Stiffening Agent for Cotton Woven Fabrics Made from Methacrylic Acid Vinyl Acetate Methylacrylate Terpolymer

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ABSTRACT: The emulsion polymerizations of methacrylic acid (MAA), vinyl acetate (VAc), and methyl acrylate (MA) in different VAc/MA molar concentrations (X_1, 0.232/0.813; X_2, 0.348/0.697; X_3, 0.456/0.581; X_4, 0.581/0.465; X_5, 0.697/0.348) and fixed MAA concentration (0.116 mol) were carried out using sodium dodecyl sulfate (SDS; 34 mmol) as emulsifier and potassium persulphate ($K_2S_2O_8$; 37 mmol) as initiator at 70 °C for 6 h in semicontinuous reaction mode. The average molecular weights (M_n, M_w) and the molecular weights distributions were determined using gel permeation chromatography (GPC). All terpolymers prepared showed monomodal molecular weights distributions. Glass transition (T_g), crystallization (T_c), and melting (T_m) temperatures and thermal stability of the prepared terpolymers were determined using differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA), respectively. The elongation percentage at rupture, tensile strength and accelerated thermal aging were determined for X_{1-5} terpolymers, as functions of the molar composition in the emulsion polymerization feed. The terpolymers prepared, X_{1-5} terpolymers, were tested as stiffening agents for cotton woven fabrics through crosslinking to cellulose, using sodium hypophosphite monohydrate ($NaH_2PO_2 \cdot H_2O$) as catalyst. The effect of X_{1-5} compositions upon the stiffening efficiency was discussed. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 852–856, 2006

Key words: stiffening agent; cotton fabrics; crosslinking; methyl acrylate; vinyl acetate; methacrylic acid; sodium hypophosphite

INTRODUCTION

Cellulose crosslinking[1–3] is a very important textile chemical process, and it is the basis for a vast array of durable press and crease-resistant finished textile products. *N*-methylol crosslinkers containing formaldehyde not only give fabrics the desirable properties of mechanical stability (e.g., crease resistance, anticurl, shrinkage resistance, durable press), but also impart strength loss and the potential to release formaldehyde, a known human carcinogen. Natural polysaccharides,[4] such as starch, were the most commonly used stiffening agents for cotton woven fabrics. Because of the stiffening undurability of these natural stiffening agents, scientists moved to synthetic stiffeners. Compounds include urea-formaldehyde or melamine-formaldehyde resins, as well as derivatives of cyclic amines and epichlorohydrin.[5] Recently, poly itaconic acid and copolymers of maleic acid have been proposed as crosslinking agents for cellulose to increase fabric stiffness.[6,7] Both maleic and itaconic acids homopolymerize with great difficulty.[8–10]

In previous researches,[11–15] the strength loss for the cotton fabric treated with multifunctional carboxylic acids was attributed to two factors: acid-catalyzed depolymerization of cellulose molecules and crosslinking of cellulose molecules. The strength of the fiber depends on how much the crosslinked chains can still be mutually displaced under tension to adequately resist the applied load.

The rigid crosslinks that are formed with the standard formaldehyde based resins and with polycarboxylic acids, such as BTCA, obviously prevent the redistribution of stresses by preventing movement within the fiber microstructure. The crosslinking of cellulose molecules with these relatively rigid crosslinks causes stiffening of the cellulosic macromolecular network and fiber embrittlement thus reducing the mechanical strength of the treated cotton fabric. These same mechanisms are responsible for the reduced mechanical properties of the fiber surface thus leading to poorer abrasion resistance. The aim of this research is to synthesize a new material poly (MAA-*co*-VAc-*co*-MA) terpolymer as an alternative for homo-polycarboxylic acids, which can impart stiffening to cotton woven fabrics and reduce the cellulose network embrittlement.

MATERIALS

Methyl acrylate (MA) and vinyl acetate (VAc), products of Aldrich, were vacuum distilled twice before

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use. Methacrylic acid (MAA), a product of Redel de Häen, Germany, was purified from inhibitor by being stirred over active alumina for 4 h. $K_2S_2O_8$, $NaH_2PO_2 \cdot H_2O$, and sodium dodecyl sulfate (SDS), products of Merck, Germany, were used as received. Isopropanol and methanol, products of Al Nasr Pharmaceutical Company, Egypt, were of analytical grade. THF HPLC grade, a product of Aldrich, was used as received. Persil commercial detergent, a washing powder for white and color fabrics produced by Henkel Technologies, Egypt SAE, was used as received.

Methods

Semicontinuous emulsion polymerization of MAA, VAc and MA

The emulsion polymerizations of MAA, VAc, and MA were carried out in a three-neck round bottom flask equipped with mechanical stirrer (100 rpm) at 70 °C under nitrogen blanket. SDS (37 mmol) was dissolved in 300 mL distilled water. MA (30 mL) was charged to the water/SDS solution. A mixture of VAc, MA, and MAA was added to the polymerization reaction medium in dropwise manner over 6 h. Five different homologous terpolymers were prepared using fixed MAA concentration, 10 mL, 116 mmol, and different VAc/MA molar ratios (X_1, 0.285; X_2, 0.500; X_3, 0.784; X_4, 1.249; X_5, 2). The overall conversions were determined gravimetrically. The terpolymers prepared, X_{1-5}, were purified by being dissolved in water/isopropanol (50/50 v/v) and precipitated in benzene twice, washed with methanol and distilled water three times, and finally dried in an electric oven at 40 °C for 48 h.

Film preparation

The terpolymers, X_{1-5} films, were prepared by casting from 10% water/isopropanol (50/50 v/v) polymer solution. The casted films were left to dry at room temperature for 7 days.

Gel permeation chromatography

The number average molecular weights (M_ns), weight average molecular weights (M_ws), and MWDs (M_w/M_n)'s were obtained with Agilent gel permeation chromatography (GPC) instrument, Germany, equipped with a series of three styregel columns (10^2, 10^3, and 10^4 Å) calibrated with a series of narrow molecular weight polystyrene standards and a refractive index (RI) detector (Agilent 1100 differential refractometer).

Mechanical properties[16]

Tensile strength and elongation percentage at rupture were determined using tensile testing machine, Zwick 1425, Germany. Accelerated thermal aging of X_{1-5} terpolymers was carried out in an air circulated electric oven at 90°C. All measurements were carried out using five replicates of dumbbell shaped X_{1-5} specimens.

Thermal analysis

T_g, T_c, and T_m of the X_{1-5} terpolymers were determined using a Shimadzu (Model DSC-50) calorimeter, Foster City, CA. The specimens were cooled to -100 °C and heated up to 110 °C to remove their thermal history. The second runs were measured at a heating rate of 10 min^{-1} under nitrogen atmosphere. Thermal degradation was studied with thermal gravimetric analyzer (Model TGA-50), by heating the samples X_{1-5} from ambient temperature to 200°C.

Measurements of stiffening efficiency

Padding procedures and crosslinking of cotton fabrics with poly(MAA-co-VAc-co-MA)terpolymers (X_{1-5})

Five terpolymer solutions were prepared by dissolving 5 g of each terpolymer (X_1, X_2, X_3, X_4, and X_5) in water/isopropanol (50/50 v/v). Cotton strips were impregnated in the terpolymer solution for 1 min in a crystallization dish, and were then squeezed to 100% wet pick-up. $NaH_2PO_2 \cdot H_2O$, 20 mL (10%) solution was sprayed over each specimen. The fabric strips were dried at 90 °C and cured at 160 °C for 2 min. The fabric specimens were washed with tap water for 5 min to remove unreacted X terpolymer and $NaH_2PO_2 \cdot H_2O$ catalyst. The cured fabric specimens were treated with 0.1N NaOH for 2 min to convert any remaining carboxylic to carboxylate groups. Finally, all specimens were dried at 85 °C for 5 min.

Washing

Fabric specimens were washed in a domestic washing machine (Ideal Zanussi) at a temperature of 40 °C for 2×5 h using Persil washing powder (1.0 g/L) and then rinsed three times with water and finally air dried.

Measurements of flexural rigidity

Flexural rigidity of cotton fabrics specimens (3×15 cm^2) were measured in six replicates for each X terpolymer, according to the ASTM Designation: D 1388–96$^{\varepsilon 1}$, using a cantilever test machine, US Testing, Fairfield, NJ. The flexural rigidity is calculated as follows:

$$G = Wc^3 \qquad (1)$$

TABLE I
TABLE I
Overall Conversions of the Emulsion Polymerizations of X_{1-5} Polymers with Their Respective M_n and (M_w/M_n)

Specimen	Overall conversion	M_n (10^{-3})	M_w/M_n
X_1	74	27.38	3.21
X_2	79	35.09	3.35
X_3	86	43.86	3.36
X_4	94	48.27	3.39
X_5	97	51.91	3.60

Figure 2 TGA trace of X_1 terpolymer.

where G is the flexural rigidity in mg cm, W is the fabric mass per unit area in mg cm^{-2}, and c is the bending length in cm.

RESULTS AND DISCUSSION

Effect of molecular monomer composition upon the total conversion and molecular weights of the prepared X_{1-5} terpolymers

The overall conversions of the emulsion polymerization of MAA, VAc, and MA using different VAc/MA molar ratios (X_1, 0.285; X_2, 0.500; X_3, 0.784; X_4, 1.249 and X_5, 2) are shown in Table I. The increase of VAc concentration in the terpolymerization feed leads to an increase in the overall conversion of X_{1-5}. Table I reveals that the increase of VAc molar ratio in the termonomer feed leads to an increase in M_n and M_w/M_n. The increase of M_w/M_n demonstrates the nonlivingness of the terpolymerization system.

A representative GPC trace of X_{1-5} terpolymers, shown in Figure 1, demonstrates monomodal M_w/M_n distributions for X_{1-5} terpolymers. Figure 2 represents the TGA of X_1 terpolymer; it reveals that X_1 is thermally stable up to 200°C, where it loses only 3.5% of its original weight. The data shown in Table II reveals that as VAc molar ratio increases in the polymerization feed, the thermal stability of terpolymers prepared decreases to some extent. The DSC thermogram
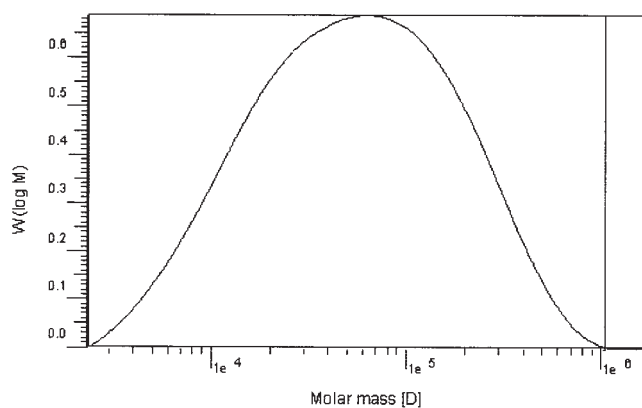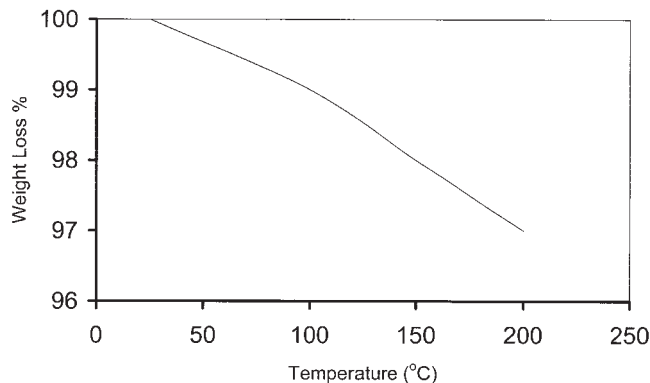
and its differential of X_1 terpolymer (Fig. 3) show T_g (first endothermic peak of the differential trace) at 10°C.

TGA and DSC of X_{1-5} terpolymers

The second peak at 18.23°C, in the DSC scan, first differential is assigned as the exothermic crystallization temperature T_c. The melting point transition appears at 23.59°C. Table II shows the T_g, T_c, and T_m of X_{1-5} terpolymers. As VAc molar ratio increases in the polymerization feed, the T_g, T_c, and T_m increase; also the exothermic T_c peak flattens, which is attributed to the change in crystal volume of higher M_n.

Mechanical properties of X_{1-5} terpolymers

The tensile strength and elongation percentage at rupture of X_{1-5} terpolymers, which are shown in Figure 4, increase upon moving from X_1 to X_5. Two dependent factors, M_n and T_g of X terpolymers, assign their corresponding mechanical properties. The slight increase in T_g of X_{1-5} series did not lead to a decrease in elongation percentage at rupture, which is attributed to the increase in molecular weights and the number of VAc copolymeric elastic species in the terpolymer molecular compositions through the series. The accelerated thermal aging of X_{2-5} specimens shows that the tensile strength (Fig. 5) and elongation at rupture percentage (Fig. 6) both decline with time. X_1 shows

Figure 1 GPC trace of X_1 (MA-VAc-MAA-terpolymer).

TABLE II
Thermal Properties of X_{1-5} Terpolymers

Terpolymer	wt % loss at 200°C	T_g (°C)	T_c (°C)	T_m (°C)
X_1	3.499	10.21	18.23	23.59
X_2	4.121	12.32	18.52	24.01
X_3	5.360	13.69	19.10	25.38
X_4	7.025	13.59	19.25	25.92
X_5	8.487	15.21	19.85	26.35

Figure 3 DSC trace of X_1 terpolymer.
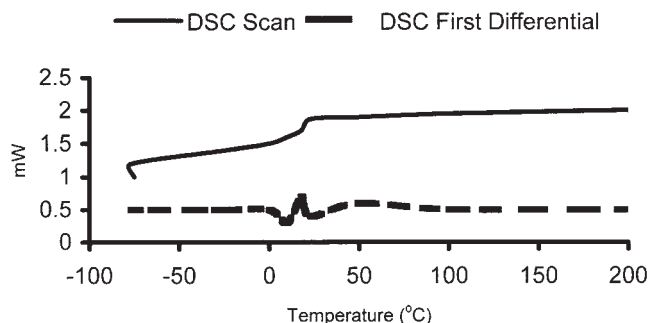

Figure 5 Tensile strength versus aging time of X_{1-5} terpolymers.

stable mechanical properties upon thermal aging; this thermal stability is in excellent agreement with its corresponding TGA thermogram. Specimens X_2 to X_5 mechanical properties decline upon accelerated thermal aging because of the increase of VAc copolymers content within the terpolymers prepared and the increase in polydispersity index (M_w/M_n) from 3.2 to 3.6; also the DSC thermograms (not shown) reveals a tendency towards amorphous state, because T_c peaks minimize and flatten as it moves from X_1 to X_5.

Flexural rigidity

The stiffening effect of the prepared poly(MAA-*co*-VAc-*co*-MA) terpolymers upon cotton woven fabrics is attributed to the crosslinking of carboxylic groups of the X_{1-5} terpolymers and cellulosic hydroxyl groups of cotton. This crosslinking is catalyzed by $NaH_2PO_2 \cdot H_2O$, which enhances the formation of cyclic anhydrides as reactive intermediates, which in turn esterify cotton cellulose.[12] Our new X_{1-5} terpolymers differ from the conventional polycarboxylic acid stiffening agents in the presence of low T_g oligomeric and polymeric segments between crosslinkable carboxylic groups (M_c) of variable molecular weights. The M_c depends on the concentration and distribution of MAA within the X terpolymers. Figure 7 shows a
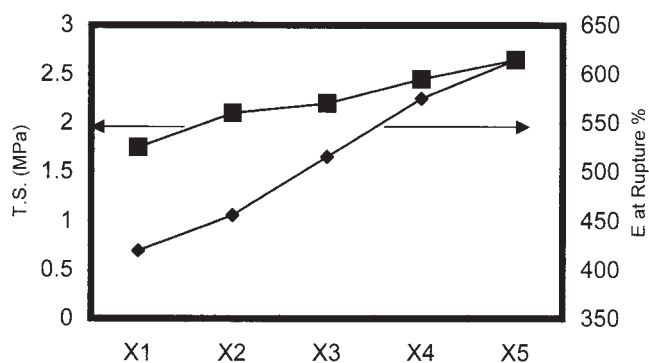
schematic representation of the proposed M_c formation. These segments should allow the redistribution of stresses upon load application to fabrics. The concentration of carboxylic groups within the terpolymer affects the stiffening efficiency of materials and also M_c, which in turn would allow easier chain displacements and hence the better mechanical properties of stiffened fibers.

The stiffening efficiency of X_{1-5} terpolymers for cotton woven fabrics was measured in function of flexural rigidity before and after washing. The data shown in Table III reveal that the average G value of control specimens is 1204 ± 4 mg cm. G values are shown to increase from X_1 to X_5 from 4.325×10^3 to 17.442×10^3 mg cm, upon increasing VAc molar ratio from 0.285 to 2. G values are shown to decline with increasing washing time. G values of X_1 declined from 4.325 to 1.358
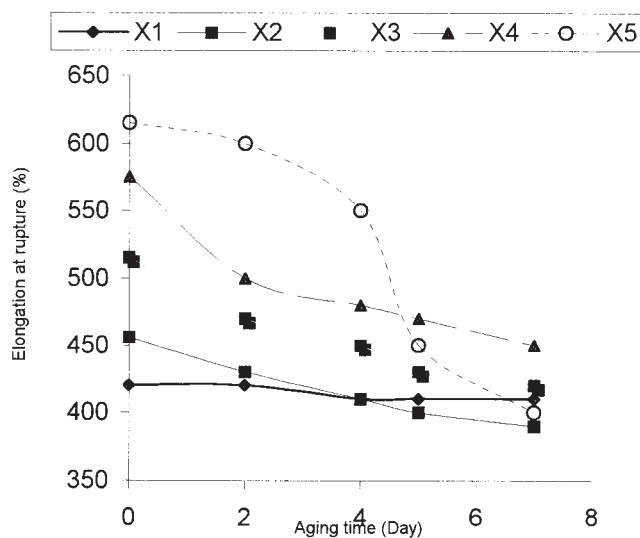

Figure 4 Tensile strength and elongation percentage at rupture of X_{1-5}.

Figure 6 Elongation at rupture percentage of X_{1-5} terpolymers.

$\times 10^3$ mg cm and from 17.442 to 15.021 $\times 10^3$ mg cm for X_5 after 10 h machine washing. Table III also shows that the rate of decline ΔG is a function of VAc molar concentration, i.e., ΔG increases with increasing VAc concentration. The previous results show that the stiffening of cotton cellulose is not only a function of carboxylic groups concentration but also is a function of the rest of X terpolymer molecular composition. The physical adhesion properties of VAc copolymers to cellulose materials make a significant contribution to the overall resultant flexural rigidity of cellulose cotton fabrics.

CONCLUSION

1. A novel stiffening agent is made from poly-(MAA-*co*-VAc-co-MA) in different VAc/MA molar ratios (X_1, 0.285; X_2, 0.500; X_3, 0.784; X_4, 1.249; and X_5, 2) and fixed MAA concentration (116 mmol).
2. X_{1-5} were characterized by GPC, TGA, and DSC; the increase of VAc concentration in the terpolymer leads to an increase in M_n and M_w/M_n, decrease in thermal stability, and increase in mechanical properties of the X_{1-5} terpolymers.
3. Tensile strength and elongation percentage at rupture of X_{1-5} increase with the increase of VAc concentration in the terpolymers and decline with thermal aging.
4. The stiffening efficiency of X_{1-5} terpolymers for cotton woven fabrics was measured in function
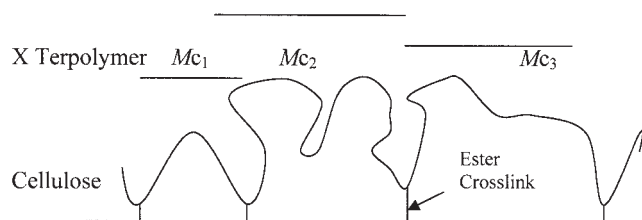

Figure 7 Schematic representation of X terpolymer interaction with cotton cellulose.

TABLE III
Flexural Rigidity of X_{1-5} Terpolymers After and Before Washing

Specimen	Before washing	Washing time (h)				
		2	4	6	8	10
Control	1.216	1.208	1.210	1.209	1.212	1.201
X_1	4.325	3.365	2.985	1.965	1.658	1.358
X_2	6.985	6.536	6.007	5.284	5.036	4.853
X_3	10.236	8.658	7.268	6.364	5.269	5.029
X_4	13.365	12.327	11.857	10.358	9.236	9.025
X_5	17.442	17.007	16.895	15.369	15.024	15.021

Flexural rigidity, $G \times 10^{-3}$ (mg cm)

of flexural rigidity before and after washing; the VAc rich terpolymer was found to have better G and ΔG values.
5. The higher the VAc concentration in the terpolymer, the less the decline in flexural rigidity of stiffened cotton fabrics.

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