Asian Journal of Chemistry; Vol. 29, No. 5 (2017), 1145-1149

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2017.20463

Synthesis of Polyacrylate Binder by Emulsion Polymerization and Application on Cotton

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Received: 22 December 2016; *Accepted*: 25 January 2017; *Published online*: 10 March 2017; AJC-18316

Present research explores the synthesis of poly-acrylate binder *via* emulsion polymerization to produces high molecular weight polymers. There is no or negligible content of volatile organic compounds where alcohol polyethylene glycol ether (AEO9), K12 were used as emulsifiers and ammonium persulphate used as an initiator and pigment printing on cotton by simple screen-printing technique. The polymerizing monomers and their charge ratio and their effects on reaction conversion rate, gel fraction rate, crocking fastness properties, solid content, emulsion stability and water resistance of samples were examined. Results showed that binder performance on these parameters were satisfactory. In addition, significantly improvement was observed on water resistant and stability parameters. The chemical structures of resulting copolymers were characterized by Fourier transform infrared spectroscopy and morphological changes of cotton fabric have been studied with the scanning electron microscope and no consequential differences were observed after characterization.

Keywords: Polyacrylate binder, Emulsion polymerization, Initiator, Water resistant, Stability.

INTRODUCTION

Cotton cellulose has exceptional properties corresponding to higher water absorbency and moisture, being snug to wear and straightforward to dye. For these factors, the apparel industry is predominantly cotton based and the share of cotton in total fiber consumption is about 50 % [1]. Pigment printing may be considered as the most often and largely used process for printing textiles due to the fact of its handy utility to a kind of fabrics and rather clean and environmentally pleasant aspects [2,3]. Printing of cellulosic fibers are viewed to account for greater than 70 % of all printed substrates and pigment printing is a fundamental process [4]. Pigment printing is just not best the oldest but additionally the easiest printing procedure so far as simplicity of application is concerned. The majority of printed fabrics had been printed with pigment dyestuff. Pigment printing has advantages similar to ease of near final print at the printing stage itself, exceptional of the prints and applicability to almost every sort of fiber or combo and the capability to prevent any washing techniques after fixation [5-7]. The binder is a film-forming substance made up of long chain macromolecules, when utilized to the textile alongside the pigment, produces a three-dimensionally network [8].

The binders used in pigment printing are usually based on styrene-butadiene, styrene-acrylate or vinyl acetate-acrylate copolymers [9]. The option of binders will consistently depend upon the ultimate fastness requisites as well as the rate specifications of the system. Determining a binder for pigment coloration is an elaborate however important step in establishing a recipe on the way to meet very distinctive standards. The place to begin to investigate which final fabric properties are important as more than a few finish use functions could require an extra polymer to obtain the desired outcome [10]. Within the field of printing ink, polyacrylate latices are probably the most commonly used binders as a result of their high-quality stability and weathering-resistance, low rate and handy instruction. Nevertheless, polyacrylate lattices possess the negative aspects of the skin tackiness at high temperature and brittleness at low temperature and drawback to balance just right mechanical properties and low temperature film forming property [11-13].

To attain an eco-friendly pigment prints, solvent-free thickening agents and low or zero-formaldehyde binding agents have been used along with other proper additives, *e.g.* cross linker, softener, active ingredients, catalyst, *etc.* [14]. Elasticity and extended adhesion of the film to the substrate is performed by crosslinking. The crosslinking responses have to produce covalent bonds, which are insensitive to hydrolyzing dealers (washing liquor, perspiration, industrial surroundings). The reaction must be activated in dry scorching air with the aid of curing method [15]. Cross linking increases the crocking, washing and dry cleaning fastness properties, but detrimentally impacts the handle of the fabric. When the binder molecule have no self-crosslinking groups, a further cross linking agent

reminiscent of urea formaldehyde or melamine formaldehyde condensate, methylolated urethane compounds *etc*., having at least two reactive groups per molecule are introduced within the binder process [16]. Emulsion polymerization is an essential industrial approach, which produces high molecular weight polymers and because there is no or negligible content of volatile organic compounds [17]. Butyl acrylate, methyl methacrylate and styrene monomers are of great importance in several commercial applications. Their poly-merization products find applications in the fields of coatings and biomaterials.

This work aimed to study the preparation of polyacrylate binder by emulsion polymerization and the influence on the crocking fastness, solid content (%), water resistance and other properties of the printed cotton fabric has also been investigated.

EXPERIMENTAL

100 % cotton scoured woven fabric having construction 28 ends/cm^2, 24 picks/cm^2 and an area density of 148 g/m^2 was used for pigment printing purpose. Butyl acrylate (BA) was used as soft monomer, methyl methacrylate (MMA) and styrene (St) as hard monomer, acrylic acid (AA) and N-methyl acrylamide (NMA) were used as functional monomer. Alcohol polyethylene glycol ether (AEO9), K12 and ammonium persulphate (APS) were used as emulsifier and initiator respectively that purchased from Sigma Aldrich. Leutexol HP was also supplied by BASF and used as a thickener.

Preparation of emulsion polymers: To study the emulsion polymerization of polyacrylate binder, emulsify the monomer with surfactants at room temperature. Then AEO9 and K12 were added 20 wt % of total water in three neck bottle flask and start stirring. Then gradually added all the monomers required amount at 5 min interval and run about 30 min with continuous stirring. Take 1/6th part pre emulsion in a three neck bottle flask and added required amount of water. Then increased the temperature up to 75 °C and simultaneously dissolve ammonium persulphate in 10 mL of distilled water and once the temperature reached 75 °C, then added 1/3th quantity of ammonium persulphate drop by drop until its colour changes to blue. When blue beam observed then remaining 5/6 parts of pre-emulsion and 2/3 parts of initiators put into the reactor simultaneously one by one in 90 min of intervals at 80 °C. Increased the temperature from 80 to 85 °C and keep it about 30 min. Stirring speed should be slower. Run the process till for observing sweet smell (if sweet smell was not observed or strong smell appeared then add 10 wt % extra initiator to the mixtures, need to run another 20 min at 85 °C). When sweet smell was observed, lower the temperature at 40 °C. Neutralizing of solutions were was done by adding ammonia water (20 wt %) to the solutions mixtures until pH = 7 was not achieved. By reducing the temperature of the solution at room temperature and collected all the segments and residue by filtration. Then washed the entire residue and dried it at 105 °C for 90 min.

Characterization: The functional groups of samples were obtained with a Bruker (Tensor 27) Fourier transform infrared spectrophotometer (FT-IR) in the range 4000-400 cm^{-1}. A standard procedure was used to create samples for SEM measurements. Samples were coated with platinum (ion-sputter, Hitachi E-1010, Japan) under vacuum and then they were used to investigate the morphology of the treated sample after printing.

Gel ratio:

$$\text{Gel ratio } (\%) = \frac{D_1}{D_2} \times 100 \quad (1)$$

where, D_1 = Dry weight of total residue; D_2 = Total weight of monomer.

Solid content: Take approximately 3 g of the sample and weigh it accurately in a glass dish. Placed it in the oven for 4 h at 110 °C. After cooling in the desiccator, weight the dish accurately.

$$\text{Solid content } (\%) = \frac{G_1}{G_0} \times 100 \quad (2)$$

where, G_1 = Constant dry weight; G_0 = Sample weight.

Conversion ratio:

$$\text{Conversion ratio } (\%) = \frac{G_1 - G_0 W}{G_0 M \times \text{Solid content}} \times 100 \quad (3)$$

where, G_1 = Constant dry weight, G_0 = Sample weight.

$$W = \frac{\text{APS} + \text{Emulsifier}}{\text{APS} + \text{Emulsifier} + \text{Monomers}} \quad (4)$$

Emulsion stability test: We have done the emulsion stability test for individual sample according to the report [8].

Dilution stability: The emulsion was diluted to a solid content of 3 % and then the emulsion was poured into 30 mL tube after dilution with the liquid column height of 20 cm, placed for 72 h and measured the volume of supernatant and precipitate upper portion.

Acid and alkali stability: In two test tubes were charged emulsion of 5 g sample tested, the two tubes were then allowed drop-wise 1 mL (1 mol/L) hydrochloric acid and 1 mL (1 mol/L) solution of KOH. After shaking, the pH test and observe the emulsion is stable. Then the two tubes placed at room temperature for 24 h and then observe the stability of the emulsion.

Electrolyte resistance stability: Added 16 mL polymer emulsion sample into the test tube, then added 4 mL of 0.5 % $CaCl_2$ solution, shake and left for 48 h, the emulsion changes observed.

Printing paste preparation and application: The print paste was prepared in soft water with heavy string by adding 10 g prepared binder separately, 12 g thickener, 6 g ammonia to attain a pH 8-9 and 0.7-0.8 % w/w fixative were also added. The viscosity of the final print paste was 28000 cps as determined with Brookfield viscometer. Then it was applied on to the fabric with the help of rubber squeeze. The angle of rubber squeeze was kept at 75 °C. The paste was applied in the form of two layers. After the application, the samples were dried at a temperature of 110 °C for 3 min [18,19].

Crock fastness testing: This test method is designed to determine the degree of colour transfer from the surface of textile floor coverings to other surfaces by rubbing. Colour fastness to rubbing (dry and wet) was assessed as per ISO 105 E04 method using a manually operated crock meter [20].

RESULTS AND DISCUSSION

Polymerizing monomers and their charge ratio: It is integral to select polymerizing monomers considering of their complementary roles in application properties. Actually, properties of polyacrylate dispersion usually lie on monomers and their charge ratio. Table-1 shows five different binder samples are made by changing the quantities of soft and hard monomers used in binder formation.

TABLE-1
SELECTION FOR BASIC MONOMERS

Samples	Methyl methacrylate (%)	Styrene (%)	Butyl acrylate (%)
A1	23	8	64
A2	20	10	65
A3	22	7	66
A4	25	9	61
A5	21	11	63

Influences of monomers ratio on properties: Fig. 1 shows the influence of monomer ratio on properties of polyacrylate binder. Fig. 1(a) deals about solid content percentage of different samples and although A3 exhibited highest solid content (%) among all provided samples but A1 and A4 has satisfactory level of solid content percentage. Fig. 1(b) denotes that conversion ratio percentage of PA binder. In this case A3 showed highest impact on conversion ratio percentage and other sample has average conversion ratio (%). Fig. 1(c) supports the gel ratio (%) of prepared binder. Furthermore, A3 showed higher gel ratio (%) among all binder samples. It can be seen that A2 and A3 samples showed similar conversion ratio (%). Actually, some oil-like matter can be observed on the surface of the emulsion and was improved as the increasing of the dose of acrylate copolymer. The cause is most likely that the molecules of copolymer can react and able to create H-bond or different bonds as a result of cohesive force [8]. The emulsion polymerization of acrylate can't be uncared for when it is dosed as a lot as ample and the copolymer of acrylate increases the gel ratio of the binder and decreases the steadiness of emulsion. Fig. 1(d) shows the performance of rubbing fastness of pigment printing fabric and it can be seen that the wet rubbing fastness is more stable than dry rubbing fastness. However, the fact that excessive amount of copolymer may induce more coagula and stabilization of the emulsion might be weakened with high amount of copolymer used is a matter of concern. Obviously, sample A-3 takes on the best integrated properties, which derive from average content of methyl methacrylate and styrene (with good film forming property) and higher butyl acrylate (with excellent flexibility and water repellency) [21].

Stability of binder: Table-2 represents the stability test of prepared binder samples. In electrolyte resistance test it can be seen that A1, A3 and A4 showed good to resistance and other samples are average to satisfactory without any precipitation. The dilution stability of all prepared samples has been passed by lab scale experiment. Furthermore, acid and alkali stability test also showed stable phenomena for all samples. It was also found that, acid and alkali stability of the emulsion improves gradually up to pH 7.

TABLE-2
STABILITY OF BINDER

Samples	Electrolyte resistance	Dilution stability	Acid and alkali stability
A1	Good	Pass	Stable
A2	Average	Pass	Stable
A3	Good	Pass	Stable
A4	Good	Pass	Stable
A5	Satisfactory	Pass	Stable

Water resistance of binder: Fig. 2 indicates that the water resistance of the prepared binder films. A3 shows the consistency to repel water among all samples. These show

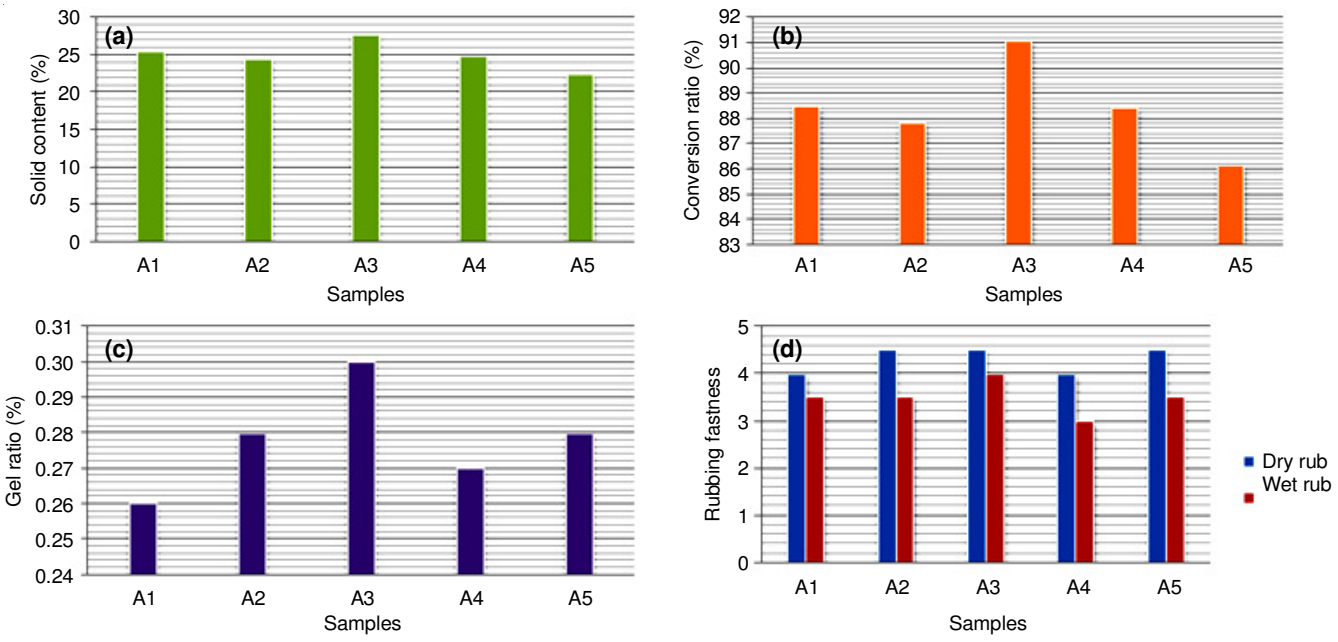

Fig. 1. (a) Solid content (%), (b) Conversion ratio (%), (c) Gel ratio (%) and (d) Rubbing fastness

that the water resistance of the film may also be multiplied, *i.e.*, the hydrophilic groups, which migrate to the skin of the movie, are lowered largely when the average amount of monomers have been brought. This is caused by the fact that monomers were copolymerized during the course of the emulsion polymerization, when desorption of emulsifiers from the particles of the binder and their migration in the movie of the binder are evaded [22]. There are several factors that affect the water resistance of binder. Initiator input method, pre emulsion pH value and dual dropping time. Initiator ammonium persulphate should be put into three parts in ratio (1:3:1). It will help in smoother reaction and conversion rate would be more. Since it helps in crosslinking in monomers and as a result conversion rate would be more but residual monomer percentage would be less. Dual dropping time should be 90 to 100 min because if time is less then reaction would be quick, exothermic reaction resulting in polymerization difficult to control and poor yield.

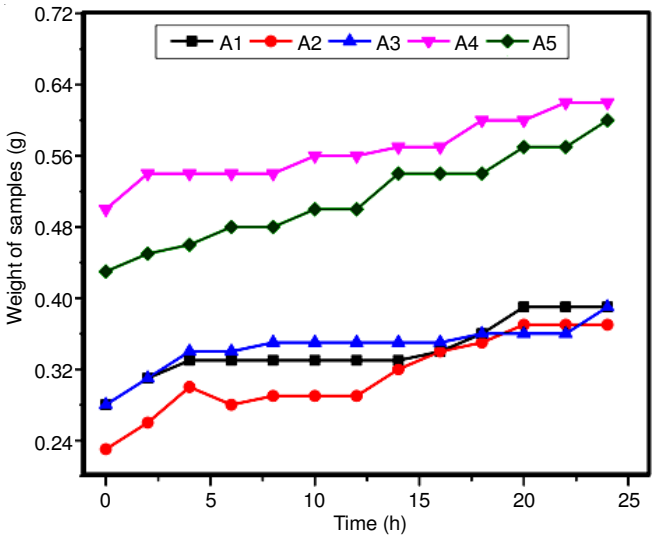

Fig. 2. Water resistance of binder

FT-IR analysis of binder: Fig. 3 represents the FT-IR spectrum of prepared binder samples. The frequency in 3500-3000 cm^{-1} region are stretching peak curves of carboxylic acid (-COOH group) which leads to its stability. It can be seen that fromA3thio group -SO_3 present in wavenumber 1500-500 cm^{-1}

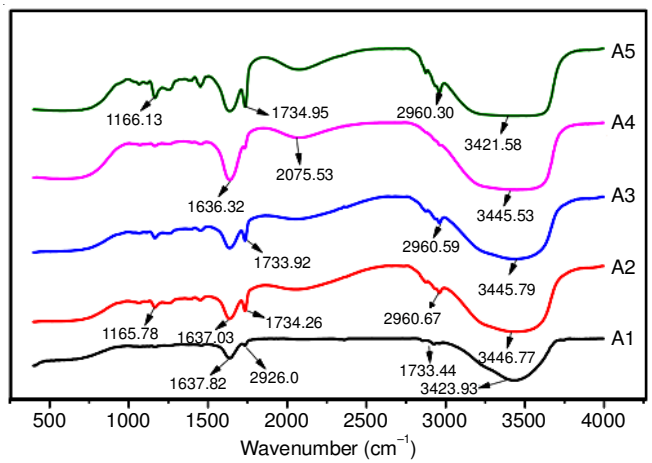

Fig. 3. FT-IR of binder

region and showed instability because of change in concentration of ammonium persulphate. Due to change in concentration of soft monomers and hard monomers in binder FT-IR graph shows variations in alkene –CH groups from wavenumber 2900-1600 cm^{-1}. So it is evident from FT-IR graph that small changes in concentration of monomers as well as initiator will lead to stability of product binder.

SEM analysis: Morphological changes of cotton fabrics treated with binder have been studied with the scanning electron microscope. Fig. 4(a) shows the surface morphology of the untreated (control) fibers from cotton fabrics. It implies that a homogeneous distribution of spherical particles deposited on the surface of the untreated cotton fiber. When fiber is treated with binder very smooth appearances and no significant changes have been observed [Fig. 4(b)].

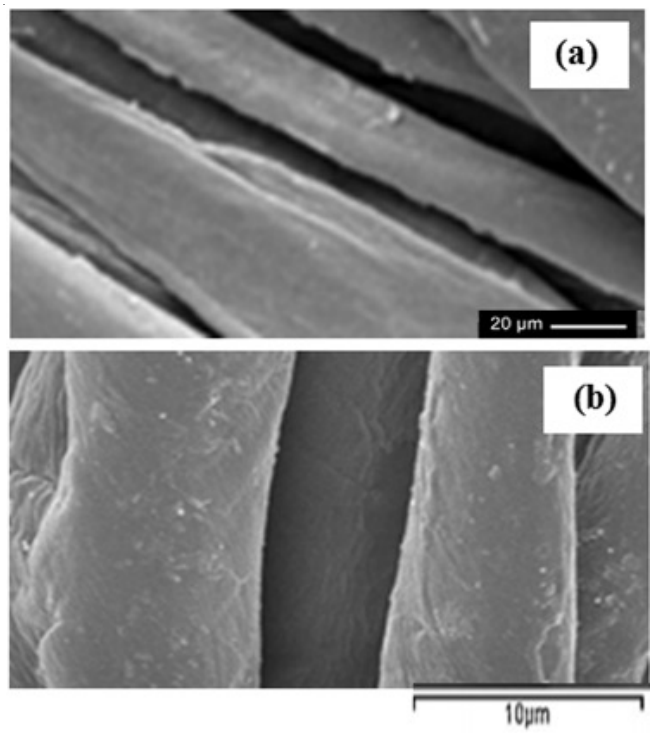

Fig. 4. SEM of (a) Untreated cotton fabric and (b) Binder treated cotton fabric

Conclusion

The present research work demonstrated the synthesis of polyacrylate binder with more stability and good application properties through most economical method *i.e.*, emulsion polymerization. Emulsifying conditions were maintained with initiator feeding was done in three parts (1:3:1) and double dropping temperature was kept at 78-82 °C for 90-95 min and then elevating its temperature 85-87 °C with pH value of pre emulsion is kept 5 and product emulsion is kept 7. In other hand when applying the binder on cotton fabric, they showed obvious improving in colour fastness to rubbing, maximum stability, minimal stiffening in handle of the textile, more water resistance. Overall research suggested that sample A3 showed best performance among all prepared samples and it could be a potential commercial binder for pigment printing of cotton textiles.

ACKNOWLEDGEMENTS

The authors express their gratitude towards Prof. Quan Heng for his constant guidance, advice and support throughout the research work. Thanks are also due to Runhe Chemical Industry, China & Colour Root (Hubei) Technology Limited, China, for providing the financial support for this research.

REFERENCES

1. S.R. Karmakar, Chemical Technology in the Pre-treatment Processes of Textiles, Elsevier, p. 12 (1999).
2. R. Eisenlohr and V. Giesen, *Inter. Dyer.*, **12**, 180 (1995).
3. M. Galgali, *Colourant*, **45**, 20 (1998).
4. M. El-Molla, *Dyes Pigmments*, **74**, 371 (2007); https://doi.org/10.1016/j.dyepig.2006.02.021.
5. S. Bahmani, G. East and I. Holme, *Color. Technol.*, **116**, 94 (2000); https://doi.org/10.1111/j.1478-4408.2000.tb00027.x.
6. M. El-Molla and R. Schneider, *Dyes Pigmments*, **71**, 130 (2006); https://doi.org/10.1016/j.dyepig.2005.06.017.
7. R.M. El-Shishtawy and S.H. Nassar, *Color. Technol.*, **118**, 115 (2002); https://doi.org/10.1111/j.1478-4408.2002.tb00367.x.
8. S. Mahmud, M.A. Habib, M.N. Pervez and A. Islam, *Am. J. Polym. Sci. Eng.*, **3**, 119 (2015).
9. D.C. Patel, Synthetic Binders for Pigment Printing, Pigment Printing Handbook, pp. 63-95 (1995).
10. M. Iqbal, J. Mughal, M. Sohail, A. Moiz, K. Ahmed and K. Ahmed, *J. Anal. Sci. Meth. Instrum.*, **2**, 87 (2012); https://doi.org/10.4236/jasmi.2012.22016.
11. C.Y. Kan, X.Z. Kong, Q. Yuan and D.S. Liu, *J. Appl. Polym. Sci.*, **80**, 2251 (2001); https://doi.org/10.1002/app.1329.
12. Y. Meng, Z. Weng, G. Shan, Z. Huang and Z. Pan, *Acta Polym. Sinica*, 367 (2004).
13. J. Zhao, H.-S. Chen and Z.-Y. Hu, *China Adhes.*, **3**, 018 (2011).
14. N. Ibrahim, M.R. El-Zairy, S. Zaky and H.A. Borham, *Polymer Plast. Technol. Eng.*, **44**, 111 (2005); https://doi.org/10.1081/PTE-200046103.
15. A. Johnson, The Theory of Coloration of Textiles, Society of Dyers and Colourists, Bradford (1989).
16. V.A. Shenai, Chemistry of Textile Auxiliaries, Sevak Publications (1976).
17. H.B. Yamak, in ed.: F. Yilmaz, Emulsion Polymerization: Effects of Polymerization Variables on the Properties of Vinyl Acetate Based Emulsion Polymers, In: Polymer Science, Intech Open Access Publisher, Chap. 2, (2013); https://doi.org/10.5772/51498.
18. A. Khan and M.N. Pervez, *Int. J. Text. Sci.*, **4**, 53 (2015); https://doi.org/10.5923/j.textile.20150403.01.
19. M.N. Pervez, A. Khan and I.A. Khan, *Am. J. Polym. Sci. Eng*, **3**, 90 (2015).
20. M.N. Pervez and M.A. Rahman, *Int. J. Sci. Eng. Res.*, **6**, 19 (2015).
21. P. Zhang and Q. Heng, *Adv. Mater. Res.*, **557-559**, 1588 (2012); https://doi.org/10.4028/www.scientific.net/AMR.557-559.1588.
22. L. Chen and F. Wu, *J. Wuhan Univ. Technol.-Mater. Sci. Ed.*, **27**, 134 (2012); https://doi.org/10.1007/s11595-012-0423-5.