

Full Length Research Paper

Perpetration of styrene–butadiene acrylate anti bacterial binders and their application on cotton/polyester printing

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This paper reports preparation of four samples of styrene – acrylic emulsion copolymers. It was performed in the presence of acrylic- acid, acryl amid, ammonium persulfate as a free radical initiator and sodium dodecyl benzene sulfate as an anionic emulsifier at 80 °C. The resulting Ag nanoparticle-loaded grafted fabric was characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) analysis. The Ag nanoparticles were almost nodisperse in nature and their average diameter was approximately 12.5 nm. The fabric shows antibacterial activity against *Escherichia coli* depending upon the extent of grafting of the polymer network onto the fabric and the amount of nano Ag loaded into the grafted fabric. The synthesized emulsion copolymers was formulated by pigmented printing paste in the presence of an acrylic thickener in two different concentrations of 3 and 5% then printed on cotton and polyester/ cotton blend fabrics and then dried at 95°C at 2 min and then fixation at 150°C at 3 min. The characteristics of cured prints such as paste add-on, colour fastness K/S together with fabrics stiffness. The highest K/S is obtained and the fastness properties range between good and excellent for samples printed using methyl metha acrylate styrene (MMA) and lowest K/S is obtained in case of using ethyl acrylate styrene (EA) as a commercial binder.

Key words: Styrene, polyester, butadiene, printing, cotton.

INTRODUCTION

Adhesion is one of the most important properties in coatings for metal protection. The loss of adhesion allows water to enter the coating/substrate interface where it acts twofold: first, expanding the detached area and hence producing blistering, and secondly, initiating corrosion (Wu et al., 2000). Acrylic lattices are among the predominant binders since they can be designed to provide either stiffness or softness, and also confer excellent properties to the fabrics (Son et al., 2006). These lattices consist in general of three or four monomers. One indeed associates very often with the basic monomers one or more monomers known as “functional” in relatively small quantity and whose role is primarily to functionalize the basic copolymer, for instance, to improve the mechanical properties of the latex film (Krumova et al., 2000). During the crosslinking treatment at high temperature of the chemically bonded on the fabric, bond formation between the polymer macro-molecules will lead to a stiff three- dimensional structure:

the viscoelastic properties of the latex will therefore change (Dusek and Duskova-Smrckova, 2000).

Recently, an awareness of general sanitation, contact disease transmission, and personal protection has led to the development of antibacterial fibers to protect wearers against the spread of bacteria and diseases rather than to protect the quality and durability of the textiles (Feulliat and Galvano, 2008). Most of the processes to create antibacterial fibers entail the attachment of biocidal or bacteriostatic agents to the fabric surface, for example, N-halamine, enzyme, quaternary ammonium salt, chitosan, or zinc oxide

The various mechanisms used to attach these agents to the fabric include the graft polymerization of N-halamine monomers onto textile substrate, the addition of N-halamine additives into the electrospinning dope of fibers, the immobilization of enzymes onto ester-cross-linked cotton fabrics the placement of quaternary ammonium salt onto cotton fabrics using a covalently

bound adduct the attachment of chitosan to chitosan fabrics via cross-linking agents and the impregnation of zinc oxide–soluble starch nanocomposites onto cotton fabrics (Chiou and Schoen, 2006).

The chemical and mechanical properties of the crosslinked polymer are thus different from those of the uncross linked one (Wicks and Jones, 2005). The hydrogen bridges between the substrate and the coating, which are responsible of adhesion of the coating, can be weakened by the action of the incoming water and the adhesion can be lost. This permits water to attack the metal surface (Mooney and Colloid, 1953). As corrosion proceeds, ferrous and hydroxide ions are formed generating an osmotic cell under the coating film. Osmotic pressure can be expected to range between 2500 and 3000 kPa, whereas the resistance of organic coatings to deformational forces is lower, ranging from 6 to 40 kPa (Verbruger and Appl, 1988). Polymer lattices used in various commercial applications are frequently prepared by copolymerization with a small amount of acrylic acid (AA) or methacrylic acid (MAA) because carboxyl groups thus introduced at the surface of latex particles stabilize lattices in alkaline solution (Gilbert, 2003). The amount of AA or MAA that can be used is limited because Coulombic repulsion exists not only among particles but also among ionized groups belonging to the same particle; thus, a particle of a carboxylated latex may swell upon alkalization or even disintegrate if the content of AA, MAA is high enough (Adamson, 1990). Aqueous dispersions of acrylate copolymers form a very important group of polymer materials, synthetic lattices, which find a variety of technical applications (Adhikari et al., 2008). Especially as water-borne paints they meet ecological requirements and have been used for many years. The utilization of these materials brings about problems related to both their rheological and film-forming properties. It has been demonstrated that the so called “alkali-swell ability” of latex particles due to dissociation of the carboxylic groups in copolymer chains is strongly influenced by copolymer composition, above all by the hydrophobicity of comonomer units (Adhikari et al., 2004).

Surfactants are commonly used during emulsion polymerization to produce latexes, stable dispersions of polymer particles in an aqueous environment the latexes produced from this process are used in applications such as adhesives, paints, and other coating applications. In these applications, the prevention of sedimentation and phase separation during the manufacture and storage of the particles is desirable (Liu and Sun, 2006).

EXPERIMENTAL

Materials

Pigmaprint red B (Alvan Sabet Co) butadiene, Roehm Company (Germany), ammonium per sulphate (Merck), ammonia (Merck) and sodium loryl ether sulphate (Henkel, Germany), styrene (Merck), sodium sulphate (Merck), acraconz BN (thickener

synthetic, Bayer Co, Germany), ammonium sulphate (NH₄)₂SO₄, (Merck). Desizing, bleached and mercerized wave cotton fabric 100 g/m² and cotton / polyester (80/20) fabric 120 g/m², supplied by by Texlab Co. Urea (Merck), emulsifier V02 (Bayer Co). Acrylamide, A, N, N'-methylene bisacrylamide (MB), and CAN were obtained from Hi Media laboratories, Mumbai, Japan. Acrylamide was recrystallized in methanol to remove the inhibitor.

Silver nitrate and sodium borhydride salts were obtained from Qualigens Fine Chemicals, Mumbai, India. Nutrient broth (NB) and nutrient agar (NA) were purchased from Hi Media laboratories. Cotton fabric was obtained from a local textile mill.

Polymerization procedure

Semi-continuous emulsion copolymerization were carried out by using a 500 ml five necked round-bottom flask equipped with a reflux condenser, stainless-steel stirrer device, and two separate feed streams. The first feed stream was a solution of butadiene – styrene and anionic surfactant. The other feed was the initiator solution before emulsion polymerization start up, the reaction vessel was first charged with the desired amounts of water, emulsifier and initiator solution. The reaction mixture was stirred at a rate of 60 rpm, and the temperature was maintained at 60°C after 5 min, 10% of total amount of the monomer mixture was added to the flask in a period of 20 min. Then the temperature was kept at 80°C until the end of polymerization and then addition sodium sulphate (antibacterial material).The polymerization was performed with feeding rate of 1.0 ml/min. The reaction was cooled to room temperature and neutralized, if necessary, to a final pH of 8.

Preparation of poly (AAm-co-IA)-grafted

All procedures, from solution preparation to the graft copolymerization, were performed at room temperature. Both the initiator (CAN) and monomer/cross-linker were dissolved in 0.1 M HNO₃ and bubbled with N₂. Unless otherwise stated, a preweighed cotton fabric piece was put in 10 ml of 20 mM CAN for 15 min, blotted with tissue paper to remove extra CAN, and then immersed in 20 ml of a solution containing predetermined quantities of the monomers AAm, IA, and the cross-linker MB. After the graft polymerization reaction, each substrate was equilibrated in distilled water to remove unreacted salts. Finally, the grafted fabric was put in acetone to remove any homopolymer formed (Taghizadeh and Darvishi, 2001) and to remove water from grafted fabric, and placed at 40°C in a dust-free chamber until the fabric was completely dry.

The percentage grafting (G) was calculated using the expression:

$$(G) = (W_g - W_o) / W_o \times 100$$

where w_o and w_g are the sample weights before and after graft copolymerization respectively.

To check the reproducibility of the grafting yield, the graft-copolymerization process was performed in triplicate and the average value of percent grafting is given in the data.

Printing recipe

Preparation of printing paste for pigment printing (Red B) was carry out according to the recipe found in Table 1 (Najafi, 2007).

RESULTS AND DISCUSSION

FTIR spectral analysis

A comparative depiction of FTIR spectra of plain, poly

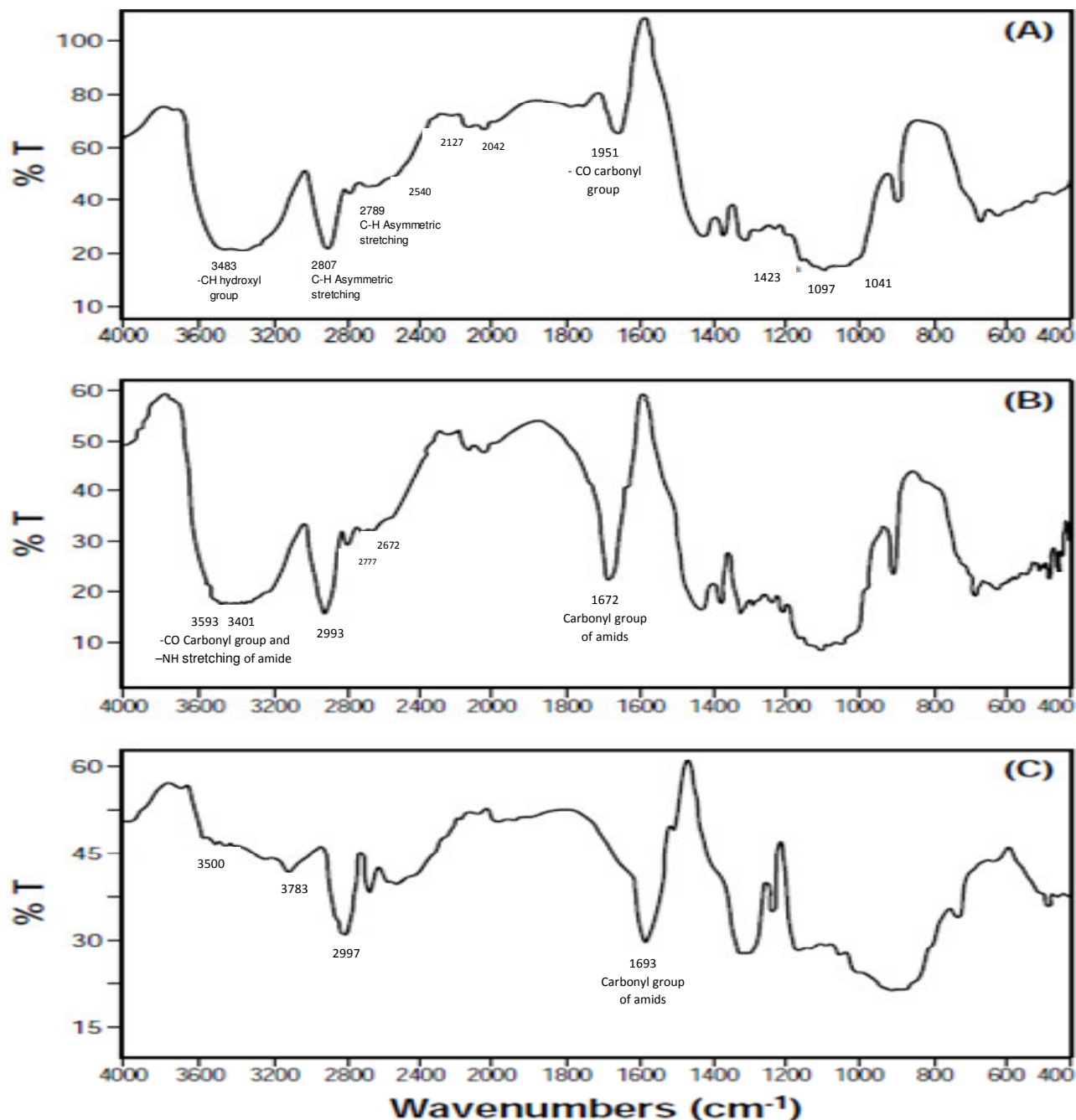


Figure 1. FTIR spectra of plain fabric (A), grafted fabric (B), Ag-loaded grafted fabric (C).

Table 1. Preparation of printing pastes for pigment.

3– 5%	Pigmaprint dye
3%	AcraconzBN
4%	Butadiene – Styrene
1%	Ammonium sulfate
0.5%	Urea

1000 Balance water.

(AAm-co-IA)- grafted, and Ag-loaded grafted fabric is shown in Figure 1A, B, and C, respectively. In Figure 3A a broad peak corresponding to the –OH hydroxyl group of cotton fabric is observed in the 3600 to 3200 cm⁻¹ range and a peak of the –CO carbonyl group is observed at 1651 cm⁻¹. Asymmetric C-H stretching is obtained in the 2500 to 2000 cm⁻¹ range, whereas the symmetric peak is obtained in the 2800 to 2600 cm⁻¹ range. Figure 5B shows a broad peak at 3400 to 3600 cm⁻¹ in the spectrum

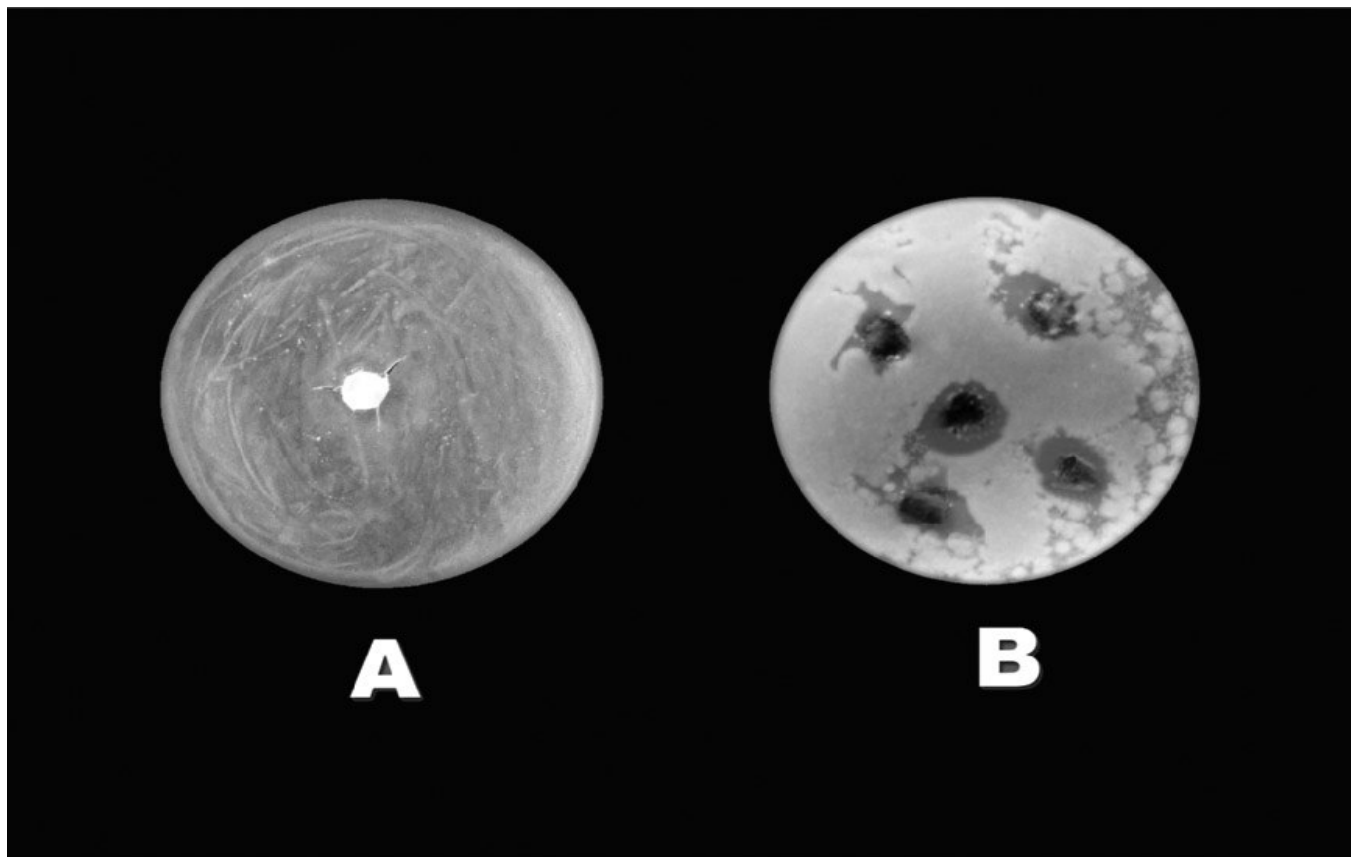


Figure 2. Antibacterial effect of Ag-loaded fabric on *E. coli*. plain fabric (A), Ag loaded fabric (B).

of the grafted sample due to both the presence of carboxylic groups of IA as well as -NH stretching of amide groups present in AAm and MB. However, in Figure 3C this broad peak almost disappears in the spectrum of Ag-loaded fabric, thus indicating the binding of Ag with N and O moieties of these functional groups. In addition, the peak at 1672 cm^{-1} , corresponding to carboxyl groups of amide functionalities in a grafted sample, is shifted to 1693 cm^{-1} in the spectrum of Ag-loaded fabric. This also indicates binding of an Ag with O in amide groups of AAm and MB.

Antibacterial action of Ag-loaded fabric

Figure 2 show the results of the antibacterial action of nano Ag-loaded grafted cotton fabric on the growth of *E. coli*. It is clear that the growth of the bacterial colonies around the Ag-loaded fabric is inhibited (Figure 2B), whereas a dense population of bacterial colonies appear in the control set that contains pieces of plain fabric in the petri dish (Figure 2A). The observed inhibiting action of nano Ag-loaded fabric is due to the release of Ag^+ ions from the Ag nanoparticles present in the fabric. These Ag^+ ions come in contact with bacterial cells and kill

them.

The results of these antibacterial tests (Figure 3), clearly indicated that the fabric prepared by immersion in AgNO_3 solution with a concentration of $50\text{ mg}/30\text{ ml}$ demonstrated greater biocidal activity as indicated by larger area of inhibition zone. Therefore, the Ag content of the fabric is a key factor in controlling its antibacterial activity.

Screen printed cotton and polyester fabrics

The effect of fixation temperature on the color strength of both samples of cotton and polyester, using EAS and BAS as syntheses binder containing Imperon brilliant red B with concentrations of 3 and 5% are shown in Figures 5 to 7. It is clear from the Figures 4 to 7 that the color strength of the printed fabrics (using either 3 or 5% dye) is nearly comparable. This may be attributed to the increase in the dye concentration needed to increase in the binder concentration to make fixation to this dye through the polymerization process to this binder. The results on Figures 5 to 7 shows that that highest and lowest color strength values K/S were obtained for MMA and BA on both polyester and cotton fabrics respectively,

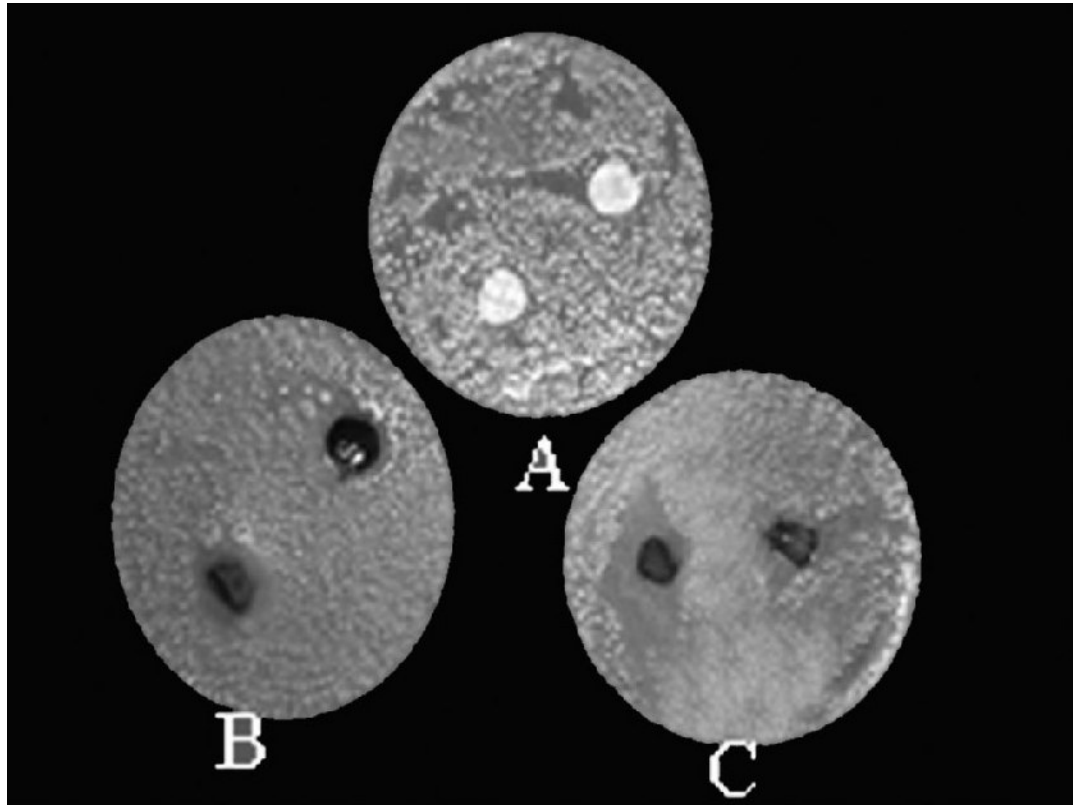


Figure 3. Effect of Ag content on bacteriostatic action (A) plain sample, (B) sample prepared in 20 mg/30 ml AgNO_3 solution, and (C) sample prepared in 50 mg/30 ml AgNO_3 solution.

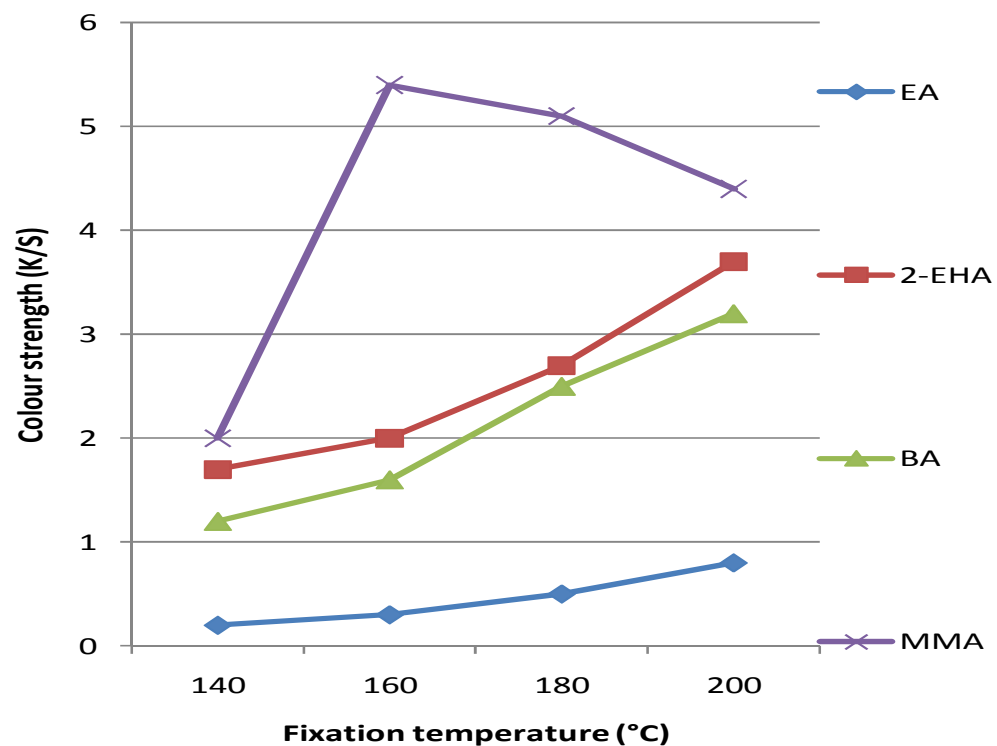


Figure 4. The effect of the type of binders used on the color strength of screen printed cotton fabrics using 3% Imperon Brilliant red B, the time of fixation is 2 min.

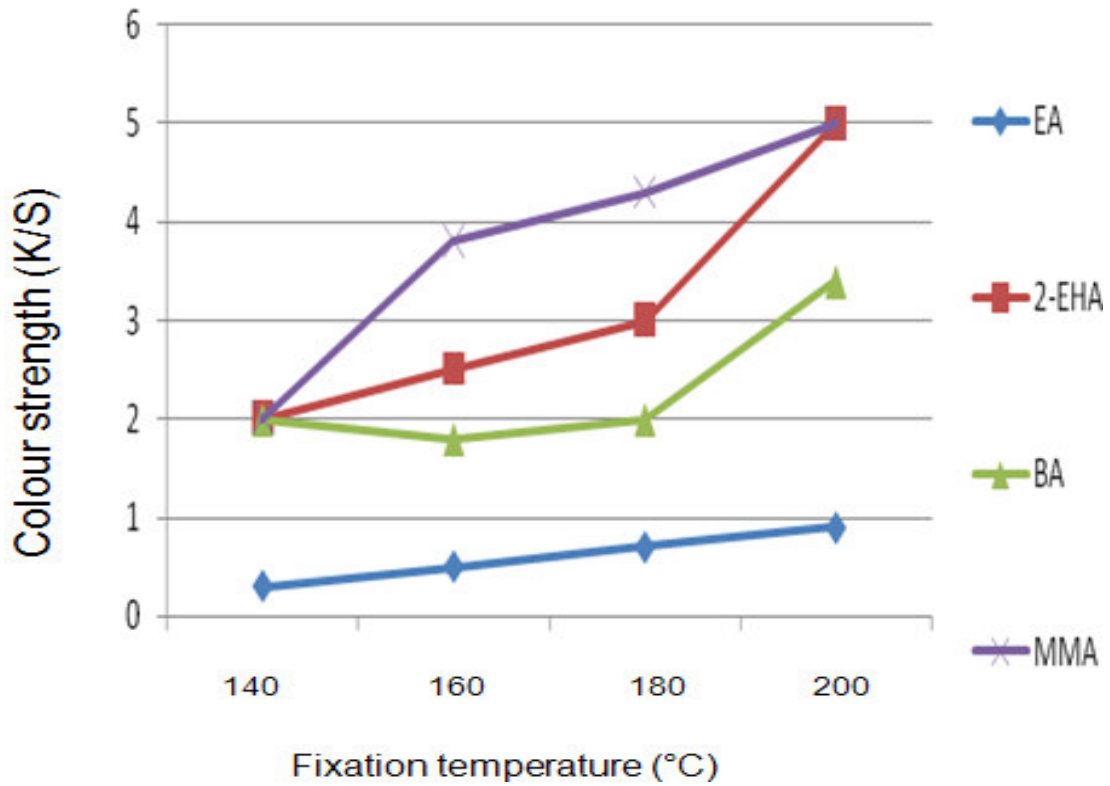


Figure 5. The effect of the type of binders used on the color strength of screen printed cotton fabrics using 5% Imperon brilliant red B, the time of fixation is 2 min.

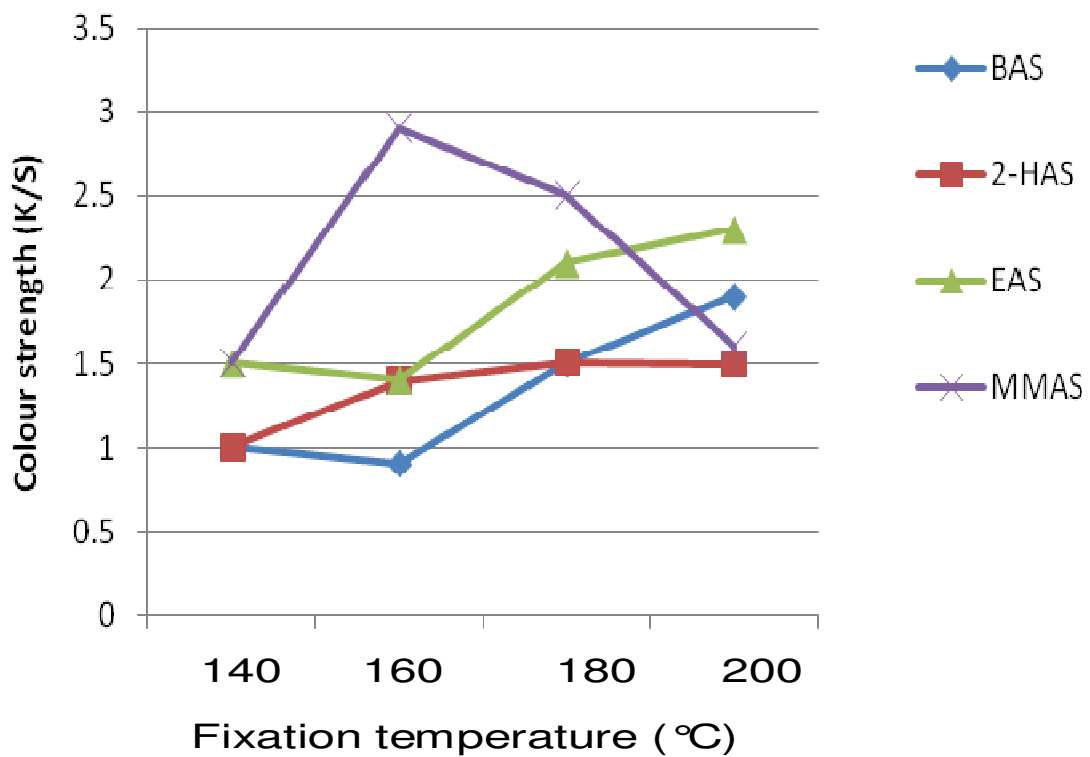


Figure 6. The effect of the type of binders used on the color strength of screen printed polyester/cotton blend fabrics using 3% Imperon brilliant red B, the time of fixation is 2 min.

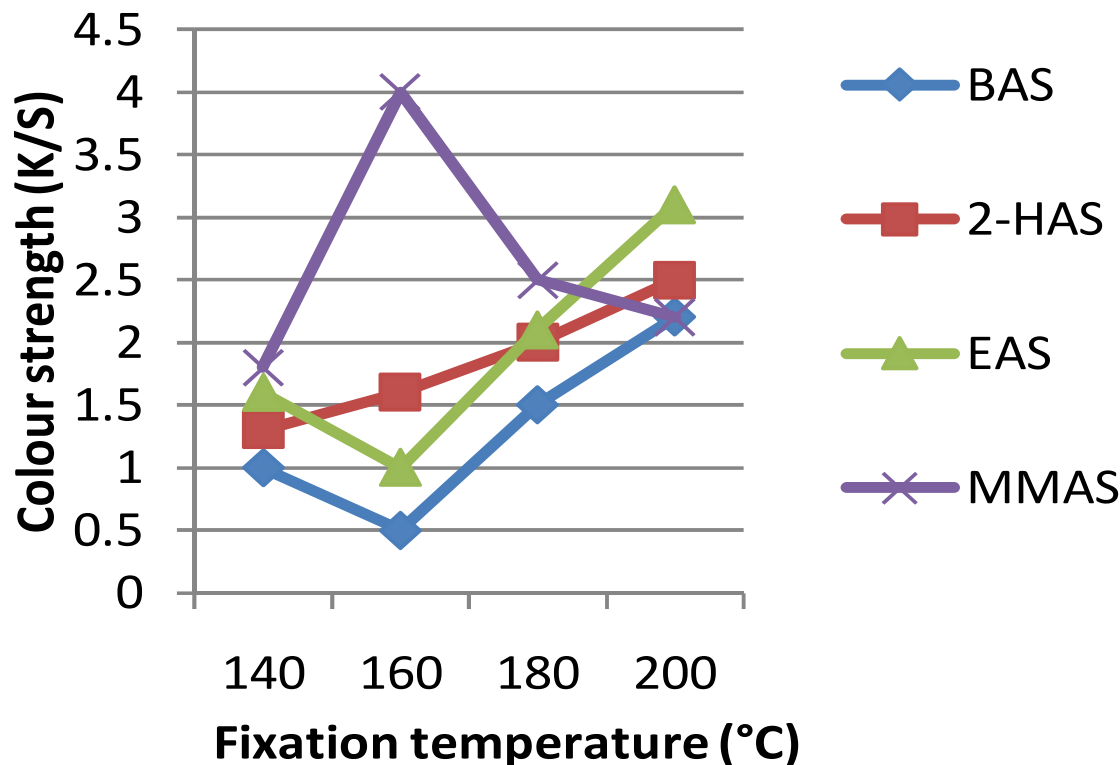


Figure 7. The effect of the type of binders used on the color strength of screen printed polyester/cotton blend fabrics using 5% Imperon brilliant red B, the time of fixation is 2 min.

when K/S value of 2-EHA higher than EA binders. It is also clear from Figures 4 to 7 that the highest color strength values were obtained in case of using styrene acrylate based as a binder in the printing paste as compared to the results obtained upon using the syntheses binder of EA, which gives the lowest value of color strength in case of screen printed cotton fabrics, while in case of using 2-EHA, the K/S values were better than the values obtained in case of using BA.

Conclusions

From this study, we concluded that the *in situ* formation of Ag nanoparticles in a grafted polymer network of cotton fabric was an effective method for the preparation of antibacterial fabrics. The almost uniform distribution of narrow dispersed Ag nanoparticles is a major advantage of this method. These fabrics show biocidal action against the bacteria *E. coli*, thus showing great potential to be used as an antiseptic dressing or bandage, which are in high demand for biomedical applications.

The results show that some novel prepared aqueous binder of styrene acrylate based on having zero volatile organic compounds can be used safely for preparing printing paste for screen printing of cotton and polyester types of textile fabrics using pigment dyes. The highest K/S values is obtained and the fastness properties range

between good and excellent for samples printed using methyl metha acrylate styrene (MMA) based, this is true irrespective of the type of printed fabric. The lowest K/S values are obtained in case of using ethyl acrylate styrene (EA) as a commercial binder.

The binder of 2-ethylhexylacrylate (2-EHA) gives K/S values better than the binder of butyl acrylate styrene (BA) for two the types of printed fabrics.

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