Graft Polymerization of Hydrophilic Monomers onto Textile Fibers Treated by Glow Discharge Plasma

ZUBAIDI[1] and TOSHIHIRO HIROTSU[2],*

[1]Institute for Research and Development of Textile Industries, Jl. A. Yani 390, Bandung 40272, Indonesia, and
[2]National Institute of Materials and Chemical Research, 1-1, Higashi, Tsukuba, Ibaraki 305, Japan

SYNOPSIS

Graft polymerization of vinyl monomers was made onto some natural and synthetic textile fibers that were pretreated by glow discharge plasmas. Among the monomers investigated, 2-hydroxyethyl methacrylate (HEMA) produced the most improved grafting effects. Effects of plasma gas source, exposing time of glow discharge, grafting time, temperature, etc., on grafting were investigated. Postpolymerization in vacuum allowing oxygen shutoff was desirable for improved grafting yield. Air exposure of the plasma pretreated textile fabrics lead to decrease of grafting yield prominently because of the deactivation of radicals by oxidation. Grafting amount was dependent also on the nature of the substrate textile fibers, and cotton was, in general, more reactive. Breaking strength of yarns increased after graft polymerization of HEMA, while the strength decreased by etching of yarns by plasma treatments using nonpolymerizable gas species. Increase of the strength in the grafted yarn is attributed to binding effect of the grafted polymers as revealed from studies of morphology by scanning electron microscopy. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Glow discharge plasma has been applied to surface modification of many polymer materials.[1,2] The modification effects are, in general, confined to the vicinity of the exposed polymer surface, and their bulk properties remain practically unchanged. Recently, modification of polymeric materials using plasma processing has been investigated from the more practical aspects in film and textile industries.[3,4] Plasma-treated fibers become somewhat more hydrophilic. Oxidation of the polymer radicals after exposure to air is also effective to impart hydrophilicity.

Radical sites are effectively generated on the surface of polymer substrates on plasma processing, and these active radicals can initiate graft polymerization of vinyl monomers.[5] Selective plasma graft polymerization was used for surface modification of polyester fibers for the purpose of increasing hydrophilicity, dying properties, and so forth. Likewise, hydrophobic nature of a fiber surface can be enhanced by graft polymerization of fluorine-containing vinyl monomers.[6]

The present work relates to modification of several conventional textile fabrics by plasma graft polymerization using selected hydrophilic monomers and the evaluation of mechanical properties of products. Studies were made mainly using 2-hydroxyethyl methacrylate (HEMA).

EXPERIMENTAL

Materials

Textile fabrics used in the present work were from cotton, cellulose acetate, rayon, and cupraammonium cellulose supplied from the Japan Industrial Standard (JIS).

Monomers used for graft polymerization onto these fabrics were reagent grade HEMA, acrylamide(AAm), N-isopropyl acrylamide (NiPAAm), acrylic acid (AA), 2-methoxyethyl acrylate (MEA), and 2-hydroxyethyl methacrylate (HEA). AAm and NiPAAm were purified by recrystallization and other liquid monomers were purified by distillation under reduced pressure.

Table I % Grafting of Monomers onto the Residual Gas Plasma-Treated Textile Fibers in Vacuum

Monomer	% Grafting[b]					
Fiber[a]	HEMA	AAm	NiPAAm	AA	MEA	HEA
Cotton	85.7	1.46	72.8	1.52	33.7	18.7
Acetate	60.1	6.12	1.9	1.18	10.7	10.3
Rayon	22.3	—	8.5	—	11.8	4.7
Cupra	10.1	0.15	1.0	—	3.5	2.3
Polyester	5.2	1.46	5.8	—	9.0	1.7
Nylon	7.6	3.0	30.8	1.8	8.9	0.9
Acrylic	2.4	—	1.5	1.83	1.3	—

[a] Residual gas plasma pretreated at 10 W for 60 s.
[b] Grafting at 60°C for 2 h with aqueous solutions of 2% for HEMA and 5% for other monomers.

Graft Polymerization

The monomers were graft polymerized in the aqueous solution in vacuum by the same procedure as described before.[7-9] A piece of a textile fabric (4.0 × 4.0 cm) was placed in a cylinder-shape reactor made of Pyrex glass tubing (30 mm i.d., 24 cm length), and exposed to glow discharge plasma generated by the radio frequency of 13.56 MHz. Previously degassed aqueous monomer solutions (40 mL) (2%, 5%) was poured into the reactor without contact with air, and the graft polymerization was carried out under shaking in a water bath at a controlled temperature.

After termination of reaction, the product fabrics were soaked in distilled water and appropriate solvents to remove the ungrafted portion of original monomer and homopolymers as much as possible. The grafting yield was evaluated from the % wt increase of the vacuum-dried polymers based on the weight of original textile fabrics.

Breaking Strength Measurements

Breaking strength of the yarns taken out from the treated fabrics was evaluated by the modified testing method of filament yarns (JIS L 1013–1992). The yarn was conditioned in standard room overnight and the breaking tensile strength was measured using a tensile meter (Tensilon UTM-111–100, Toyo Baldwin Co. Ltd., Japan) with a gauge distance of 20 mm and at an operating rate of 50 mm/min. The measurements were taken for 10 different yarns, and the average was taken.

Scanning Electron Microscopy

Scanning electron microscopy was taken at an accelerating voltage of 10 kV, using an apparatus of a Dual-Stage Electron Microscope (Type DS-720, Topcon, Japan), and the surface morphology of fibers was observed.

RESULTS AND DISCUSSION
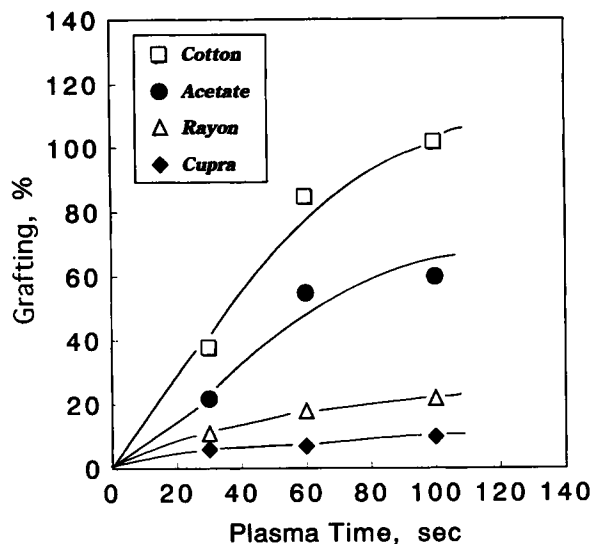
Plasma Graft Polymerization

Monomer Reactivity

Graft polymerization is commonly influenced by the reactivity of the substrate polymer and the monomer used. The reactivity was assessed considering the grafting effects at 60°C for 2 h onto the textile fabrics pretreated with the residual gas plasma at 10 W for 60 s.

One can see from data summarized in Table I: (1) graft polymerization yield was dependent on the textile substrates, and natural fibers composed of cellulose, especially cotton are in general more reactive; (2) HEMA was graft polymerized more readily than other monomers investigated, especially onto cotton and acetate; (3) NiPAAm was graft polymerized to cotton and nylon in good yield; (4) the less hydrophilic monomer of MEA was more graft polymerized onto these fibers than HEA.

Effects of Plasma Gas Species

Effects of a change in plasma gas species on the graft polymerization were initially investigated using HEMA. Textile fabrics were treated with plasmas of argon (Ar) and O_2 at the flow pressure of 13.3 Pa and to the residual gas plasma (1.33 Pa) generated at 10 W for 60 s; HEMA was then reacted in 2% aqueous solution at 60°C for 2 h. Higher grafting yields of poly(HEMA) were obtained when the textile substrates were pretreated with residual gas plasma and Ar-gas plasma, although the yield

Figure 1 Dependence of graft polymerization of HEMA (2%, 60°C, 2 h) on time of exposure to the residual gas–plasma (10 W).

changed somewhat depending on the type of substrates.

The smaller grafting yield on the O_2 plasma-pretreated textile fibers was attributed to the deactivation of polymer radicals during contact to oxygen after even shorter time of plasma.

Effects of Plasma Pretreatment

Residual gas plasma was commonly used for fabric pretreatments before graft polymerization to achieve more effective graft polymerization. Dependence of graft polymerization of HEMA on the time of residual gas plasma pretreatment time is shown in Figure 1. Plasma was generated at 10 W, and the fabrics were treated for 30, 60, and 100 s. HEMA was reacted in 2% aqueous solution at 60°C for 2 h, and the reactivity of pretreated substrates was compared. With the increase of plasma pretreatment time, % grafting followed an initial increasing trend up to 60 s and then leveled off.

According to independent experiments, etching of fabrics under the same pretreatment condition linearly increased with time, and the weight loss after the residual gas–plasma exposure for longer time of 20 min was estimated 1.9% for cotton, 3.8% for acetate, 7.0% for rayon, and 5.6% for cupraammonium. (When the substrate fabrics were exposed to the oxidative plasmas, the weight loss was naturally much greater.) Weight loss of the fibers was, therefore, estimated to be less than 0.5% after plasma exposure for 100 s, and actually the degradation was supposed to be negligible under the given conditions

of pretreatment for graft polymerization. Therefore, the graft polymers have been formed onto fiber substrates that remained practically unaffected due to pretreatment.

Figure 2 shows dependence of discharge power on % grafting of HEMA onto cotton and acetate fibers. Here also, the substrates were exposed by plasma of residual gas for 60 s, and 2% aqueous HEMA solution was reacted in vacuum at 60°C for 2 h. Discharge power as low as 5 W was quite effective and produced optimum effects in graft polymerization and % grafting followed a decreasing trend for discharge power higher than 30 W. Extensive fabric etching rather than active radical formation on them is attributed to decrease in % grafting with increase in discharge power beyond 30 W.
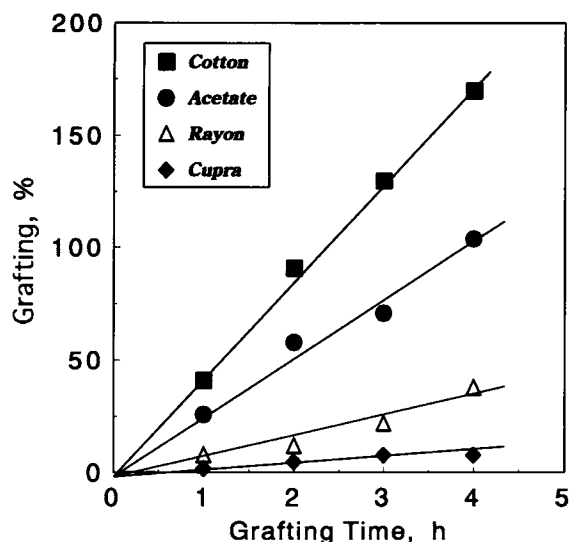
Grafting Time Dependence

Time variation of % grafting of HEMA on four different pretreated fabrics is shown in Figure 3. Percent grafting under the given condition increased linearly with the grafting time within the time range investigated. The aqueous monomer solution became turbid during reaction, and partial formation of homopolymers was indicated. The initiation of homopolymerization in the system is attributed to the radical transfer from the activated fiber surface to a monomer. The activated monomer should attack the adjacent monomers to lead to homopolymerization. However, it should be noted that the homopolymer ratio to the grafted poly(HEMA) was comparatively small.

Considering the linear increase in % grafting with the reaction time as in Figure 3, reaction rate anal-
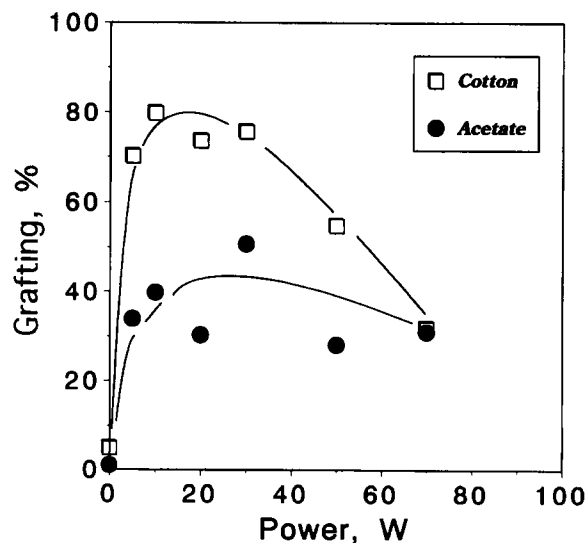
Figure 2 Dependence of graft polymerization of HEMA (2%, 60°C, 2 h) on discharge power (60 s).

Figure 3 Dependence of graft polymerization of HEMA (2%, 60°C) on grafting time onto the residual gas plasma treated fabrics (10 W, 60 s).

yses at 60°C were attempted based on the first-order kinetics of monomer consumption. The overall rate of polymer formation (R_p) is given in eq. (1), where k_g and k_h are rate constants of graft polymerization and homopolymeization, respectively:[7]

$$R_p = -d[M_t]/dt = (k_g + k_h)[M_t] \qquad (1)$$

Here, $[M_t]$ is the monomer concentration at time t.

Considering that homopolymerization of HEMA was negligible, the rate constant of graft polymerization of the monomer is given by eq. (2):

$$k_g = -\ln(1 - [M_{gt}]/[M_o])/t \qquad (2)$$

Here, $[M_{gt}]$ and $[M_o]$ are, respectively, concentration of the monomer that was grafted at time t and of that taken initially. Negligible homopolymerization under the given condition was characteristic of HEMA.

Reaction rate constants (k_g) as calculated for graft polymerization of HEMA at 60°C on different fabrics are: 2.34×10^{-5} s^{-1} for cotton, 0.903×10^{-5} s^{-1} for cellulose acetate, 0.250×10^{-5} s^{-1} for rayon, and 0.056×10^{-5} s^{-1} for cupraammonium cellulose. The rate of graft polymerization of HEMA onto cotton is much faster than that on any other textile species.

Effects of Variation of Temperature

Grafting behaviors of HEMA on the residual gas–plasma-treated cotton fabrics (10 W, 60 s) were also investigated at different temperatures (40–70°C),

and the results are shown in Figure 4. Exposure of the preactivated substrate cotton to air for 10 min caused a drop in % grafting at all temperatures of grafting. In each case, there appeared an optimum temperature for graft polymerization around 60–65°C, and, therefore, % grafting followed a dropping trend.

The fall in % grafting above 65°C may be due to a drop in efficiency of initiation. Such effects of heating causing decrease in grafting were confirmed by independent experiments as follows; the plasma-treated fabrics were heated to 70–90°C and then graft polymerization was likewise carried out at 60°C, all in vacuum. Lower grafting yield observed in such cases suggests substrate deactivation on heating over the higher temperature range.

Effect of Time of Air Exposure of the Pretreated Fabrics

Actually ESR signals of polymer radicals formed on activation by glow discharge plasma are reported to suffer drastic changes in the peaks or in the state of radicals on exposure to air by Kuzuya et al.[10,11] However, if graft polymerization could be achieved effectively even after exposure to air, then the pre-treatment process and the graft polymerization in the next step could be separated and carried out independently with some practical advantage.

Several reports on graft polymerization of vinyl monomers onto the air-exposed pretreated polymer
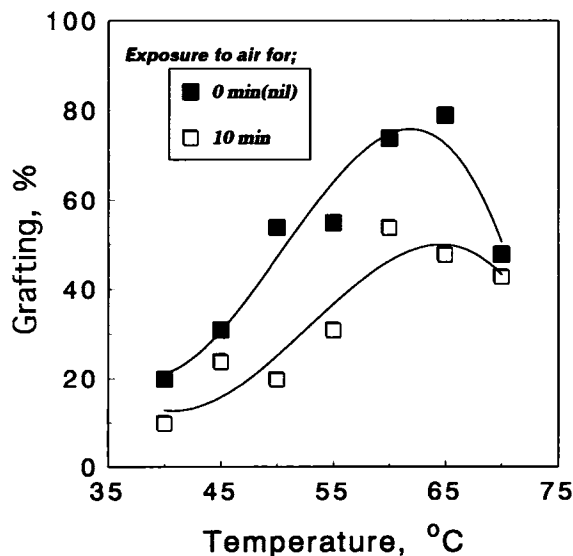

Figure 4 Temperature dependence of the graft polymerization of HEMA (2%, 60°C, 2 h) onto the residual gas plasma treated cotton and air-exposed cotton for 10 min.

surfaces are available.[12-14] However, studies of the effects of variation of air exposure time may prove interesting. Graft polymerization in vacuum was, therefore, studied using pretreated fabrics exposed to air for 0–100 min. The relevant sequence of processing was as follows: (1) residual gas plasma pretreatment at 10 W for 60 s, (2) exposure to air for 0–100 min, (3) evacuation of the system, and (4) graft polymerization using the aqueous HEMA solution of 2% at 60°C for 2 h.

Relevant results using three different fabric substrates and the monomer HEMA are shown in Figure 5. Compared to % grafting for a process carried out fully in vacuum, the grafting suffered a sharp drop over the initial period (up to 20 min) of air exposure, then highlighting a prominent retarding role of air, which, however, tends to level off for longer time of exposure. The trends of observation for other monomers were similar.

Breaking Strength of Textile Yarns

The breaking strength of cotton yarns grafted with HEMA to different % grafting was measured. In addition, yarns etched by plasma treatments were used and the strength was compared. Relevant showing plots of relative breaking strength (RBS) vs. weight % gain or loss on HEMA grafting or plasma etching, respectively, are given in Figure 6. Here, RBS = [strength of the treated yarn]/[strength of the original untreated yarn]. The breaking strengths of the three original textile yarns studied here are: 54.4
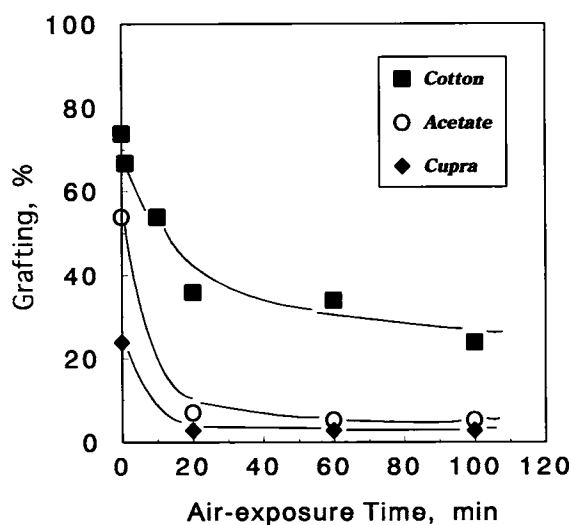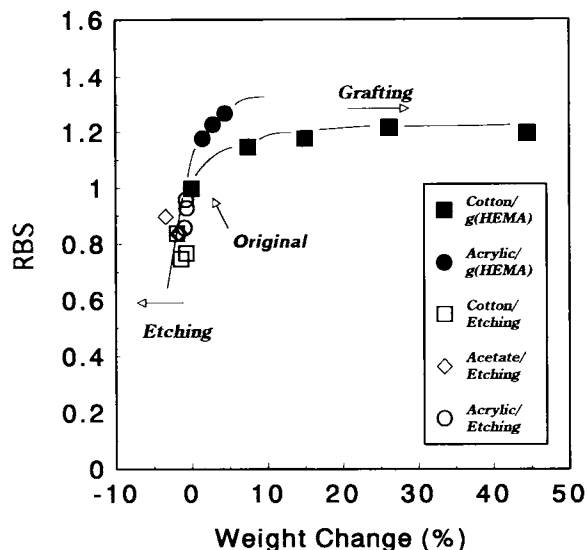
Figure 6 Relative breaking tensile strength (RBS) of HEMA-grafted and plasma-etched yarns; RBS = [strength of treated yarn]/[strength of the untreated yarn].
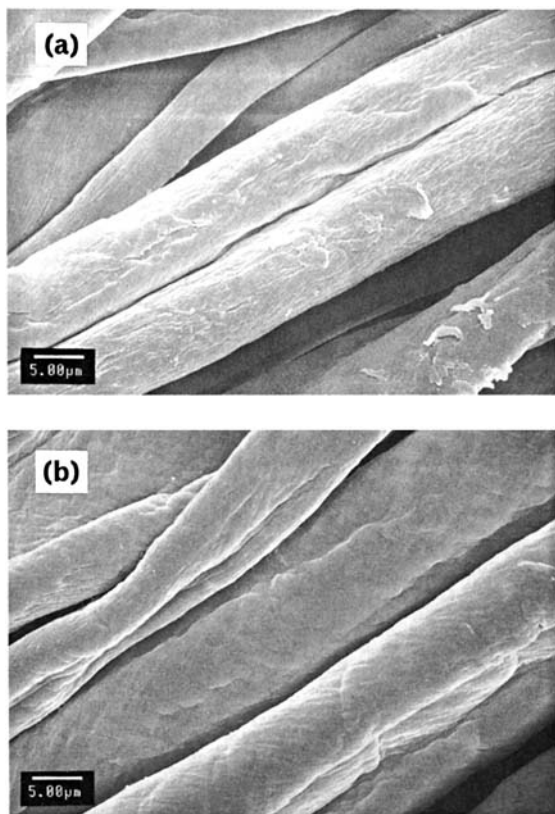
g/yarn for cotton, 17.0 g/yarn for cellulose acetate, and 40.7 g/yarn for an acrylic yarn.

A drop in breaking strength due to etching on plasma treatment was commonly observed for all the fabrics studied, and the drop is in the order of cotton > acetate > acrylic. The change in the mechanical strength of textile yarns has been extensively studied by Yasuda et. al.,[15] and the lowering in breaking strength on plasma etching is attributed to some degradation and mass loss that lead to additional voids and development of micro cracks.

Small extents of grafting of HEMA, on the other hand, led to an increase in breaking strength of the yarns up to about 10% grafting, and thereafter a leveling of trend followed. The fact was confirmed from the results of acrylic yarns with the smaller grafting amounts of poly(HEMA).

It may be said from additional revelation from studies of surface morphology of the yarns/fibers using scanning electron microscopy that increase in the breaking strength is associated with the fiber structure after graft polymerization. Figure 7 shows the SEM pictures of Ar–plasma-treated cotton fiber at the weight loss of 2.55% (a), and HEMA-grafted fiber at 6.2% (b), respectively.

After Ar–plasma treatments, the cotton fiber was slightly etched and the characteristic surface morphology with small cavities and cracking along the fibrils was observed. On the contrary, the surface of the HEMA-grafted cotton yarn was covered with the graft polymer, and the swollen surface morphology was observed.[16] From the comparison of SEM pictures, the bonding of the fibrils by graft

Figure 5 Effects of air exposure on graft polymerization of HEMA (2%, 60°C, 2 h) onto the residual gas–plasma-treated cotton, cellulose acetate, and cupraammonium cellulose (10 W, 60 s).

Figure 7 SEM pictures of Ar–plasma-treated cotton fiber at 10 W for 20 W at the weight decreasing ratio of 2.55%(a), and HEMA-grafted cotton fiber at the weight gain of 6.2% (b).

polymers was indicated and, thus, the increase in the mechanical strength of yarns is attributed to the effective bonding of the fibrils composing the yarns. In other words, the surfaces and cavities of the fiber were filled with a graft polymer, and the bulk properties of fiber was changed. It should be noted that the smaller grafting of a few % weight gain by poly(HEMA) was effective for the increase.

CONCLUSION

Important aspects found in the present work are summarized as follows:

1. Grafting was influenced by various conditions derived from the plasma pretreatments and the followed graft polymerization. Among the monomers investigated, HEMA was the best graft polymerized and NiPAAm was followed.

2. There appeared an optimum temperature for the grafting of HEMA at 60–65°C. Grafting degree rather decreased in the temperature range higher than this.
3. Grafting yield decreased prominently on the air-exposed substrates with the time. The vacuum processing is therefore inevitable for the effective polymerization.
4. Breaking strength increased in the yarns grafted with HEMA, while that decreased by etching after Ar–plasma treatments. Increase in the strength is attributed to the binding of fibrils by graft polymers.

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