

Design and Development of Bilayer Composite using Different Cross-linkers

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Abstract - Composites can be assumed as a boon for enhancing the mechanical strength of hydrogels. In the present study, bilayer composites are developed using cotton substrate and poly (acrylamide-co-acrylic acid) hydrogel system through free radical polymerization. The parameters for the development of bilayer composites were optimized in terms of grafting yield. The maximum grafting with 0.1 % by (w/w) PEG and 0.3% (w/w) MBAAm was 102% and 184%. The optimised conditions for maximum grafting (0.23 ± 0.08 mm thick layer) were initiator concentration 5% (w/v), monomer molar ratio 1:1, monomer concentration 15%, reaction time 55 minutes and reaction temperature 50°C. Morphology of the composites was characterized by Fourier Transform Infrared spectroscopy (FTIR), and their mechanical properties were tested using Universal Tensile Machine (UTM). The stress-strain curve data suggests higher mechanical strength of composites as compared to hydrogel film. These results support the reinforcement of the strength of the hydrogel after converting it into a composite.

Keywords - Bilayer composite, Cross-linker, Grafting, Hydrogel, Mechanical strength

I. INTRODUCTION

The cross-linked three-dimensional hydrophilic materials¹ infiltrated with water, called 'hydrogel,' have a wide range of closely related applications with biological organisms such as controlled drug delivery^{2,3}, tissue engineering, biological research. Their biocompatibility, softness, wetness, responsiveness, and bioactivity make them useful in sensors, optics, electronics, water harvesters, dye removal^{4,5}, dehydration⁶, water purification⁷, etc. Most of them are smart due to their quick responsive nature towards environmental factors⁸ like pH, temperature^{9,10,11}, concentration, electricity, etc. polyacrylic polymers are highly significant in this regards¹². But their weak mechanical strength limits their uses for the applications occurring in aqueous or wet medium¹³.

Composites are bi, tri, or multi-layered materials with strength greater than any individual constituent layers. These may be natural or synthetic or a combination of both. However, the composite with a combination of natural and synthetic material has much more strength than its components. So efforts have been made to convert the hydrogel into composite form by grafting them with some

support like cotton¹⁴, cellulose^{7,15}, chitosan¹⁶, gelatine¹⁷, clays¹³, silk sericin¹⁸, etc.

In the grafting reaction role of initiator and crosslinker is highly crucial. A major drawback associated with these systems is excessive homo polymerization due to the initiator's presence in the whole reaction mixture leading to less yield of the grafted copolymer. In our system, we used surface grafting method in which the presence of the initiator only at the substrate's surface restricts the homopolymerization reaction. Such a method was reported by Purwar *et al*¹⁴. For the polymer system based on acrylic monomers, MBAAm¹⁹ was the widely used crosslinker, but in some cases cross-linking by PEG¹⁴ has also been reported. However, the effect of using different crosslinkers on grafting and swelling of composites is not explored completely. Thus, in this study, we explored the effect of these two crosslinkers on bilayer composite characteristics. For our study, the selected crosslinker was PEG and MBAAm. This is because MBAAm is a widely used crosslinker for this polymeric system. In contrast, PEG has unique properties like biodegradability, biocompatibility, etc. The composite prepared by it exhibits more swelling than that developed by using MBAAm as a crosslinker.

II. EXPERIMENTAL

A. Materials

Reagent grade Acrylamide from Sisco Research Laboratories (Mumbai, India), Acrylic acid (AAc), Methylene bis acrylamide (MBAAm) and Ammonium persulphate from Central drug house (Delhi, India), Polyethylene glycol (PEG 6000) from LOBA CHEMI (Mumbai, India), Cotton fabric (139 g/m²), All experiments were carried out using distilled water.

B. Method of preparation

The development of bilayer composite is a three-step process. In the first step, a 3×3 cm² sample of the support, i.e., cotton fabric, is activated by treating it with an initiator, Ammonium persulphate (APS) at 52 ± 5°C for about 30 minutes. The activated substrate was then treated with monomers acrylic acid (AAc) and acrylamide (AAm) for about 55 minutes at temperature 50 ± 5°C to graft a layer of their copolymer over the surface of the substrate. Then a calculated quantity of cross-linkers PEG or MBAAm was added, and the reaction was continued for 15 minutes to induce cross-links in the



grafted copolymer. A Schematic diagram showing the development of bilayer hydrogel composite is shown in Fig. 1.

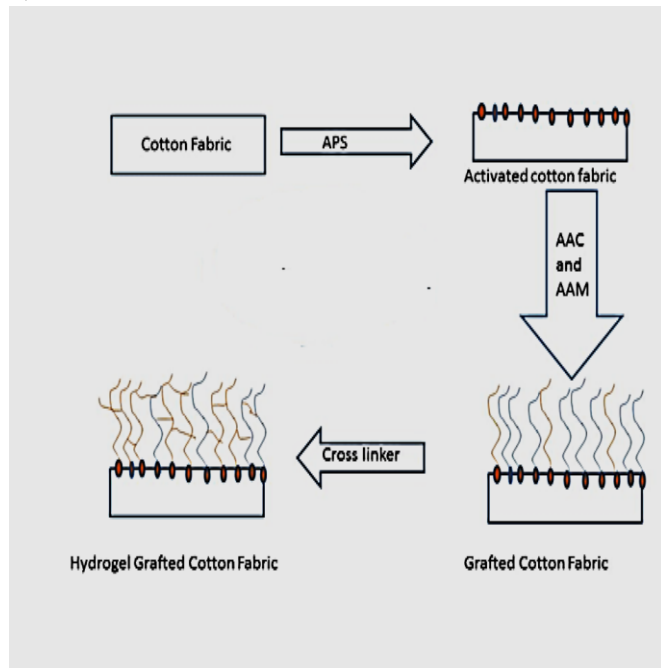


Fig 1. Schematic diagram showing the development of bilayer composite

C. Characterisation

a) Optimisation of the conditions for maximum grafting:

The conditions for composite preparation were optimized by plotting grafting yield obtained by varying a single parameter fixing the others as constant. Grafting yield of dried and weighed poly (acrylic acid co acrylamide) hydrogel grafted cotton fabric was calculated using the formula

$$\text{Grafting yield} = \frac{w_g - w_d}{w_d} \times 100\% \quad \text{-----(1)}$$

W_g = Weight of the hydrogel grafted cotton fabric, w_d = Weight of the cotton fabric taken.

(i) Initiator concentration

Cotton fabric was kept in APS solutions of concentrations 1 % to 7 % (w/V) at 50°C for about 30 minutes to create active sites over its surface. The initiator's presence only at the surface avoids the homopolymerization of acrylic acid or acrylamide during graft copolymerization reaction. Grafting yield was calculated in each case, keeping other parameters constant.

(ii) Monomer concentration

The grafting copolymerization reaction was carried out varying monomer concentration from 5 % to 15 % (w/v) to optimize monomer concentration. The monomers taken here were acrylamide and acrylic acid in 1:1. This is because of larger pore unable to hold water results in excess of acrylic acid. However, pH sensitivity gets diminished in its absence; hence the composite is of no use for control drug release²⁰. The monomer concentration is plotted with the respective

grafting yield of the hydrogel composite.

(iii) Nature of monomer

Different hydrogel systems of acrylamide and acrylic acid (i.e., Polyacrylamide, polyacrylic acid, poly acrylamide-co-acrylic acid) were grafted PEG or MBAAm crosslinkers keeping other parameters the same.

(iv) Temperature

The polymerization reaction temperature varied from 30-60°C, keeping the other variables constant and plotted with grafting yield to predict optimum temperature for maximum grafting.

(v) Reaction time

The grafting reactions were varied from 15 min to 55 min keeping other variable constant and plotted with grafting yield to predict the time taken to obtain requisite yield.

(vi) Effect of crosslinker

The introduction of cross-links makes the hydrophilic polymer chains insoluble in an aqueous environment. Here cross-links were introduced using two different crosslinkers, i.e., PEG and MBAAm. In each case, grafting yield and percent swelling were studied with varying cross linker concentrations from 0.05 to 1% of monomer weight and keeping other variables constant.

b) Fourier Transformed Infrared spectroscopy (FTIR):

The bilayer composite was analyzed using Thermo-scientific Nicolet 380 spectrophotometer, USA, in ATIR mode. For Scanning, the selected frequency range was 500- 4000 cm^{-1} and the resolution was 4 cm^{-1} .

c) Mechanical testing:

Bilayer composites of Polyacrylamide, poly acrylic acid, poly (acrylic acid –co- acrylamide) developed using PEG, and MBAAm crosslinkers were tested mechanical strength wet condition using a Universal tensile machine (UTM, Instron – 2700) in tension mode. The bilayer composite sample of the size (70×10×0.4) mm was fixed in between the two clamps. In this experiment, the sample's gauze length was taken as 50 mm, and the stretching rate was 5 mm min^{-1} . The results were reported in the form of the stress-strain curve.

III. RESULTS AND DISCUSSION

A. Development of bilayer composite

When the substrate was treated with APS solution (initiator) at 50 ± 5°C for 30 minutes, it abstracts a proton from the cellulosic substrate to produce cellulose radicals. These radicals react with one of the monomers, i.e., acrylamide present in the reaction mixture, forming a new free radical. This new radical combines with another monomer, i.e., acrylic acid, to produce another free radical. In this way, a chain reaction starts. Subsequent addition of the acrylic acid and acrylamide monomers to the activated chain propagates the grafting reaction over the substrate. Coupling, disproportionation with a crosslinker, or combination with the initiator may lead to the chain's termination.

When the copolymer's requisite thickness is achieved, PEG

or MBAAm is added to insert cross-links among poly (acrylamide co acrylic acid) chains. Polyethylene glycol (PEG) causes cross-linking by inserting an ester linkage between the chains. Contrary to this, methylene bisacrylamide (MBAAm) inserts an amide group between the polymeric chain by reacting with unsaturated chains and generating new free radicals. The mechanisms of both cases are given in Figure 2.

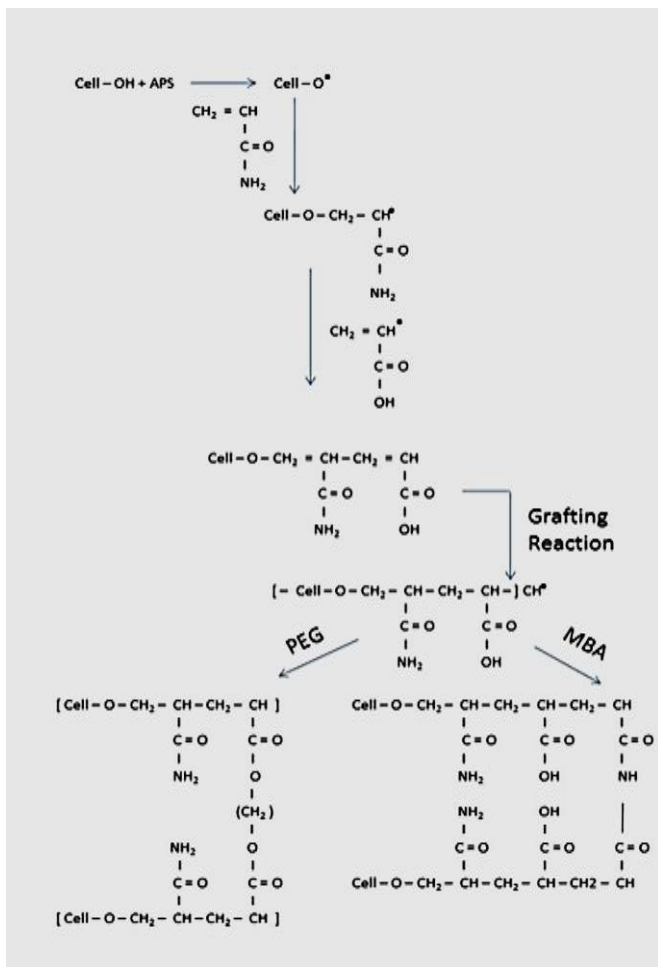


Fig 2. Mechanism showing the development of bilayer composite using two different crosslinkers

B. Effect of initiator concentration

Figure 3 reveals a hike in grafting yield with a rise in APS concentration. It shows APS is responsible for generating active sites over the surface of the substrate. A 0.30 mm thick hydrogel layer was grafted using 5 % (w/V) APS concentration. A higher APS concentration may weaken the bonds present among fibers leading to the rupturing of fabric. At 5% (w/V) APS concentration, the grafting yield was 102% and 184% using PEG and MBAAm (cross-linkers), respectively.

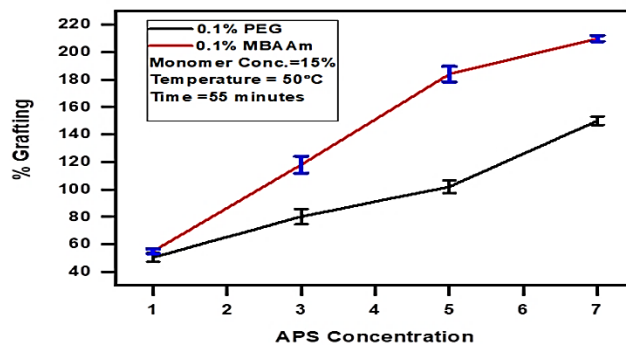


Fig 3. Effect of Initiator concentration on percentage grafting

Others reported an initial increase and then decreased percentage grafting with increasing APS concentration showing more homo polymerization due to the initiator's presence in complete reaction solution²¹. In our case, homopolymerization is almost negligible as the initiator is available only over the substrate surface.

For further studies, the optimized APS concentration was 5% (w/V) as it leads to the grafting of a sufficiently thick hydrogel layer over cotton fabric.

C. Effect of acrylamide and acrylic acid (monomer) concentration

The results are revealed in Figure 4.

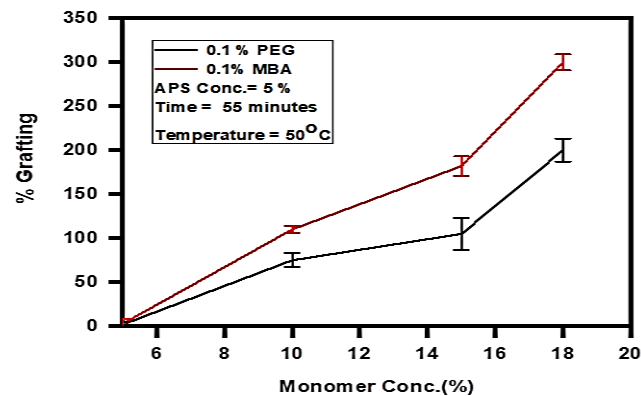


Fig 4. Effect of monomer concentration on percentage grafting

This figure indicates a gradual increase in percentage grafting with increasing monomer concentration. It may be justified with the availability of more reaction sites at higher monomer concentration. Sufficiently thick (0.23 mm thick resembling with a thickness of the cotton fabric) hydrogel layer was grafted with 15% (w/v) monomer concentration. Grafting gradually increases with a rise in monomer concentration. Chun et al. also observed the same findings for acrylic acid-acrylamide grafted polypropylene²². Although a thicker hydrogel layer left the fabric surface when equilibrated with water. Rupture of forces between

hydrogel and cotton owing to the bulkiness of hydrogel film in wet conditions may be a reason.

At 15% monomer concentration, the grafting yield was found 105% and 182% using PEG and MBAAm as a crosslinker, respectively.

For further studies, the optimized monomer concentration was 15 % (w/V).

D. Effect of Monomer Type

The results are shown in fig 5.

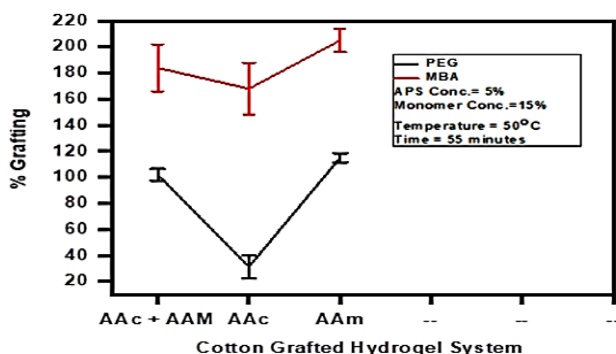


Fig 5. Effect of monomer nature on percentage grafting

The figure reveals the highest grafting for the polyacrylamide system, followed by grafting of its copolymer.

E. Effect of temperature

The results are shown in Figure 6.

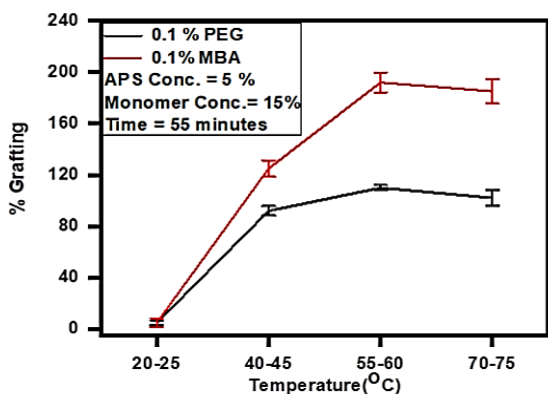


Fig 6. Effect of reaction temperature on percentage grafting

The figure reveals a rise in % grafting up to 50 ± 5°C in both the cases, i.e., with PEG and MBAAm and then a decrease in it. This is because the initial increase in temperature increases the initiator's dissociation rate and the monomer's diffusion and mobility from the aqueous phase to the fabric phase. Hence, the grafting yield increases. A further rise in temperature (above 50±5°C) may accelerate radicals' termination, leading to a decrease in % grafting.

F. Effect of reaction time

The results have reported the figure 7.

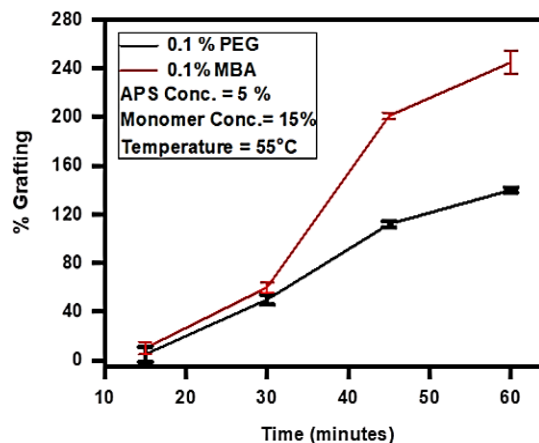


Fig 7. Effect of reaction time on percentage grafting

The results suggest that grafting yield increases with an increase in time, and 55 minutes is sufficient to graft a hydrogel layer of requisite thickness over the fabric.

G. Effect of crosslinker

The results are shown in figure 8.

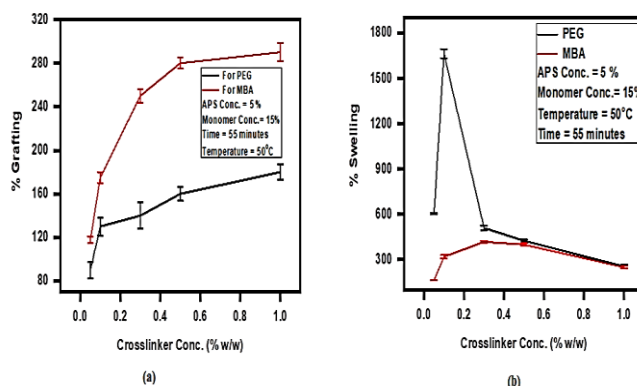


Figure 8. Effect of crosslinker concentration on (a) Percentage Grafting (b) Percentage Swelling

Figure [8(a)] indicates a regular increase in grafting yield with increasing crosslinker concentration but a decrease in percentage swelling after a certain crosslinker concentration [Fig 8(b)]. This may be attributed to reduced space present between the polymer chains with raising crosslinker concentration²⁰.

H. Morphological study

The morphology of the composites was studied by FTIR spectroscopy. Figure 9 shows the FTIR spectra of the cotton, poly (acrylic acid-co-acrylamide) hydrogel film, and composites prepared using PEG and MBAAm as a crosslinker. Figure 9(a) shows the characteristic peaks of

cotton at 3000 cm⁻¹ (for COOH), 1670 cm⁻¹ (C=O), and 1020 (C—O str.). Figure 9(e) reveals the characteristics peaks of acrylamide at 3443 cm⁻¹ (for N-H stretching) and 1656 cm⁻¹ for C=O stretching (C=O of amide group). A weak peak at 2832cm⁻¹ may be due to -OH of water molecules present in hydrogel.

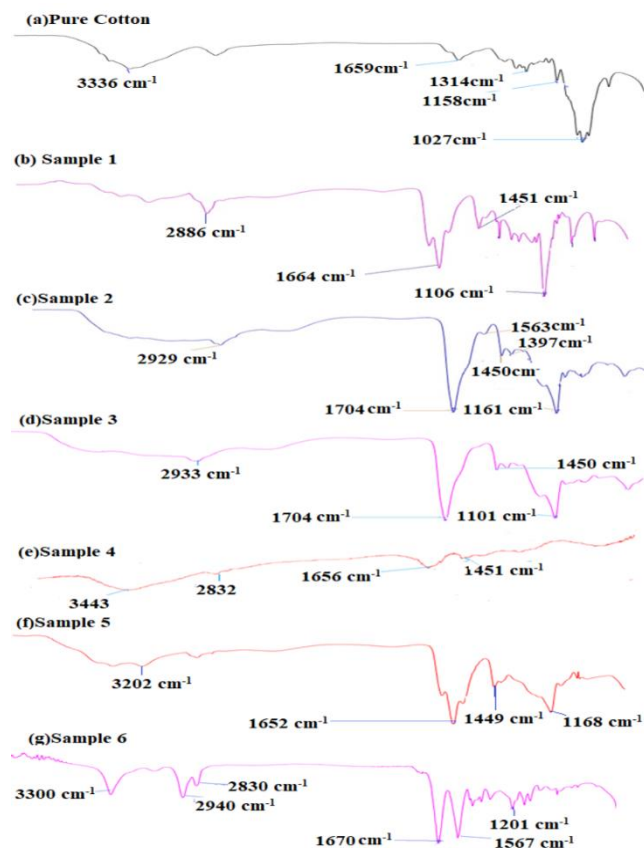


Fig 9. FTIR results

Figures 9(c) and 9(d) reveal the characteristics peaks of acrylic acid at 3400cm⁻¹ (for OH stretching) and 1704 cm⁻¹(for C=O of the acidic group). The main point of difference here is a peak of 1563 cm⁻¹ for the N-H group in figure 9(c). Figure 9(e) reveals the characteristic peaks of polyacrylic acid and Polyacrylamide. N-H is stretching at 3336 cm⁻¹, C=O (C=O of acrylamide group) stretching at 1638 cm⁻¹. Figures 9(f) and 9(g) reveal the characteristic peaks of polyacrylic acid, acrylamide, and PEG but not of cotton at 3000 cm⁻¹. These exhibit N-H was stretching at 3442 cm⁻¹, C=O (C=O of the acidic group) stretching at 1732 cm⁻¹. C=O (C=O of acrylamide group) stretching at 1660 cm⁻¹. Cross-linking by PEG in the hydrogel is revealed by a characteristic peak of C-O-C stretching at 1168 cm⁻¹, which is not found in the case of sample 6, showing the absence of ester linkage in it.

I. Mechanical testing

The results are shown in Table 1, and plots of composites with high modulus and pure hydrogel film are shown in Figure 10(a-c). Table 1 shows tensile strength is lower, but extension at break is much higher in hydrogel film than hydrogel composites. Moreover, a high modulus for composite prepared using MBAAm as crosslinker also supports its high mechanical strength. These results support the reinforcement of the power of the hydrogel after grafting over the fabric.

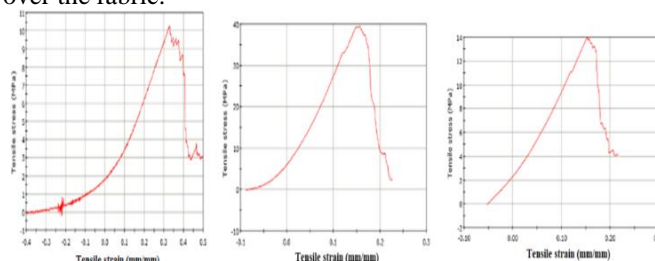


Fig 10. Stress-strain curve for (a) Sample 1 (b) Sample 7 and (c) Sample 6

Table 1. Mechanical properties of hydrogel film and bilayer composites

Materials	Tensile Stress at max load (MPa)	Tensile modulus (MPa)	Extension at Break (mm)
Sample 1 ^a	2.97±.5 (0.03)	32.3±1.4(0.03)	23.8±5(0.02)
Sample 3 ^b	3.69± 0.5(0.02)	73± 2.5(0.02)	7.75± 0.8(0.01)
Sample 2 ^c	3.97± 0.5(0.05)	85± 1.5(0.03)	7.95± 0.4(0.02)
Sample 4 ^d	4.87± 0.5(0.04)	243.67± 2.7(0.02)	8.04± 1.2(0.02)
Sample 5 ^e	5.59± 0.5(0.02)	256.8± 4.5(0.01)	8.65± 0.5(0.02)
Sample 6 ^f	4.21 ± 0.5(.01)	91.6±5 (.02)	7.48±0.6 (.01)
Sample 7 ^g	6.28± 0.6(.03)	277.37±4.9 (.04)	9.62±1.7 (0.05)

^a Hydrogel film, ^b Cotton g (Polyacrylic acid) hydrogel composite using PEG, ^c Cotton- g- (Polyacrylic acid) hydrogel composite using MBAAm, ^d Cotton -g- (Polyacrylamide) hydrogel composite using PEG, ^e Cotton-g- (Polyacrylamide) hydrogel composite using MBAAm, ^f Cotton-g- (Polyacrylic acid -co-acrylamide) hydrogel composite prepared using PEG, ^g Cotton-g-(Polyacrylic acid -co-acrylamide) hydrogel composite prepared using MBAAm.

Values in the bracket show coefficient of variation (CV).

IV. CONCLUSIONS

Bilayer composite of poly (acrylamide -co acrylic acid) grafted cotton fabric is prepared. The optimized conditions for the development of bilayer composites were initiator concentration 5%(w/V), Monomer ratio 1:1 (in mole),

monomer concentration 15%, reaction time 55 minutes, and reaction temperature $50 \pm 5^\circ\text{C}$. The crosslinker concentration was found to be 0.1 % (w/w) in PEG, whereas it was found to be 0.3 % (w/w) in the case of MBAAm as a crosslinker. The stress-strain curve reveals the higher mechanical strength of composites as compared to hydrogel film. Moreover, composite prepared using MBAAm as crosslinker has higher mechanical strength as supported by its high modulus than that prepared by using PEG crosslinker. These results support the reinforcement of the strength of the composites. Such composites may include the materials of great importance in the applications which require a hydrogel system with more strength.

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