Fabrication of Poly (Methacrylic Acid) functionalized cellulosic Fibers with Cationic Dye Uptake Capacity for Textile Applications

Sananda Nag[1], Nilesh Waghmare[1], Vishvajit Juikar[2]

[1]*Research Scientist, Pulp & Fiber Research Centre, Grasim Industries ltd., Mumbai, India*
[2]*General Manager, Pulp & Fiber Research Centre, Grasim Industries ltd., Mumbai, India*

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Abstract - *Natural as well as regenerated cellulosic fibers such as cotton and viscose are usually dyeable with reactive dyes. Functional modification has been done onto viscose by in-situ polymerization along with grafting approach in order to develop cationic dyeability in the fibre. Salt free dyeing, nearly complete dye uptake, up to two or three times lesser dye consumption to achieve similar shades, brighter colors etc. are considered as advantages of cationic dyeable cellulosic fibers over otherwise reactive dyeable viscose. Cationic dyeable viscose therefore is likely to possess enhanced environmental sustainability in addition to its performance and cost benefits. Structural inclusion of anionic polymers like poly (methacrylic acid) in viscose by in-situ polymerization and grafting of methacrylic acid onto viscose fiber is explored for the first time, leading to significant improvement in cationic dyeability.*

*Key Words***:** Viscose1, Cationic dyes2, Poly (methacrylic acid) 3, Anioinic4, Tannic acid5

1. INTRODUCTION

Basic dyes generally possess cationic groups, capable of forming electrovalent bond with anionic groups in fibers like acrylic [1], delivering vibrant shades. Basic dyes are known to possess advantages such as high tinctorial value, brighter and attractive shades at much lower dye content compared to reactive dyes. More over basic dyes may lead, to up to hundred percent dye bath exhaustion which is in favor of environmental sustainability and pollution control. Salt and soda free dyeing process with basic dyes is an added advantage considering carbon foot print and environmental concern. Cost of dyeing is also two to three times lower with basic dyes compared to reactive dyes because of lesser dye requirement and the dyeing process being salt and soda free. However natural or regenerated cellulosic fibers, in spite of being weekly anionic due to hydroxyl functionalities, are commonly unable to uptake cationic dyes to significant extent. Introduction and fixation of sufficient anionic functionality might lead to cationic dye uptake capacity in cellulosic fibers. Viscose, a regenerated cellulose fiber, is considered as the closest matching alternative of cotton. Viscose is a manmade textile fiber from natural resources [2]–[4].

Either sulfonation or carboxylation can be considered as most favorable route of anioinization of cellulosics [5], [6]. Over the last few decades, considerable amount of work has been reported on treatment of cotton fibers with different metallic moderants or fixatives in order to achieve improved affinity towards cationic and natural dyes [7]–[9]. Natural fibers like silk although can be dyed with basic dyes, wash fastness properties are normally very poor. Poor wash fastness properties of basic dyed silk can however be improved by back tanning [10]. Tannic acid due to its hydroxyl and carboxylic acid groups possess affinity towards basic dye stuff and forms sparingly water soluble dyestuff-tannic acid complex and further reacts with tarter emetic leading to completely water insoluble dyestuff-tannic acid-tarter emetic complex which improves wash fastness properties of basic dyed silk fibers to significant extents [11]–[13].

Although few researchers has reported the potential role of polyacrylic acid functionalization on mulberry silk and bamboo rayon [14]–[17], there is till now no report on anionic functionalization of viscose or cellulosic staple fibers particularly with poly(methacrylic acid).

In the present article, in-situ polymerization as well as grafting of methacrylic acid has been carried out on viscose fiber using potassium per sulfate as an initiator.

2. Materials and Methods:

2.1 Ingredients:

Cationic dye coracryl red C4G supra supplied by Colourtex Industries Ltd. was used. Laboratory grade methacrylic acid and potassium per sulfate were used as received. Pharma grade tannic acid SCPL 66 was supplied by Samana chemicals and potassium antimony tartrate was used as received from Neelkanth chemicals.

2.2 Methods of Functionalization

1.0% potassium per sulfate was dissolved in water followed by addition of measured quantity of methacrylic acid ranging from 5-15% on the basis of water under stirring. Measured amount of viscose staple fiber was dipped into the monomer solution keeping fiber to monomer solution ratio approximately 1:10. Polymerization of methacrylic acid was allowed to take place for 30 - 45 minutes, maintaining the temperature between 60-80℃. The fibers were collected and washed thoroughly with hot and cold water until free from residual monomer and water soluble homopolymer. Finally, the washed fibers were subjected to drying. In situ

polymerization as well as grafting of methacrylic acid onto viscose fibers is expected to happen as shown in Fig 1. Each of the polymerization conditions are tabulated in Table 1. From the weight gain measurement, the percentage of grafting of poly(methacrylic acid) on viscose fibers were found to be 5, 10 and 15% with respect to cellulose content respectively when polymerization was allowed to happen. Also the effect of varying temperature on polymer grafting was checked by carrying out the polymerization at different selected temperatures.

Half of each of the fiber compositions thus obtained were dipped into 0.5% aqueous solution of tannic acid and 0.5% aqueous solution of Potassium antimony tartrate one by one, keeping a dip time of 5 minutes and temperature at 50°C.

Table-1: In-situ polymerization conditions of methacrylic acid in presence of viscose fiber

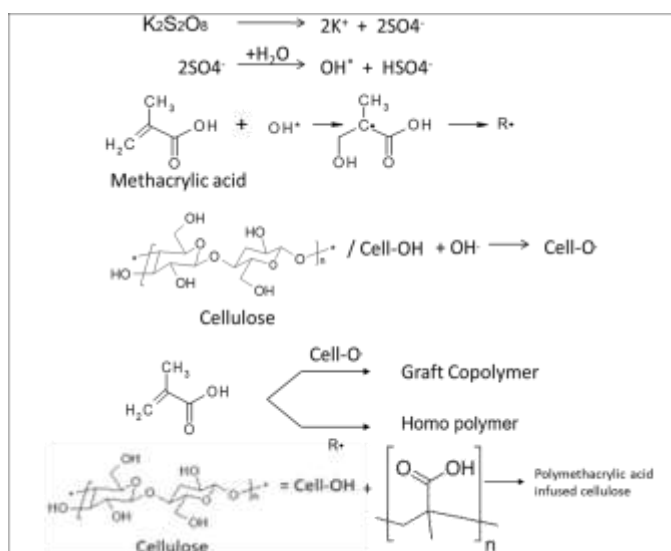| Sample Name	Temperature	Monomer (g) in in 100mL water
PMA-VSF5/ISP	80°C	5
PMA-VSF10/ISP-60	60°C	10
PMA-VSF10/ISP-70	70°C	10
PMA-VSF10/ISP-80	80°C	10
PMA-VSF15/ISP	80°C	15

Fig -1: Infusion of poly(methacrylic acid) on viscose by Insitu polymerization and grafting of methacrylic acid

The details for each of the poly(methacrylic acid) functionalized viscose fiber samples thus made are tabulated in Table 2.

Table-2: Compositions of poly(methacrylic acid) modified viscose fibers made in different methods

Sample Name	% of polymer grafted	Additional additive if any
PMA-VSF5/ISP	5	-
PMA-VSF10/ISP-60	5	-
PMA-VSF10/ISP-70	7	-
PMA-VSF10/ISP-80	10	-
PMA-VSF15/ISP	15	-
PMA-VSF5/ISP/TK	5	0.5% TA+0.5% KAT one by one
PMA-VSF10/ISP/TK	10	
PMA-VSF15/ISP/TK	15	

3. Results and Discussion:

3.1 Method of dyeing:

Each of the fiber samples were subjected to dyeing with cationic dye coracryl red C4G supra with 1% dye with respect to fiber at a pH of 5. Fiber to liquor ratio were maintained at 1:30 and fibers dipped into dye bath were dyed in dye master beaker dyeing machine heated at a rate of 1.4°C/min up to 105°C and kept on hold for 45 minutes followed by cooling up to 40°C. The dyed fibers were subjected to soaping with 2 gpL nonionic detergent at 70°C for 20 minutes followed by cold and hot rinses. The exhausted dye baths were also collected for measurement of dye bath exhaustion.

3.2 Measurement of color intensity:

Colour measurements were done using Konica Minolta spectrophotometer C-3600A where K/S values were measured considering corresponding dyed acrylic fiber as the benchmark with K/S 100. The color measurement data is tabulated below in Table 3. K denotes absorption coefficient and S denotes scattering coefficient.

$K/S = (1-R^2)/2R$, where R is the reflectance at complete opacity.

Closer the K/S value towards 100, the higher the color strength. Also L*, a*, b* values help to evaluate the color differences between different shades. Higher the value of L*, the darker is the shade. Redness in a dyed fiber increases

with increase in positive values of a*, Green ness in a dyed fiber increases with increase in negative values of a*. Similarly yellowness in a dyed fiber increases with increase in positive values of b*, and blueness in a dyed fiber increases with increase in negative values of b*.

As observed in Table 3, K/S values poly (methacrylic acid) modified viscose fibers made by in-situ polymerization, increases with increasing percentage of grafted polymer. poly (methacrylic acid) acid being an anionic polymer incorporates anionic sites to the cellulosic fiber for cationic dye uptake. Unmodified viscose does not possess any affinity towards cationic dyes as reflected in poor K/S value of cationic dyed unmodified viscose, while K/S value increases progressively from 34.59 to 73.86 with increasing content of polymerized methacrylic acid from 5 to 15%

When the same modified fibers were treated with 0.5% tannic acid and 0.5% potassium antimony tartrate, further improvement of K/S values up to 10% PMA content were observed in addition to improved wash fastness. The progressive increase in K/S value with increasing poly(methacrylic acid) content is clearly visible in Fig 2. ISP indicates PMA modified VSF by in-situ polymerization and ISP-TK designates ISP with additional TA/KAT treatment. However compared to dyed acrylic fibers, b* values of poly(methacrylic acid) modified viscose were found quite low, indicating decreased yellow ness. Particularly for tannic acid treated modified viscose fibers exhibit negative b* values, indicating towards increased blue ness in the dyed fiber.

Table -3: Color measurement data of dyed fibres considering acrylic fiber as bench mark with K/S 100

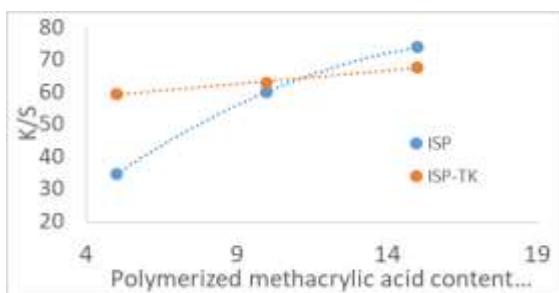| Data Name	L*	a*	b*	K/S
Acrylic Fiber	51.17	77.78	32.77	------
Unmodified Viscose Fiber	82.76	4.21	4.61	0.45
PMA-VSF5/ISP	53.76	73.24	2.1	34.59
PMA-VSF10/ISP	48.6	73.75	3.18	60.05
PMA-VSF15/ISP	45.9	72.47	5.57	73.86
PMA-VSF5/ISP/TK	39.14	62.8	-4.85	59.54
PMA-VSF10/ISP/TK	40.15	64.59	-5.28	63.01
PMA-VSF15/ISP/TK	39.5	63.98	-3.19	67.54

Fig -2: K/S values as a function of poly(methacrylic acid) content

3.3 Measurement of Dye bath exhaustion:

Solution of cationic dye coracryl red C4G supra were made in water in various concentration and UV-Visible spectroscopy were done as shown in Fig 3. Absorbance of Characteristic peak at 530 nm were noted and plotted against concentration in ppm. A straight line passing through origin is obtained following Lambert Beers law as depicted in Fig 4. Absorbance of different exhausted dye baths used for different fibers were measured by UV-vis spectroscopy as in Fig 5. Using these absorbance data from Fig 5 along with calibration curve (Fig 4), the concentration of remaining dye in an exhausted dye bath could be measured which easily give us quantitative information of dye bath exhaustion (DBE).

As observed in the calibration curve in Fig 4, the obtained equation following Lambert Beers law is y=0.0954x (R^2=9.9964), whereas y is absorbance at 530nm and x is concentration of dye in ppm. Using this equation the remaining concentration of dye in a dye bath after exhaustion was measured from the detected value of absorbance at 530nm which can be easily converted into dye bath exhaustion (DBE %) as the initial concentration is known.
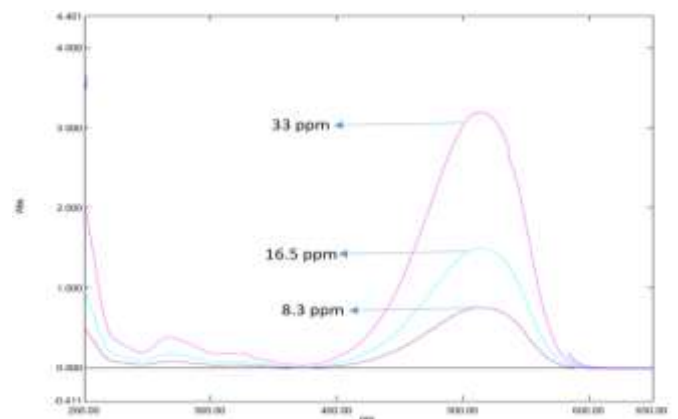
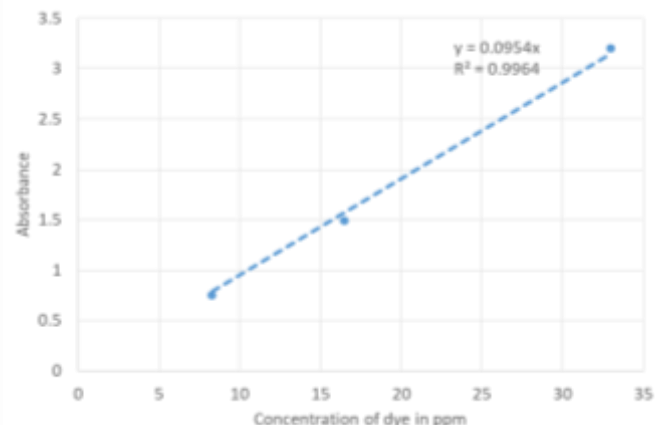**Fig -3:** UV-Visible spectrum of red coracryl cationic C4G dye at varying concentration

Fig -4: Calibration curve of red coracryl cationic C4G at absorbance at 530nm as a function of concentration in ppm

As observed in Table 4, the dye bath exhaustion increased from 90.22% to 92.98% with increase in the concentration of in situ polymerized methacrylic acid from 5 to 15%; whereas the same fibre compositions after treatment with 0.5% tannic acid and 0.5% potassium antimony tartrate, shows DBE in the range of 95.86% to 98.38%. For the understanding of role of TA/KAT post treatment, regular (unmodified) viscose fiber is treated with 0.5% TA and 0.5% KAT which after dyeing under same conditions show a dye bath exhaustion <80%.

As per our observations, the poly (methacrylic acid) enters into the structure of viscose providing anionic carboxylic acid groups suitable for cationic dye uptake, whereas improved wash fastness could be achieved only after treatment with 0.5% TA and 0.5% KAT which helps in the formation of an water insoluble complex on the surface of the fiber, and prevents poly (methacrylic acid) groups to get leached out during the wash cycles.
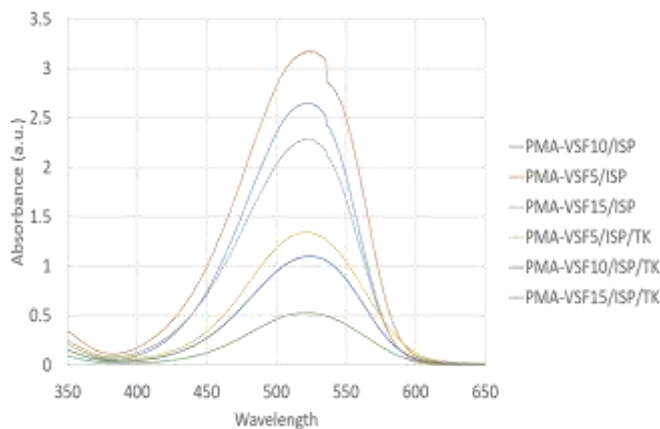

Fig -5: UV-Visible spectrum of exhausted dye bath (red coracryl cationic C4G dye) of different viscose fibers as mentioned

Table 4: Table of absobance at 530nm measuring the dye bath exhaustion (DBE %)

Sample	Abs. at 530 nm	Remaining concentration in dye bath	DBE (%)
PMA-VSF5/ISP	3.172	0.033	90.22
PMA-VSF10/ISP	2.645	0.028	91.85
PMA-VSF15/ISP	2.276	0.024	92.98
PMA-VSF5/ISP/TK	1.344	0.014	95.86
PMA-VSF10/ISP/TK	1.099	0.012	96.61
PMA-VSF15/ISP/TK	0.527	0.006	98.38

3.4 Measurement of Denier and Tenacity

Denier is an important parameter for polymeric fibers which is defined as weight in gram per nine thousand meters of a fiber. As observed in Table 5, denier of unmodified VSF was measured to be 1.26. Denier value in regenerated fibers is normally controlled through diameter of holes of spinneret during fiber regeneration as well as draw ratio of the regenerated fibers. All of these conditions like draw ratio, flow rate and spinneret dimensions being kept same, denier of 10% poly(methacrylic acid) infused VSF by in-situ polymerization method was found to be as high as 1.75. About 38% enhancement of denier value is therefore realized. Coating as well as structural incorporation of polymerized methacrylic acid could be achieved in this process, which lead to increased denier value.

The tenacity of viscose fibers got reduced from 2.82 to 2.00 grams/denier leading to reduction in tenacity of 41%. Grafting of poly methacrylic acid therefore reduced the tenacity to significant extent although variation in elongation at break was minimum (about 4%).

Table -5: Denier and tenacity measurement data of modified fibres compared with unmodified VSF

Sample Code	Denier den (%CV)	Tenacity g/den (%CV)	Elongation % (%CV)
Unmodified Viscose Fiber	1.26 (5.35)	2.82 (7.95)	20.48 (15.63)
PMA-VSF10/ISP	1.75 (9.35)	2.00 (6.89)	19.84 (12.81)

3.5 Scanning electron Microscopy:

In transverse section, the control viscose fiber (as in Fig 6a) appears to be having regular serrated cross section; whereas the poly(methacrylic acid) grafted viscose fibers made by in-situ polymerization appears to be with reduced serrations and the cross section is found to be smoothened with kidney bean or circular shape occasionally (as in Fig 6b). This observation supports the fact that poly(methacrylic acid) has been grafted and/or coated on the surface of viscose fiber although non uniformly when made in in situ polymerization approach. Considering the longitudinal sections, the control viscose is observed to be uniformly serrated (as in Fig 6c) while modified versions possess reduced serrations and irregular grafting of poly(methacrylic acid) on the surface is visible (as in Fig 6d).
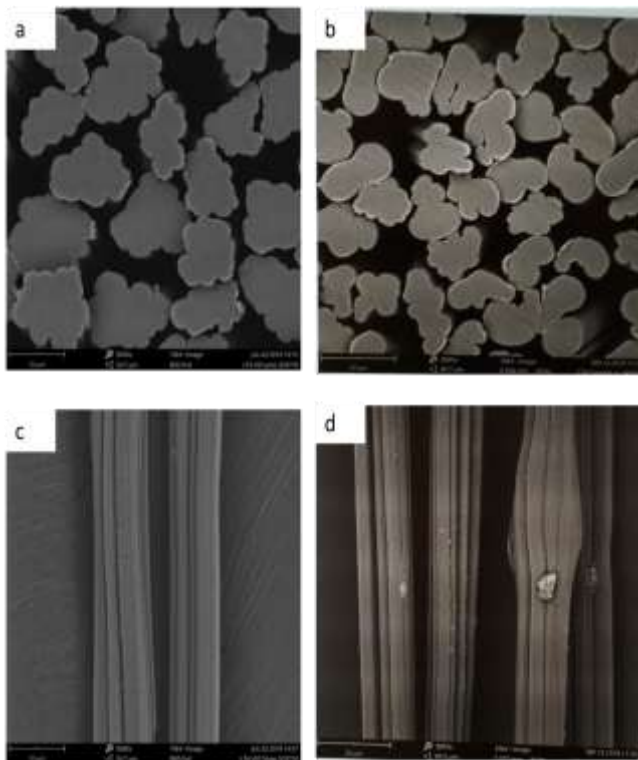
Fig -6: Scanning electron microscopic images in transverse sections of control viscose (a) and poly(methacrylic acid) modified viscose (b) and longitudinal sections of control viscose (c) and poly (methacrylic acid) modified viscose (d)

Fig -7: Thermo gravimetric analysis of poly(methacrylic acid) modified viscose

Fig -8: Differential scanning calorimetry of poly(methacrylic acid) modified viscose in comparison to unmodified VSF

3.6 Findings from Differential Scanning Calorimetry (DSC) and Thermo gravimetric Analysis (TGA)

Fig 7 and Table 6 provides a group of information considering the effect of poly(methacrylic acid) grafting on viscose fiber. In thermo-gravimetric analysis, the first stage of mass loss at 100℃ is due to evaporation of sorbed water by the fiber. Second stage degradation in unmodified viscose generally onsets at 250 ℃ as in Fig 7 as well as supported from existing data [19], [20]. Moisture content in the fiber was found to be increasing progressively from 7 to 12℃ with increasing amount of poly(methacrylic acid) grafting as depicted from TGA. This indicates higher moisture holding capacity of poly(methacrylic acid) grafted VSF when stored in same conditions. Higher polarity in viscose due to additional carboxylic acid groups coming from grafted poly(methacrylic acid) might be a reason for this behavior. Onset of second stage degradation in TGA increased progressively from 250 to 290℃ indicating influence of poly(methacrylic acid) grafting towards enhancement of thermal stability of viscose. Overall percentage of residue decreased from 17 to 12% with increasing amount of poly(methacrylic acid) grafting as expected. As observed in Fig 8, in DSC at higher PMA content, an endothermic peak is observed at 236℃ which might be due to melting of surface coated poly(methacrylic acid) content.
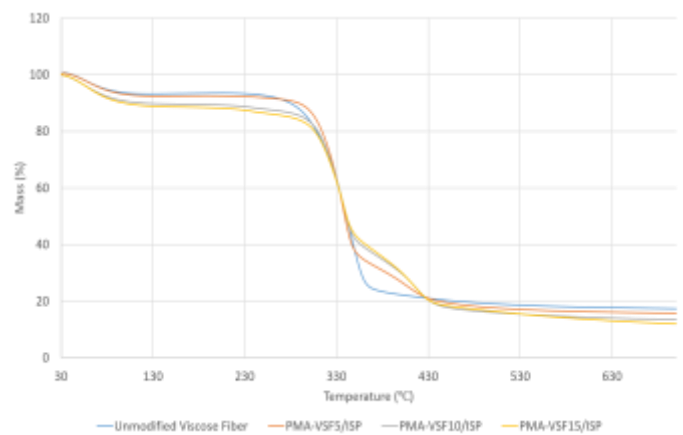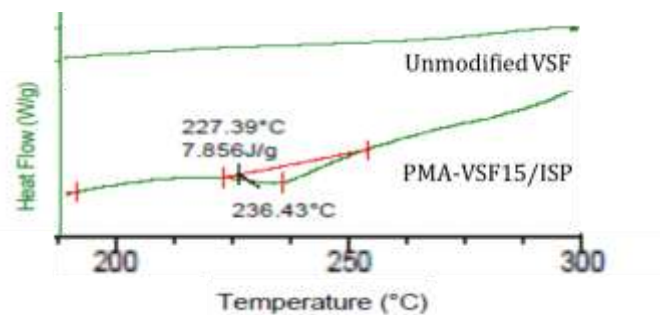
Table-6: Effect of poly(methacrylic acid) grafting on VSF by DSC and TGA

Sample	Findings from TGA			Findings from DSC
	Degradation up to 100℃	Initiation of 2nd stage degradation	residue up to 700℃	Endothermic shift position
Unmodified VSF	7%	250℃	17.37%	-
PMA-VSF5/ISP	8%	280℃	16.51%	-
PMA-VSF10/ISP	10%	285℃	13.44%	236℃
PMA-VSF15/ISP	12%	290℃	12.02%	236℃

3.7 Fourier transfer Infrared spectroscopy (FTIR)

As observed in FTIR spectroscopy of poly(methacrylic acid) modified VSF and control-VSF in Fig 9, an additional peak at 1710cm^{-1} is observed after modification of viscose with poly(methacrylic acid) due to the carbonyl stretching of carboxylic acid groups of poly(methacrylic acid). However the hydroxyl stretching frequency at 3400cm^{-1} got reduced in intensity as most of the hydroxyl groups of cellulose got blocked for grafting poly(methacrylic acid). Overall the Fig 9 supports successful grafting of poly(methacrylic acid) onto viscose fibers.
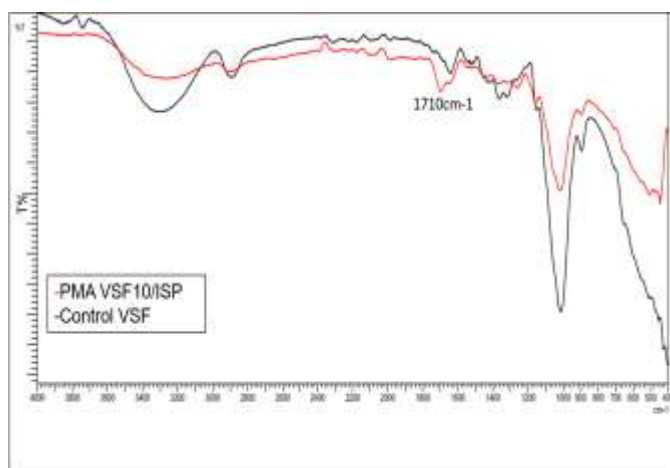

Fig -9: FTIR spectroscopy of poly(methacrylic acid) modified viscose (red) and unmodified VSF (black)

4. CONCLUSION

Incorporation of poly(methacrylic acid) into viscose fiber by in situ polymerization based grafting leads to significant improvement in cationic dye uptake in viscose fiber unlike standard/regular viscose fiber. Further improvement of color intensity along with reduced color bleeding or wash fastness, could be achieved by post treatment of the same modified fibers with 0.5% tannic acid and 0.5% potassium antimony tartrate in separate baths. Thus poly(methacrylic acid) functionalized viscose fibers can be dyed efficiently in a cost effective, salt and soda free environment friendly method leading to nearly complete dye pick up.

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