.06	25	6.0-7.5

TABLE-3
COATING FORMULATIONS

Coating formulations	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8
Ingredients	Dry parts added							
Commercial clay	100	80	100	80	–	–	–	–
Nano-sized clay	–	20	–	20	–	–	–	–
Commercial $CaCO_3$	–	–	–	–	100	80	100	80
Nano-sized $CaCO_3$	–	–	–	–	–	20	–	20
Styrene/*n*-butyl acrylate copolymer	10	10	–	–	10	10	–	–
Acrylic/vinyl acetate copolymer	–	–	10	10	–	–	10	10

TABLE-4
OPTICAL AND PHYSICAL PROPERTIES OF COATED RECYCLED PAPERBOARD SAMPLES

Coating formulations	Brightness (%)		PPS Roughness (μ)		PPS porosity (mL/min)		Permeability (nm²)		Machine direction (MD) hunter gloss 75º (%)		Cross direction (CD) hunter gloss 75º (%)		Thickness (mil)	
	Ave	Std	Ave	Std	Ave	Std	Ave	Std	Ave	Std	Ave	Std	Ave	Std
No. 1	78.6	0.2	1.7	0.1	7.5	0.2	195.3	0.1	43.1	2.1	42.1	1.9	21.1	0.2
No. 2	78.9	0.2	1.6	0.1	7.8	0.3	205.7	0.0	39.8	0.6	38.1	0.3	21.3	0.1
No. 3	77.9	0.3	1.9	0.3	8.7	0.2	232.2	0.0	26.7	1.7	24.5	1.1	21.4	0.1
No. 4	79.7	0.2	2.1	0.2	8.9	0.3	235.4	0.0	31.8	1.4	30.1	1.4	21.4	0.1
No. 5	81.2	0.9	1.9	0.1	8.2	0.2	219.7	0.0	27.5	0.4	26.3	0.7	21.6	0.1
No. 6	80.0	0.6	1.8	0.1	10.0	0.3	261.3	0.1	41.1	0.8	39.9	0.8	21.0	0.2
No. 7	79.6	0.9	1.7	0.1	8.8	0.2	233.8	0.0	29.9	0.5	29.0	0.5	21.4	0.1
No. 8	82.0	0.5	1.8	0.1	10.6	0.1	281.3	0.0	39.4	1.0	38.6	1.0	21.3	0.2

effect on print density as porosity. Print density is affected by the kind of coating pigment and ink ingredients used. Mechanical and environmental print conditions are also determinate factors for optimal print density[10].

Both paperboard permeability and ink absorption were affected by pigment type. Fig. 1 shows that the highest print density values were measured in the printed-coated recycled paperboards that contained commercial pigments with styrene/*n*-butyl acrylate copolymer. However, the use of acrylic/vinyl acetate copolymer significantly decreased the print density values of printed-coated recycled paperboards with commercial pigments. Changing the copolymers did not have an important effect on the print density of printed-coated recycled paperboards that contain nano-sized pigments. As, the use of nano-sized pigments with styrene/*n*-butyl acrylate copolymer decreased print density, the use of nano-sized pigments with acrylic/vinyl acetate copolymer increased print density compare to using commercial pigments. On the other hand, the pigment type did not demonstrate a positive or negative effect on print density. The ink absorption of the printed-coated recycled paperboards was increased due to an increase in porosity and permeability, resulting from an increase in the use of nano-sized pigments in the coating formulation.

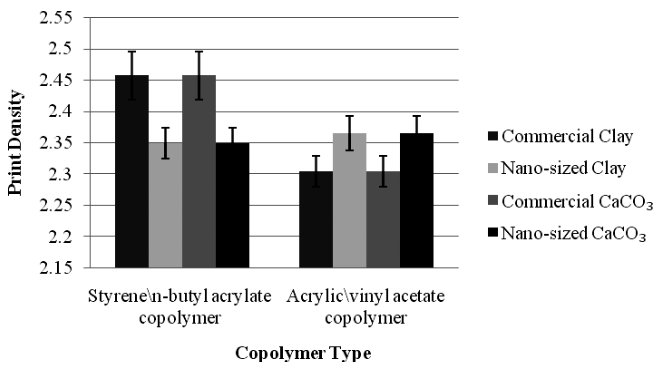

Fig. 1. Print density

Print contrast is a percentage value of tone difference between the ink density of a solid area and the ink density in a 75 % tint. Low dot gain and high print contrast indicate for a good print that is obtained with a well adjusted printing press. In other words, printing press quality will increase print contrast[11]. Changing the copolymer type did not exhibit a significant effect on the print contrast of printed-coated recycled paperboards. In addition, the pigment types did not affect print contrast, except in the formulation that included nano-sized $CaCO_3$. Nano-sized $CaCO_3$ increased print contrast, thereby giving good tone values for flexographic printing. In other words, a quality print with better shadow detail can be obtained from the use of coating formulation with nano-sized $CaCO_3$ (Fig. 2).

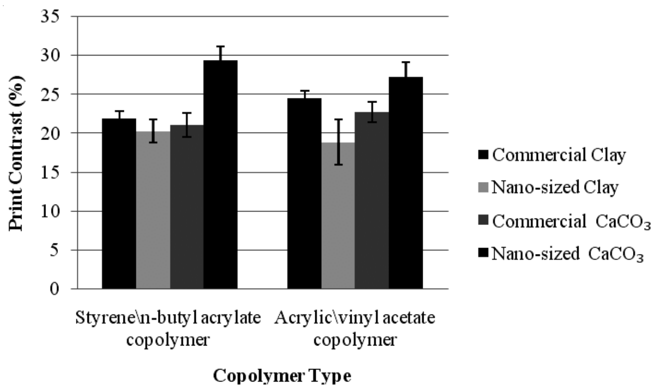

Fig. 2. Print contrast

Delta gloss, which is the difference between the gloss before printing and the gloss after printing (all at the same angle)[12], is an indicator of a good glossy print. Final gloss values may increase or decrease, depending on surface roughness and porosity properties of paper and ink ingredients[13]. In particular, the binder of ink ingredients and its amount are a significant predictor of a glossy print quality[14].

Fig. 3 shows that no noticeable change in the delta gloss values, in the machine direction (MD) of coated recycled paperboards with commercial $CaCO_3$ and nano-sized $CaCO_3$, was associated with copolymer types in each formulation. However, in coating formulations that included commercial clay and nano-sized clay, the machine direction delta gloss values decreased in using acrylic/vinyl acetate copolymer. In addition, decreased particle size of pigments slightly decreased delta gloss in all pigment types. The machine direction delta gloss values of coated recycled paperboards were higher than the unprinted machine direction gloss values of coated recycled paperboards. In other words, after printing, the printed-coated recycled paperboards had a high print gloss. Obtained cross direction delta gloss values were close to machine direction delta gloss values (Fig. 4).

Chroma refers to "colour" and it can be measured through colour intensity or saturation[15]. High chroma indicates high colour saturation, which is an important property for good quality prints, which including high colour gamut. The print chroma value was calculated as:

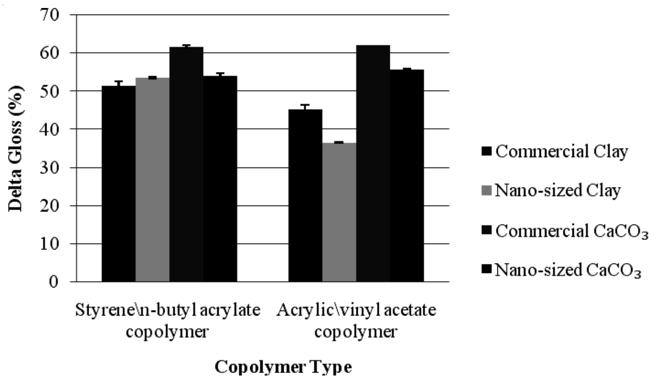

Fig. 3. Machine direction (MD) delta gloss

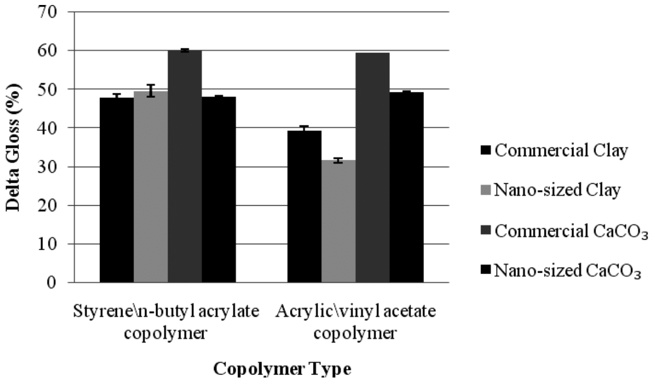

Fig. 4. Cross direction (CD) delta gloss

$$C = \sqrt{a^{*2} + b^{*2}}$$

From the results shown in Fig. 5, it is obvious that the use of nano-sized $CaCO_3$ in coating formulations significantly increased print chroma in each copolymer type, which indicated a larger colour gamut to be obtained. However, nano-sized clay did not show a significant effect on print chroma. On the other hand, the use of styrene/*n*-butyl acrylate copolymer in coating formulation increased the print chroma values of printed-coated recycled paperboards. Increased print chroma presents a larger colour gamut which is the most important determinant for good quality print in flexographic printing.

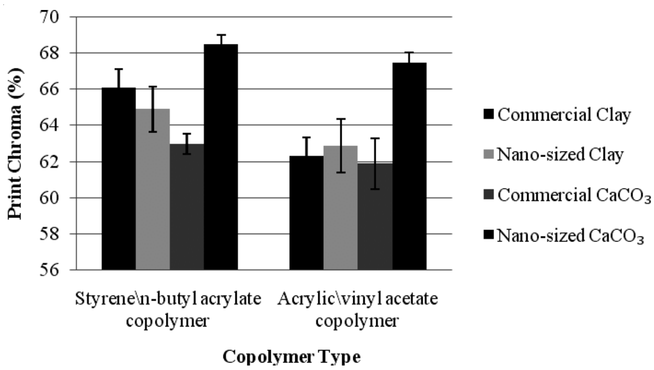

Fig. 5. Print chroma

Mottle, which indicates non-uniform ink coverage, is also an important aspect of print quality. The differences on papers surface structure and base paper properties are significant indicators of the mottling index. Therefore, pigment coating has a positive effect on the mottling index due to increased smoothness. However, the mottling index may increase or decrease depending on which pigment or which binder is in the coating formulation[16]. Heiser[3] noted considerable differences in latex concentrations at the coating surface were found, depending on binder migration conditions. As a result, the surface of coated recycled paperboard may have a different ink receptivity that increases print mottle. Decreased mottle provides a good print quality. The mottle values for the 100 % solid areas were measured.

Fig. 6 demonstrates that the use of commercial clay increased the print mottle. In addition, decreased clay particle size increased print mottle. By contrast, the use of nano-sized $CaCO_3$ decreased print mottle compare to commercial $CaCO_3$. While the use of acrylic/vinyl acetate copolymer had a positive effect on print mottle values of nano-sized clay, print mottle values of nano-sized $CaCO_3$ decreased. The print mottle values of printed-coated recycled paperboards with commercial $CaCO_3$ were higher than nano-sized $CaCO_3$ in each copolymer type (Fig. 6).

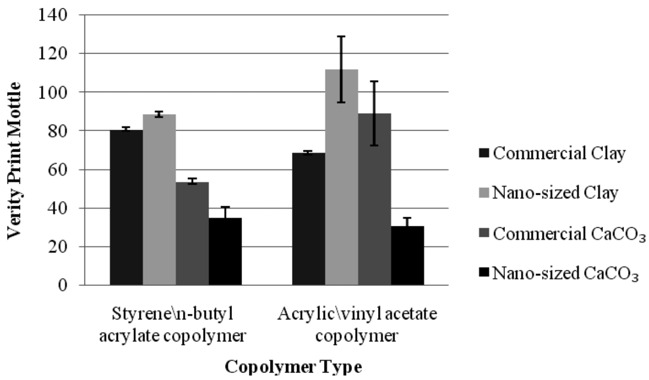

Fig. 6. Print mottle

Dot gain is known to increase the size of the half-tone dots over the period between the pre-press and printing processes. The surface smoothness affected the uniformity of the dot shape and size. Low dot gain and rounder dot shape are important properties to obtain a good print. Generally, dot gain is affected by both the anilox roller and the plate for flexographic printing[10]. Table-5 demonstrates that the use of commercial clay with styrene/*n*-butyl acrylate copolymer in coating formulations slightly increased dot gain relative to acrylic/vinyl acetate copolymer. The particle size of pigments did not show a positive or negative effect on dot gain.

The measure of dot roundness is a method to be used for the quantification of dot quality. This measurement, together with dot gain, gives a good characterization of an ink dot. An ideal circular dot has a dot roundness value of 1.00, which is the maximum value for a closed figure[17]. Table-5 shows the dot roundness values for each coating. The values, being close to one, are all within acceptable tolerance limits. Table-5 demonstrates that the change in copolymer types, pigment types and particle sizes did not show significant effect on dot area and roundness values.

TABLE-5
DOT GAIN, AREA AND ROUNDNESS VALUES

Coating formulations	Styrene/*n*-butyl acrylate copolymer						Acrylic/vinyl acetate copolymer					
	Dot gain		Dot area		Dot roundness		Dot gain		Dot area		Dot roundness	
	Ave.	Std.	Ave.	Std.	Ave.	Std.	Ave.	Std.	Ave.	Std.	Ave.	Std.
Commercial clay	66	3	0.02	0.01	0.98	0.04	60	1	0.02	0.01	0.98	0.03
Nano-sized clay	65	2	0.02	0.01	0.98	0.04	61	1	0.02	0.01	0.98	0.03
Commercial $CaCO_3$	58	3	0.02	0.01	0.98	0.02	62	2	0.02	0.01	0.98	0.02
Nano-sized $CaCO_3$	60	1	0.02	0.01	0.98	0.02	58	2	0.02	0.01	0.98	0.02

Conclusion

This study examined the effects of copolymer type on printability properties of coated recycled paperboards using nano-sized pigments. Acrylic/vinyl acetate copolymer increased PPS porosity and permeability properties of coated recycled paperboards negatively affecting print properties. Especially, print density decreased and print mottle increased. In addition, print chroma significantly decreased. However, the use of styrene/*n*-butyl arcylate copolymer in coating formulations resulted in an increased print density, print gloss, print chroma and a decreased print mottle. These indicators provide better colour reproduction in flexographic printing.

This study also revealed that the effects of pigment types and their particle sizes on the print quality of coated recycled paperboards. Pigment type did not show a significant effect on print quality. However, particle size slightly affected the print properties of coated recycled paperboards. Specifically, the use of nano-sized $CaCO_3$ significantly increased print chroma and decreased print mottle relative to the use of nano-sized clay in each copolymer type, which is an important property for a good quality print. In addition, nano-sized $CaCO_3$ had a positive effect on print density according to commercial $CaCO_3$. Pigment type and its particle size did not demonstrate any significant effect on the printed dot quality.

REFERENCES

1. K. Femi, Coating Formulations Evolve to Support New Customer Demands, Pulp & Paper (2003).
2. http://worldaccount.basf.com/wa/NAFTA~en_US/Catalog/Functional-Polymers/doc4/BASF/Industry/paper
3. E.J. Heiser, Review of Latex Binder Formulations, Effects on Coated Paper Properties, Pulp & Paper, pp. 29-35 (1985).
4. J.S. Preston, A.G. Hiorns, D.J. Parsons and P.J. Heard, Design of Coating Structure for Flexographic Printing, Coating and Graphic Arts Conference, pp. 85-117 (2007).
5. H.K. Lee, H.J. Youn, K.H. Lee, C.H. Kim, J.D. Kim and C.Y. Chen, Development of New Coated Linerboard by Combining Condebelt Drying and Curtain Coating Technologies, 63rd Appita Annual Conference and Exhibition, p. 203 (2009).
6. L. Pal, M.K. Joyce and P.D. Fleming, *TAPPI J*., **5**, 10 (2006).
7. R. Rosenberger, The Correlation of Macro Print Mottle to Surface Topography as Measured by an Optical Surface Topography System, Proceedings TAGA (2003).
8. Y. Kipman, The Role of Quantitative Data in Graphic Arts Production Facilities, International Conference on Digital Production Printing and Industrial Applications, pp. 373-377 (2001).
9. Y.H. Zang and J.S. Aspler, *TAPPI J*., **78**, 23 (1995).
10. J. Johnson, C. Andersson, M. Lestelius, L. Jarnstrom, P. Ratto and E. Blohm, *Appita J*., 371 (2009).
11. H.N. Dharavath, T.M. Bensen and B. Gaddam, *J. Ind. Technol*., **21**, 2 (2005).
12. M. Juuti, T. Prykäri, E. Alarousu, H. Koivula, M. Myllys, A. Lähteelä, M. Toivakka, J. Timonen, R. Myllylä and K.E. Peiponen, *Colloids Surf. A*, **299**, 101 (2007).
13. M.C. Béland and J.M. Bennett, *Appl. Optics*, **39**, 2719 (2000).
14. J.S. Presto, N.J. Elton, J.C. Husband, J. Dalton, P.J. Heard and G.C. Allen, *Colloids Surf. A*, **205**, 183 (2002).
15. P.P. Veazie, K.C. Julie, D.P. Sam and R. Warren, *J. Sci. Food Agric*., **81**, 983 (2001).
16. P. Rajala, N. Milosavljevic, H. Kiiskinen and M. Hendrickson, *J. Appl. Thermal Eng*., **24**, 2527 (2004).
17. P.D. Fleming, J.E. Cawthorne, F. Mehta, S. Halwawala and M.K. Joyce, *J. Imaging Sci. Technol*., **47**, 394 (2003).