Effect of MAA/MAM Pregrafting on DMEU Finishing of Cotton Fabrics

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SYNOPSIS

Cotton fabrics were pregrafted with mixed monomer of methacrylic acid (MAA) and *N*-methylolacrylamide (MAM) before undergoing finishing with 1,3-dimethylolethylene urea. Experiments show that when the molar ratio of MAA and MAM is 4 : 6 the finished fabric has the maximum nitrogen content (N%) and crosslinking density. The pregrafting can improve the wet crease recovery angle and the moisture regain, can reduce the tensile strength retention, and has little effect on the dry crease recovery angle. In addition, at a pregrafting ratio of 4 : 6, the finished fabric has the highest crease recovery angle and moisture regain. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

In the past there are many reports on using vinyl monomer to graft cotton fabrics for modifying chemical properties.[1-11] Most of these reports are based on single monomer grafting, with a few using mixed monomer to pregraft before resin finishing. In addition, Hebeish et al. reported about first finishing cotton with *N*-methylolacrylamide (MAM) and then grafting.[12] On the other hand, Negishi and Reinhardt et al. used various single vinyl monomers to first pregraft the cotton fabrics and then finish with MAM.[13,14] The results show that when the fabrics are pregrafted first and then finished with resin, the finished fabric shows great improvement of its physical properties. However, these reports concern only the physical changes in the finished fabrics. There is no research report on the crosslinking and physical properties of pregrafted fabrics, nor the use of mixed monomers for pregrafting and then resin finishing. Thus in this work, two monomers, methacrylic acid (MAA) and MAM, were mixed in different molar ratios to pregraft cotton fabrics for resin finishing. In addition, the relationship between the physical properties and crosslinking structure of the fabrics, after pregrafting and resin finishing, was studied.

EXPERIMENTAL

Materials

The cotton fabric, 40s * 40s ends (100) and picks (80), was desized, scoured, and bleached. MAM and MAA were purified according to the standard procedures.[15,16] Sodium hydroxide, ferrous ammonium sulfate, hydrogen peroxide, selenium mixture catalyst, sulfuric acid, boric acid, pyridine zinc nitrate, etc., were of reagent grade. The finishing agent 1,3-dimethylolethylene urea (DMEU) was synthesized according to the Hoover and Voals method.

Methods

Grafting Procedure

The sample of cotton fabric was first impregnated in freshly prepared aqueous ferrous ammonium sulfate (0.03%) for 15 min at 25°C under a material-to-liquor ratio of 1 : 100. The sample was then squeezed, washed thoroughly with distilled water, and dried. Accurate weight of the Fe^{2+}-containing sample was immersed in an aqueous solution containing the monomer or the mixture monomer, hy-

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drogen peroxide, under a material-to-liquor ratio of 1 : 100. The reaction was then allowed to proceed while stirring at 75°C for 90 min. The grafted sample was washed with distilled water and then extracted with boiling water for 2 h in a Soxhlet apparatus to remove the homopolymers formed.[18] Afterwards the sample was washed with distilled water, dried at 105°C for 2 h in an oven, and then cooled in a desiccator. The graft yield was determined gravimetrically.[19,20]

Crosslinking Procedure

The grafted cotton fabrics were first impregnated in a solution containing finishing agent (2–8% DMEU) and zinc nitrate (10% of the weight of DMEU) for 10 min at room temperature followed by squeezing to a wet pickup of 90%, pinned on a frame without tension, dried at 80°C for 5 min, and cured at 150°C for 3 min. After curing, the samples were thoroughly washed in a solution containing 2 g/L soap and dried at ambient conditions.

Analysis

The tensile strength of warp yarns was measured using an Instron tester. The dry and wet crease recovery angles (DCRA and WCRA) were determined according to ASTM standard D1295-67. Moisture regain was determined by the standard method.[21] Formaldehyde and nitrogen content were determined using the chromotropic acid method[22] and the Kjeldahl method, respectively. The number of crosslinks per anhydroglucose unit (CL/AGU) and the formaldehyde crosslinks (CL length) were calculated from the contents of nitrogen and formaldehyde of the sample with the method reported by various workers.[23,24]

RESULTS AND DISCUSSION

Effect of Molar Ratio of Mixed Monomer

Because the monomer MAM itself has nitrogen, the graft content of the fabrics grafted from the mixture of two monomers can be calculated from the nitrogen content and the graft yield on the finished cloth. Figure 1 shows that the graft content of MAA increased gradually with the increase in its proportion in the mixed monomers. The increase of the graft content became steeper starting from the molar ration of 4 : 6, especially at the higher concentration of 4%. The graft content of MAM increased gradually with its molar ratio, and reached the maximum

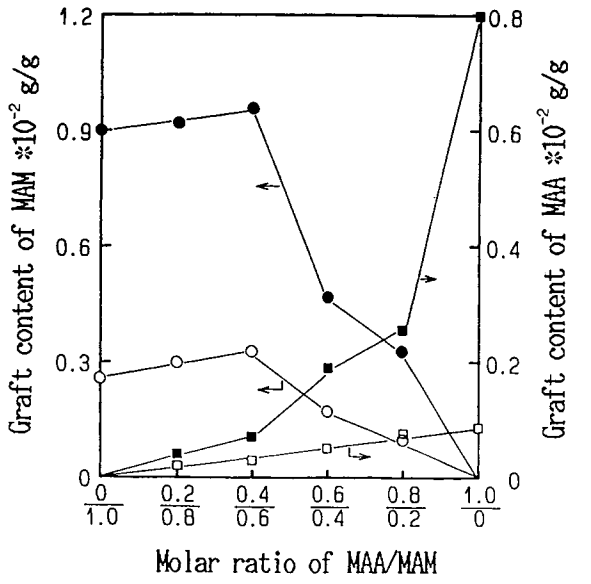

Figure 1 The relationship between molar ratio of MAA/MAM and graft content of every monomer on only grafted cotton fabrics by change concentration of mixture monomer solutions: (○, □) 1%; (●, ■) 4%; (□, ■) MAA; (○, ●) MAM.

at the molar ratio of 4 : 6. The complex formation seems to have considerable influence on the rates of reaction during the grafting process. This effect may be due to the following reasons.

1. The complex formation reduced the mobility of the reacting species in the solution, and hence the rate of homopolymerization.
2. When one monomer molecule diffused into the fiber structure, it automatically brought in the other monomer molecule of the same complex, thus increasing the monomer concentration in the fiber phase, which is very favorable for higher graft–copolymer formation.
3. When the monomer reacted with the free radicals on the backbone of the polymeric molecule, the chain propagation was enhanced due to the complex, and, hence a higher amount of monomer molecules was utilized, thus resulted in the synergistic effect.[13,25–27]

To investigate the effect of resin finishing on cotton fabrics grafted with mixed monomers, the pregrafted fabric was resin finished. The total nitrogen content and the total formaldehyde content of the finished fabric were measured and listed in Table I. The data in this table show that the nitrogen content

and formaldehyde content of the pregrafted resin finished fabric were generally higher than that of the resin finished fabrics without pregrafting. This means that pregrafting with monomers was beneficial to the reaction between resin finishing agent and the fabrics. Furthermore, from Table I and Figure 2, we know that the finished fabric has the highest nitrogen and formaldehyde contents at the mixing ratio of 4 : 6. This may be related to the grafting process. Table I also shows that the physical properties of pregrafted fabrics, DCRA, WCRA, and moisture regain (MR), were much better than those without pregrafting. The exception is the fabrics pregrafted with 4% MAA, which has the lowest DCRA and WCRA and the highest MR. Because of the pregrafting, all the values of TSR of the resin finished fabrics were lower. When the molar ratio of MAA to MAM is at 4 : 6, DCRA and WCRA were better. This is because the monomer at this molar ratio had a synergism effect, as indicated in Figures 1 and 2.

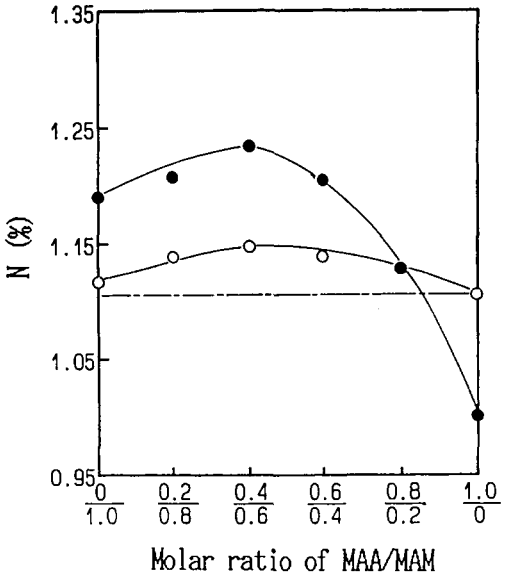

Figure 2 The relationship between molar ratio of MAA/MAM and N content: (○) 1%; (●) 4%; (—) total nitrogen; (----) control nitrogen.

Effect of Concentration of Finishing Agent

As indicated by the discussion in the previous section, the best physical properties achievable by pregrafting was with a mixing ratio of 4 : 6. Thus to investigate the effect of the concentration of resin finishing agent, DMEU, the mixing ratio was fixed at 4 : 6. The results are tabulated in Table II. As shown in Table II, N%, DCRA, and WCRA of treated fabrics all increased with the concentration of DMEU. The values of N%, DCRA, and WCRA also increased with the concentration of the mixed monomer. On the other hand, MR and tensile strength retention (TSR) decreased with the increase of the concentration of DMEU. However, the values of MR still increased with the concentration of monomer. The effect of the concentration of DMEU on the properties of the treated fabrics is illustrated by graphing DCRA, WCRA, MR, and

Table I Nitrogen, Formaldehyde Content, Physical Properties, and Length of Crosslinks in Cotton Fabrics

Monomer Concn. (%)	MAA/MAM Molar Ratio	CH_2O (%)	N (%)	Mole/AGU CH_2O	Mole/AGU N	CL/AGU	CL Length	DCRA $(W + F)°$	WCRA $(W + F)°$	TSR (%)	MR (%)
Control		1.69	1.01	0.0949	0.1215	0.0341	1.78	275	250	53.7	5.06
1	0/10	1.85	1.11	0.1043	0.1340	0.0373	1.80	281	254	52.0	5.30
	2/8	1.88	1.13	0.1060	0.1366	0.0377	1.81	285	259	51.2	5.40
	4/6	1.91	1.14	0.1078	0.1378	0.0389	1.77	287	260	50.4	5.51
	6/4	1.86	1.11	0.1048	0.1340	0.0378	1.77	285	257	50.0	5.72
	8/2	1.85	1.12	0.1043	0.1353	0.0367	1.84	285	251	48.8	6.03
	10/0	1.80	1.09	0.1014	0.1315	0.0357	1.84	282	247	48.4	6.94
4	0/10	1.98	1.19	0.1120	0.1442	0.0400	1.80	292	257	46.8	5.76
	2/8	2.00	1.20	0.1131	0.1454	0.0404	1.80	295	262	45.6	5.80
	4/6	2.04	1.22	0.1155	0.1480	0.0415	1.78	298	265	45.2	5.86
	6/4	1.98	1.19	0.1120	0.1442	0.0400	1.80	293	258	44.8	6.73
	8/2	1.87	1.12	0.1054	0.1353	0.0378	1.79	279	247	43.1	7.62
	10/0	1.64	0.99	0.0920	0.1190	0.0325	1.83	263	237	40.0	10.10

Values are for cotton fabrics grafted with different molar ratios of mixture monomer and concentration of monomer under 8% DMEU.

TSR versus N%, as shown in Figures 3, 4, 5, and 6, respectively. At the same N%, the values of DCRA, WCRA, and MR of the pregrafted finished fabrics were higher. The higher the concentration of the monomer was, the higher the values. Figure 6 shows that the TSR of finished cotton fabrics was lower for pregrafted fabrics. The above results show that the pregrafted cotton fabrics can exhibit improved physical properties. The difference of these physical properties in fabrics treated with different agents may be due to the influence of grafting treatment on the distribution and structure of crosslinking. The correlations of DCRA and WCRA with respect to MR, as plotted in Figure 7, show that pregrafted cotton fabrics had higher DCRA, WCRA, and MR. This suggests that the quality of the finished fabrics can be improved by pregrafting.

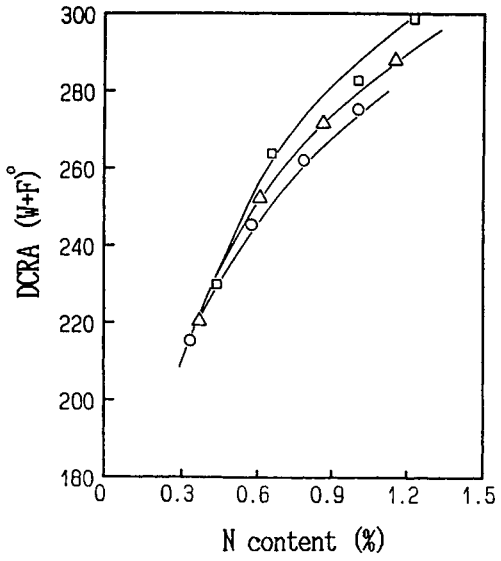

Figure 3 The relationship between DCRA and N% of grafted cotton fabrics with different concentration of mixture monomer: (○) 0%; (△) 1%; (□) 4%.

Effect of Grafting on Crosslinking Structure

The crosslinking structure of the grafted fabrics is characterized by the crosslinking density (CL/AGU) and crosslinking length (CL/length). These two quantities are calculated from the amount of formaldehyde and nitrogen contained in the grafted fabrics according to the equations reported by Frick et al.,[23] and are listed in Tables I and II. The results in Table I show that crosslinking density of pregrafted cotton fabrics was higher than those not pregrafted. The higher the concentration of the grafting monomer was, the higher the density of crosslinking. At the mixing ratio of 4 : 6, the density of crosslinking was the highest, but the crosslinking length was little affected. Thus pregrafting cotton fabrics can influence the crosslinking density more that indirectly affected the physical properties of the finished fabric. As shown in Table II, the crosslinking density increased with the concentration of the finishing agent as well as the pregrafting monomer. The crosslinking length also increased with the concentration of DMEU. This result is similar to the earlier reports.[23,28,29] However, the crosslinking

Table II Nitrogen, Formaldehyde Content, Physical Properties, and Length of Crosslinks in Cotton Fabrics

Monomer Concn. (%)	Resin Concn. (%)	CH_2O (%)	N (%)	Mole/AGU		CL/AGU	CL Length	DCRA $(W+F)°$	WCRA $(W+F)°$	TSR (%)	MR (%)
				CH_2O	N						
0	2	0.60	0.31	0.0328	0.0363	0.0147	1.24	215	203	70.0	5.50
	4	1.08	0.57	0.0596	0.0674	0.0259	1.30	245	220	64.7	5.35
	6	1.38	0.78	0.0768	0.0930	0.0303	1.53	262	243	58.3	5.10
	8	1.69	1.01	0.0949	0.1215	0.0341	1.78	275	250	53.7	5.06
1	2	0.69	0.36	0.0378	0.0422	0.0167	1.26	220	208	67.4	5.85
	4	1.13	0.60	0.0625	0.0711	0.0269	1.32	252	235	61.5	5.74
	6	1.50	0.85	0.0837	0.1016	0.0329	1.54	271	252	55.1	5.64
	8	1.91	1.14	0.1078	0.1378	0.0388	1.77	287	260	50.4	5.51
4	2	0.79	0.44	0.0434	0.0518	0.0175	1.48	229	213	61.3	6.83
	4	1.21	0.65	0.0670	0.0771	0.0284	1.36	264	240	56.0	6.37
	6	1.73	0.99	0.0971	0.1190	0.0376	1.58	282	256	51.5	6.34
	8	2.04	1.22	0.1155	0.1480	0.0415	1.78	298	265	45.2	5.86

Values are for cotton fabrics grafted with different concentrations of mixture monomer and resin under constant molar ratio of monomer (MAA/MAM = 4/6).

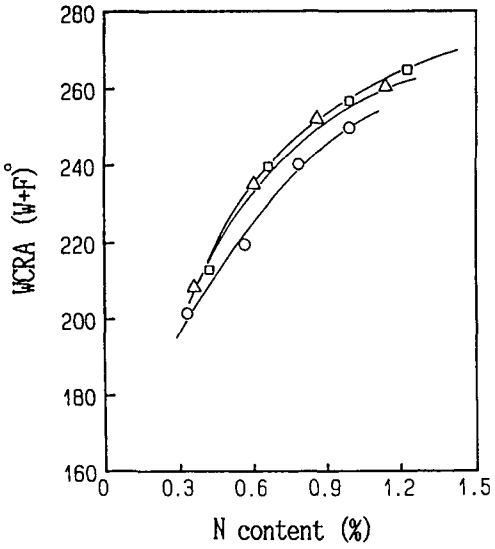

Figure 4 The relationship between WCRA and N content of grafted cotton fabrics with different concentrations of mixture monomer. The symbols are the same as Figure 3.

length of cotton fabrics seems to be little affected by the concentration of the pregrafting monomer, which is the same as the reported result. The influence of the crosslinking density on the physical properties of cotton fabrics are depicted in Figures 8–11. As shown in Figures 8–10, DCRA, WCRA, and TSR were linearly dependent on the crosslinking density, which is similar to the reported results.[23,28,29] Both DCRA and WCRA increased with CL/AGU, whereas TSR decreased with CL/AGU. This is because the grafting polymer swelled the fiber,[13] which is beneficial to the reaction of resin finishing agent and makes the crosslinking centralized.[30] Similarly, the swelling of the fiber structure can improve MR. As shown in Figure 11, cotton pregrafted with higher concentrations of monomer had higher MR.

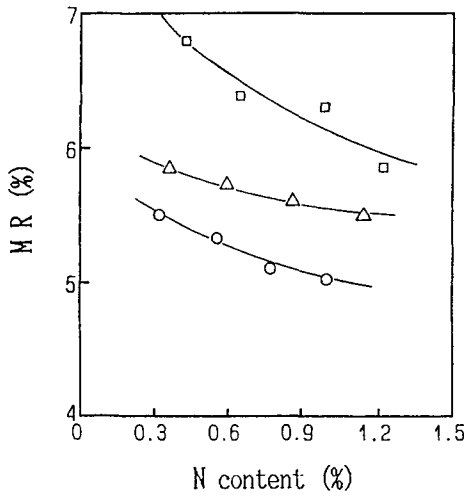

Figure 5 The relationship between MR% and N content of grafted cotton fabrics with different concentrations of mixture monomer. The symbols are the same as Figure 3.

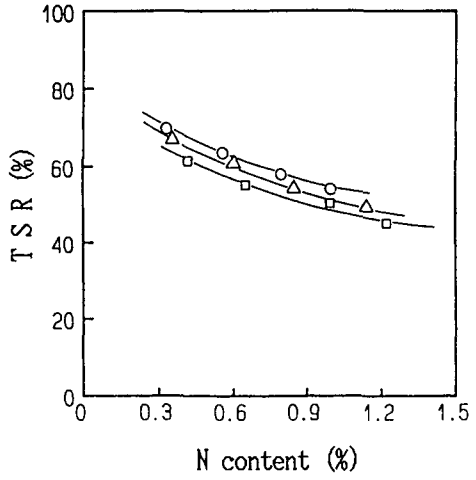

Figure 6 The relationship between TSR% and N content of grafted cotton fabrics with different concentrations of mixture monomer. The symbols are the same as Figure 3.

CONCLUSION

This research investigated the influence on the properties of resin finished cotton fabrics by pre-

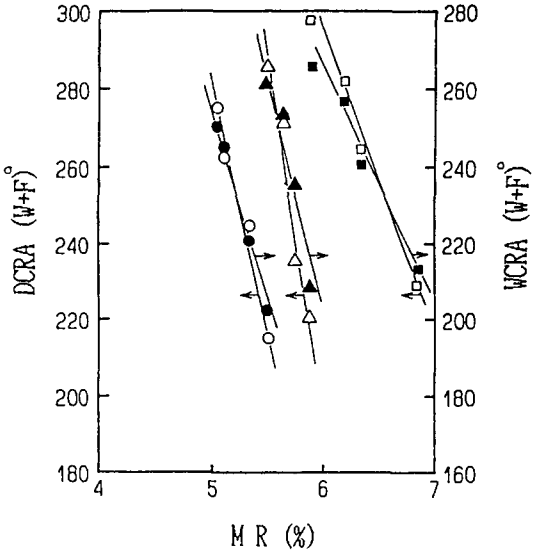

Figure 7 The balance of DCRA, WCRA, and MR% of grafted cotton fabrics with different concentrations of mixture monomer. (○, △, □) DCRA; (●, ▲, ■) WCRA; (○, ●) 0%; (△, ▲) 1%; (□, ■) 4%.

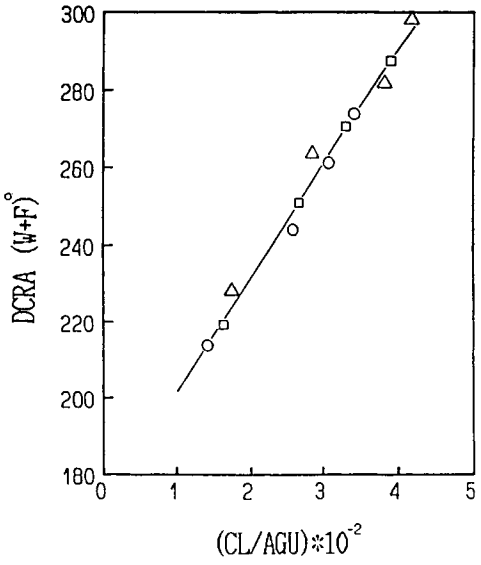

Figure 8 Plots of DCRA vs. CL/AGU for grafted cotton fabrics with different concentrations of mixture monomer. The symbols are the same as Figure 3.

grafting the fabrics with mixed monomer MAA and MAM at different molar ratios. The experimental results can lead to the following conclusions.

1. When the molar ratio of MAA to MAM was 4 : 6, the finished fabric has the highest nitrogen content and crosslinking density.
2. When the molar ratio of MAA to MAM was 4 : 6, N%, DCRA, and WCRA increase with the concentrations of pregrafting monomer and the finishing agent, but TSR decreases with both concentrations. The moisture regain increases with the increase of the concentration of the pregrafting monomer and the decrease of the concentration of the finishing agent concentration.
3. At the same N%, DCRA, WCRA, and MR increase with the concentration of the pregrafting monomer. The trend is reversed for TSR.
4. At the same CL/AGU, DCRA is little affected by the concentration of the pregrafting

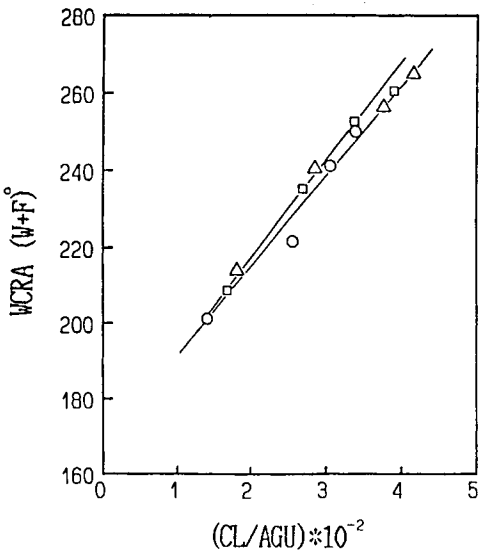

Figure 9 Plots of WCRA vs. CL/AGU for grafted cotton fabrics with different concentrations of mixture monomer. The symbols are the same as Figure 3.

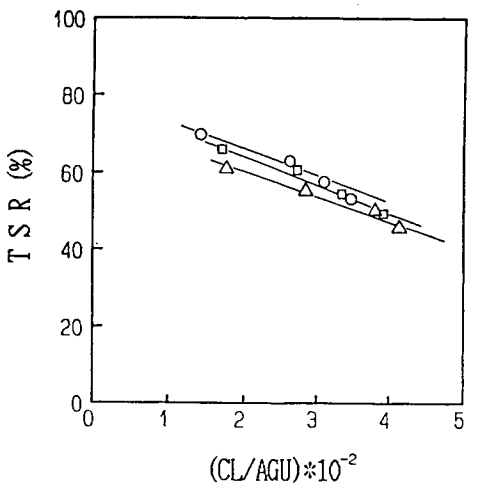

Figure 10 Plots of TSR vs. CL/AGU for grafted cotton fabrics with different concentrations of mixture monomer. The symbols are the same as Figure 3.

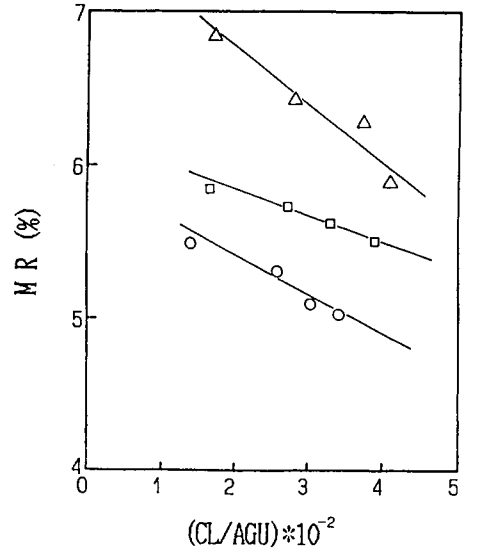

Figure 11 Plots of MR% vs. CL/AGU for grafted cotton fabrics with different concentrations of mixture monomer. The symbols are the same as Figure 3.

monomer, but WCRA and MR increase with the concentration of the pregrafting monomer. However, the trend is reversed for TSR.

5. At the pregrafting molar ratio of 4 : 6, the treated cotton fabric has the highest DCRA, WCRA, and MR.

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