

# Studies on Thermal Activities of Fabrics Treated by Polyethylene Glycol

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**ABSTRACT:** In this study, the special adjusting-temperature function of polyethylene glycol (PEG) with low molecular weight was introduced. PEGs and a two-group mixing system of PEGs of different molecular weights were added to fabrics, respectively, and the thermal activities of modified fabrics were studied. In addition, the thermal stability of PEG and fabric at a higher curing temperature was also discussed in detail. The results showed that the thermal properties of PEG decreased after being crosslinked to fabrics and the thermal activity parameters of treated fabrics

could be changed and adjusted by selecting an appropriate two-group mixing system. Some thermolysis and thermooxidative degradation of PEG and fabric used in the investigations might take place at higher curing temperatures. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2288–2292, 2003

**Key words:** thermal properties; crosslinking; crystallization; phase behavior; fibers

## INTRODUCTION

Polyethylene glycol (PEG) of low molecular weight as a “phase-change” material has special thermal activities. By transformation of the crystalline phase, polyethylene glycol has novel thermal storage and release properties during the heating/cooling cycles. When subjected to a hot environment, its crystalline phase is in the melt state and absorbs heat, giving a cooling effect; when subjected to a cooling environment, it recrystallizes and releases heat, providing a warming effect. It can be durably bonded to many kinds of fabrics (such as cotton, wool, nylon, blends of polyester/cotton, etc.) by means of a crosslinking reaction between polyethylene glycol and fiber in a pad-dry-cure process, to impart to fabrics thermal activity and adjusting-temperature function in the textile’s finishing process, which can help people maintain a constant temperature in either a hot or a cool environment. Aside from the novel thermal activities, PEG can also improve other properties of fabrics, such as increased moisture content, enhanced antistatic charge, and resistance to abrasion and pilling, for example. At the same time, however, the breaking strength of the treated fabrics can generally be decreased as a result of the crosslinking reaction.<sup>1–3</sup>

It has been proved that the thermal properties of fabrics finished by PEG through a crosslinking reac-

tion are directly affected by many factors such as, for instance, the types of fibers, the molecular weight and the concentration of PEG, the kinds and the amounts of crosslinking agents and acid catalysts, and the treating temperature and time.<sup>4</sup>

The thermal activity parameters analyzed in the experiments were the melting temperature  $T_m$ , the crystallizing temperature  $T_c$ , the heat of fusion  $H_f$ , and the heat of crystallization  $H_c$ . In recent investigations, we focused on the changes of thermal activities before and after the crosslinking reaction between PEG and various fibers, which could indicate the influences of crosslinking on the thermal properties. A mixing system of two groups of PEGs of different molecular weights was used, which enabled us to adjust the phase-change temperature on purpose. Study of the thermal stability of PEG and fabric was a primary focus of our investigations. During the curing process at higher temperature, PEG and fabrics might be thermolabile and might give rise to thermooxidative degradation, which could directly affect the thermal activities of treated fabrics. These results are very significant to working out the treating process and making the most of thermal activities of PEG. This study reports our recent investigations in detail.

## EXPERIMENTAL

### Materials

The fabrics used in the investigations were 65/35 polyester/cotton blend and 100% cotton (supplied by Tianyi Textile Inc., Tianjin, China); both had been desized, scoured, and bleached.

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Chemical agents included polyethylene glycols (MW from 400 to 1500); acid catalysts  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and citric acid (all supplied by Tiantai Chemical Reagent Inc., GuangDong, China); and a polyfunctional crosslinking agent, dimethyloldihydroxyethyleneurea (DMDHEU, solid content 40%; provided by Tianjin Chemical Reagent Manufactory, China). Deionized water was used to make up the solutions.

## Methods

PEGs of low molecular weight were crosslinked to fabrics by a pad-dry-cure process in the presence of DMDHEU. Fabrics were immersed in a finishing bath, which contained 50% of single PEG or 50% of the mixing system of PEGs of different molecular weights (PEG-400 + PEG-1000, molar ratios 1 : 1, 1 : 2, 2 : 1), 10.5% of DMDHEU (solid content 40%) as crosslinking agent, and 3% of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ /citric acid (molar ratio 5 : 1) as acid catalyst.

After two immersing-padding cycles, the extra liquid was removed by passing the fabrics through the pad rolls with high pressure; the wet pickups of fabrics were kept at 100% and then the fabrics were dried at 80°C for 6 min and cured at 140–190°C for 2–10 min. Finally, the fabrics finished by PEG were washed at 70°C for 10 min.

The thermal activity parameters of the finished fabrics were measured on a Perkin-Elmer differential scanning calorimeter DSC-7 (Perkin Elmer Cetus Instruments, Norwalk, CT). The velocity for scanning was at 10°C/min.

To study the thermal stability of PEG and fabric used in the experiment during the curing process, the weight loss of the fabric containing PEG (uncured) was tested by means of thermogravimetric analysis (TGA) on a thermobalance PR-1. Two methods were designed as follows for the purpose of investigating whether a higher curing temperature could result in thermolysis and thermooxidative degradation:

**TABLE I**  
Changes in Thermal Activities of PEGs After Crosslinking Reaction

State of PEG	MW of PEG	$H_f$ (J/g)	$H_c$ (J/g)	$T_m$ (°C)	$T_c$ (°C)
Uncrosslinked PEG	400	117.20	106.75	11.0	-4.3
	600	130.88	122.18	33.1	8.2
	800	131.17	128.45	51.2	16.4
	1000	121.05	116.54	49.7	12.7
	1500	178.95	162.51	55.5	26.0
Crosslinked PEG	400	12.18	20.17	-12.0	-23.1
	600	77.03	62.57	16.4	-6.0
	800	68.84	65.12	19.8	0.0
	1000	80.51	78.21	31.5	7.1
	1500	90.53	96.17	43.7	12.7

**TABLE II**  
Thermal Activities of Polyester/Cotton-Blended Fabric Treated with Different Molecular Weights of PEGs

MW of PEG	Add-on (%)	$H_f$ (J/g)	$H_c$ (J/g)	$T_m$ (°C)	$T_c$ (°C)
400	37.1	2.88	4.77	-12.0	-23.1
600	37.5	18.52	15.05	16.4	-6.0
800	36.4	18.85	17.22	19.8	0.0
1000	36.2	19.23	18.68	31.5	7.1
1500	36.7	21.32	22.57	43.7	12.7

1. The weight loss of fabric containing PEG (uncured) was determined on a thermobalance PR-1 at increasing temperature. The temperature of the thermobalance was controlled and increased at a rate of 10°C/min, and then the weight loss, which varied with the treating temperature, could be studied.
2. By keeping the temperature of the thermobalance at 140, 160, and 190°C, respectively, changes in the weight loss of fabric containing PEG (uncured) were recorded as the time increased, which indicated the effects of the treating time on the weight loss.

## RESULTS AND DISCUSSION

Under conditions of proper treating temperature and time, and introducing a crosslinking agent (such as DMDHEU, or 2D for short) as a bridge, the chemical crosslinking reaction between low molecular weight PEG and fiber can be conducted.<sup>5,6</sup>

Table I shows the changes in thermal activities of PEGs (MWs 400–1500) before and after crosslinking. Both  $H_f$  and  $H_c$  of the crosslinked samples decreased significantly, which meant that their endothermic and exothermic abilities had been weakened. At the same time,  $T_m$  and  $T_c$  were also obviously altered. The reason for this result was that during the crosslinking, the original molecule shape, orientation, and crystalline structure of PEG had noticeably changed, varying from uncrosslinked-PEG to crosslinked-PEG, such that the linear macromolecular structure is destroyed, thus directly reducing the crystallinity. As a result, the  $T_m$ ,  $T_c$ ,  $H_f$ , and  $H_c$  of crosslinked-PEG clearly varied compared with those of the original PEG (uncrosslinked).

Table II presents the thermal activities of polyester/cotton-blended fabric treated with PEGs of different molecular weights (PEG-400 to PEG-1500). The add-ons were kept at 36–38% for all samples. Because fabric is introduced as a participator and plays an important part in the reaction, the situation becomes more complicated; finally, a PEG-fiber net structure is formed.<sup>7</sup> With increases in molecular weight, the melting temperature of crosslinked-PEG on the fabric  $T_m$ ,

at which the cooling effect was provided, ranged from a low of  $-12.0^{\circ}\text{C}$  with PEG-400 to a high of  $43.7^{\circ}\text{C}$  with PEG-1500. The crystallizing temperature  $T_c$ , at which the warming effect was exhibited on the finished fabric, ranged from a low of  $-23.1^{\circ}\text{C}$  with PEG-400 to a high of  $12.7^{\circ}\text{C}$  with PEG-1500.

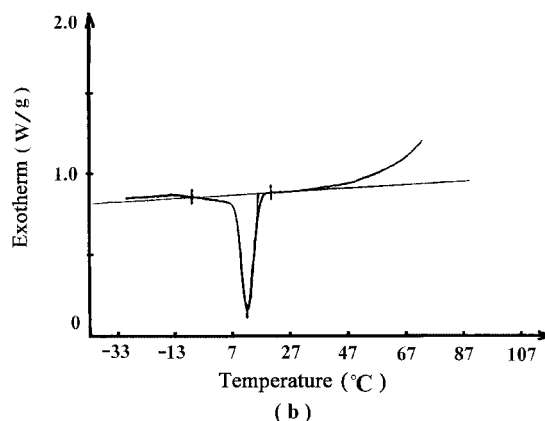
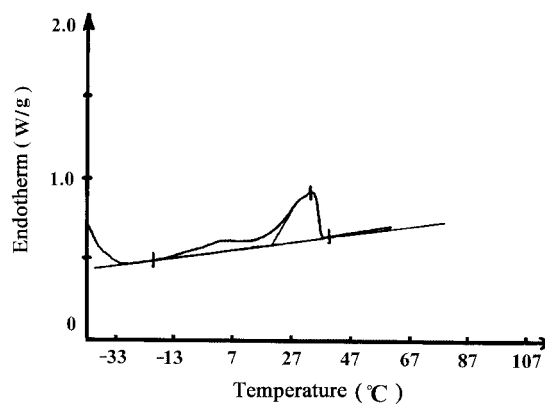
Molecular weight is a key factor to the thermal activities. Generally speaking, for most samples, the endothermal effect and the exothermal effect tended to be enhanced as the molecular weight increased (shown in Tables I and II). This might be attributed to the enhanced crystallinity in higher molecular weight PEG. In a certain range, the PEG with higher molecular weight has better flexibility and is characterized by stronger force between macromolecules, so a greater number of more nearly perfect crystals may be exhibited and higher crystallinity may be obtained, thus conferring better thermal activities.

However, after the crosslinking reaction, a sharp decline in the thermal activities of PEG-400 may be observed from the given tables. This may mainly be attributable to the fact that a higher mole fraction of reactive hydroxyl end groups is given in PEG-400 because of its lower molecular weight, which implies a better crosslinking activity compared with that of the other samples; thus a more complicated crosslinking reaction and more intricate or stiffer PEG-fiber net structure will be acquired, which gives rise to the significantly acute decrease in thermal activities. Therefore, Table II shows that there was no significant thermal activity in the polyester/cotton-blended fabric modified with PEG-400; both  $H_f$  and  $H_c$  were at reduced levels (only 2.88 and 4.77 J/g). As a result, there was a sharp increase in  $H_f$  and  $H_c$  from PEG-400 to PEG-600. When the molecular weight was above 600, the thermal properties varied smoothly. Also, Table I exhibited the same tendency for crosslinked-PEG.

The work on thermal activities of fabric modified with PEG makes it possible to manufacture garments that have an adjusting-temperature function and can maintain a constant temperature to allow people to feel more comfortable. In the investigations,  $T_m$  and  $T_c$

**TABLE III**  
Thermal Activities of the Polyester/Cotton-Blended Fabric Treated with a Mixing System of PEG-400 + PEG-1000

MW of PEG	$T_m$ ( $^{\circ}\text{C}$ )	$T_c$ ( $^{\circ}\text{C}$ )	$T_m - T_c$ ( $^{\circ}\text{C}$ )	$H_f$ (J/g)	$H_c$ (J/g)
400	-12.0	-23.1	11.1	2.88	4.77
1000	31.5	7.1	24.4	19.23	18.68
400 + 1000 (1:1)	29.2	-1.1	30.3	26.42	14.09
400 + 1000 (1:2)	30.4	2.2	28.2	28.51	19.60
400 + 1000 (2:1)	31.9	12.2	19.7	21.41	12.63



**Figure 1** DSC spectra of polyester/cotton-blended fabric treated with a mixing system of PEG-400 + PEG-1000 (molar ratio 2 : 1).

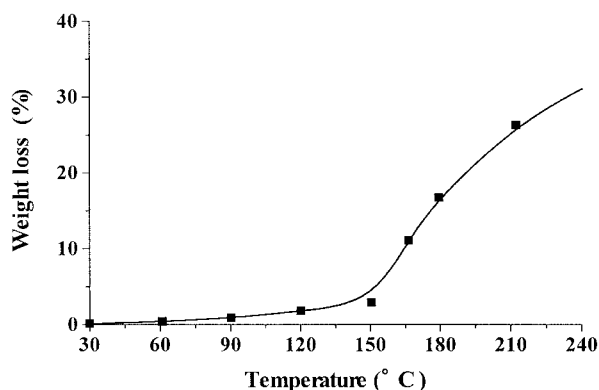
are the other two key thermal activity parameters as well as  $H_f$  and  $H_c$ : they must be in accordance with the natural environment, which means that they have to be within the varying range of the natural climate temperature and should be changed or adjusted on purpose consistent with different areas and different climate temperatures. It was found in our experiments that  $T_m$  and  $T_c$  could be adjusted by means of the mixing system of PEGs of different molecular weights. PEG-1000 was mixed with PEG-400 at molar ratios of 1 : 1, 1 : 2, and 2 : 1, respectively. The shifts of thermal activity parameters of the treated polyester/cotton-blended fabrics are listed in Table III. From Table III, it may be seen that for all samples finished by the mixing system, their  $T_c$  values varied greatly compared with those of PEG-400 and PEG-1000, whereas their  $T_m$  values were nearly identical to that of PEG-1000. In addition, their  $H_f$  and  $H_c$  parameters varied as well. It was obvious that the changes of thermal activities in the mixing system of PEGs largely depended on the molar ratios and the difference in molecular weights of two kinds of PEGs.

Figure 1 shows the heating and cooling thermal DSC scanning spectra for the polyester/cotton-blended fabric treated with the mixing system of two

kinds of PEGs: PEG-400 + PEG-1000 (molar ratio 2 : 1). There were two endothermic peaks that differed in size [Fig. 1(a)] and an exothermic peak [Fig. 1(b)] in the DSC spectra, which indicated that the physical shapes of PEGs in the mixing system were different from that of a single PEG (unmixed) and some physical properties could be altered. In the mixing system, the molecules of PEGs might reorientate, reorder, and recrystallize, which caused obvious changes in the thermal activities ( $T_m$ ,  $T_c$ ,  $H_f$ , and  $H_c$ ). Further research in this field is presently being conducted.

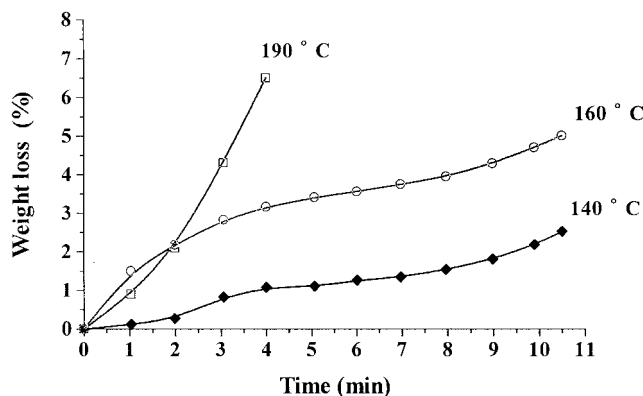
In the presence of polyfunctional crosslinking agents, the crosslinking reaction between PEG and the fiber is conducted by the pad-dry-cure method. It was found in the experiment that the PEG and the fabric used might be thermolabile and could result in thermooxidative degradation during the curing process, which had a great influence on the thermal activities of the treated fabric. From this point of view, it was significantly more important to study the thermal stability of the fabric containing PEG. The thermal stability was studied with thermobalance PR-1 by the TGA method and the weight loss of the fabric containing PEG (uncured) was determined. The experimental results are shown in Figures 2 and 3.

Figure 2 presents the weight loss that varies with the treating temperature for polyester/cotton-blended fabric containing PEG-800. It may be observed that the weight loss increased with increasing treatment temperature. The graph shows a slight tendency for weight loss to increase at temperatures lower than 150°C (which means a better thermal stability) and then increase sharply at temperatures above 150°C (which implies a worse thermal stability). This exper-



**Fabric:** Polyester/Cotton blend,  
**PEG-800:50%, No DMDHEU,**  
**No  $MgCl_2 \cdot 6H_2O$  / citric acid**  
**Process:** pad-dry (uncured), pickup:100%

**Figure 2** Changes in the weight loss for polyester/cotton-blended fabric treated with PEG-800 as the treating temperature increases.



**Fabric:** Polyester/Cotton blend,  
**PEG-800:50%, No DMDHEU,**  
**No  $MgCl_2 \cdot 6H_2O$  / citric acid**  
**Process:** pad-dry (uncured), pickup:100%

**Figure 3** Changes in the weight loss for polyester/cotton-blended fabric treated with PEG-800 as the treating time increases under three different constant treating temperatures.

imental result demonstrates that some thermolysis and thermooxidative degradation in the PEG-800 and the polyester/cotton-blended fabric might take place at sufficiently high curing temperatures, where 150°C is the critical turning point.

Figure 3 presents information about weight loss for polyester/cotton-blended fabric with PEG-800 under three constant treating temperatures. Weight loss (WL) evidently increased as the treating time increased, and a higher treating temperature produced increased weight loss, especially at 190°C. The experimental results were as follows:  $WL_{160^\circ C} > WL_{190^\circ C} > WL_{140^\circ C}$  when the treating time was less than 2 min and  $WL_{190^\circ C} > WL_{160^\circ C} > WL_{140^\circ C}$  when the treating time was more than 2 min. The weight loss had already reached 2.7% under the processing condition of 160°C for 3 min, but only 0.87% under 140°C for 3 min, which demonstrated that when the treating time was controlled for 3 min, the fabric containing PEG-800 had better thermal stability at 140°C than that at 160°C and had the worst thermal stability at 190°C.

To validate the fact that the thermal stability could eventually affect thermal properties, a corroborating experiment was designed. Table IV lists the thermal activities of cotton and polyester/cotton-blended fabric finished with PEG-800 under 140 and 160°C, respectively, for 3 min. It is obvious that the sample cured at 140°C had better thermal activities ( $H_f$  and  $H_c$ ) than that cured at 160°C. Results fully confirmed the conclusion on thermal stability mentioned above.

**TABLE IV**  
**Contrast of the Thermal Activities of Fabrics Treated**  
**with PEG-800 Cured at 140 and 160°C, Respectively**

Type of fabrics	Curing temperature (°C)	$H_f$ (J/g)	$H_c$ (J/g)
Cotton	140	38.04	36.99
	160	29.47	28.84
Polyester/cotton	140	34.03	31.39
	160	28.42	26.04

### CONCLUSIONS

The conclusions from our investigations may be summarized as follows:

1. After the crosslinking reaction between PEG and the fiber, the crystalline structure and state of PEG had been greatly altered, causing the thermal activities of treated fabric to decrease as a result. Besides, the thermal activities were significantly linked with the molecular weight of PEG.
2. The thermal activity parameters (such as  $H_f$ ,  $H_c$ ,  $T_m$ , and  $T_c$ ) could be changed and adjusted by means of a mixing system of PEGs of different molecular weights. The adjusting range depended on the difference in the molar ratios and the molecular weight of two kinds of PEGs, which made it possible to manufacture the ad-

justing-temperature garments in accordance with the natural environment.

3. When cured at higher temperature, PEG and fabric might be thermolabile and could result in thermooxidative degradation, which directly affects the thermal activities. The weight loss for fabric containing PEG increased as the treating temperature increased. The fabric containing PEG-800 had a better thermal stability at 140°C than that at 160°C and had the worst thermal stability at 190°C. In the practical treating process, it is very important to determine a reasonable curing temperature that not only can allow the crosslinking reaction to proceed normally, but also can avoid thermooxidative degradation at the same time.

### References

1. Bruno, J. S.; Vigo, T. L. *Textile Res J* 1987, 57, 7427.
2. Lamb, G. E. R.; Kepda, S.; Miller, B. *Textile Res J* 1991, 61, 169.
3. Mishra, S. P.; Sundareswaran, K. *J Appl Polym Sci* 1989, 37, 371.
4. Bruno, J. S.; Vigo, T. L. *J Coat Fabrics* 1987, 16, 264.
5. Ma, X.-G.; Guo, H. -J.; Jin, X. -N. *Dyeing Finishing (China)* 1997, 23, 10.
6. Ma, X.-G.; Yu, Y. -J.; Yu, Z. -X. *Dyeing Finishing (China)* 1996, 22, 9.
7. Goynes, W. R.; Bruno, J. S. *Textile Res J* 1990, 60, 277.
8. Leonas, K. K.; Malkam, S. *Am Dyestuff Rep* 1996, 85, 41.
9. Bruno, J. S.; Vigo, T. L. *J Coat Fabrics* 1989, 19, 16.