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THERMAL ANALYSIS OF FIBROUS SUBSTRATES CONTAINING CROSSLINKED POLYOLS

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ABSTRACT

Various structurally diverse fibrous substrates (e.g., cellulosics, polyolefins, polyesters and fiber blends) have been treated with solutions of low molecular weight polyethylene glycols (M_n 1000 and 1450) containing an appropriate crosslinking agent (a polyfunctional methylolamide, DMDHEU) and a mixed acid catalyst. The crosslinked polyols are subsequently bound to the fabrics by curing under various conditions, and possess enthalpies of fusion and crystallization (H_f and H_c) at different melting (T_m) and crystallization temperatures (T_c). These thermal properties have been observed to vary due to the degree of crosslinking in the amorphous and crystalline regions of the semi-crystalline polyols bound to the various fibrous substrates.

INTRODUCTION

The polyethylene glycols are of interest because they are considered phase change materials (PCMs). This classification is due to their high enthalpy values in the uncrosslinked (water-soluble) state, which range from ca. 30 to 45 cal g^{-1} depending on the molecular weight and degree of crystallinity of these polymers. Methods for physically incorporating and for insolubilizing these polyols on various fibrous substrates have been reported [1–4]. The objective of the later studies was to impart several improved functional properties to the substrates containing the bound polymer. These include enhanced thermal storage and release due to enthalpy changes, increased hydrophilicity, wear, and improvement of other functional properties. It was recently observed that the curing conditions chosen for a selected group of nonwoven substrates exerted a marked influence on the maximum melting temperature and minimum crystallization temperatures of the crosslinked polyols bound to fibers [5]. This investigation is concerned with a comparison of the thermal behavior of crosslinked polyols bound to a variety of fibrous substrates under different curing conditions, and with the theoretical and practical consequences of the results obtained.

EXPERIMENTAL

Materials

The following fibrous substrates/fabrics were used: (a) woven fabrics–100% cotton printcloth (126 g m^{-2}; thickness 0.021 cm; 35/65 cotton/polyester printcloth (175 g m^{-2}; thickness 0.029 cm), and 100% polypropylene taffeta (157 g m^{-2}; thickness 0.044 cm); (b) nonwoven fabrics—75/25 thermally point-bonded cotton/polyester (152 g m^{-2}; thickness 0.067 cm); hydroentangled 55/45 pulp/polyester (80 g m^{-2}; thickness 0.021 cm), and melt-blown polypropylene (34 g m^{-2}; thickness 0.025 cm). All fabrics were obtained from commercial sources except the nonwoven 75/25 cotton/polyester and melt-blown polypropylene, which were provided to us by the Textile Processing Laboratory, University of Tennessee, Knoxville.

Poly(ethylene glycol)s (PEG) (M_n 1000 and 1450) were commercial grade obtained from Dow Chemical or Union Carbide *. The crosslinking agent was Hylite LF (40% aq. dimethyloldihydroxyethyleneurea, DMDHEU) obtained from National Starch & Chemical Co. Acid catalysts (combinations of $MgCl_2 \cdot 6H_2O$ and citric acid) and NaCl were J.T. Baker reagent-grade chemicals. Deionized water was used to make up aqueous solutions.

Treatment of fibrous substrates

Woven and nonwoven fabrics were immersed in aqueous PEG solutions containing the resin and acid catalysts, then put through squeeze rolls under pressure to obtain uptakes of 60–380% above dry substrate weights. Fabrics were then cured in a one-step process (0.8–6 min at 80–100 ° C), whereby network polymerization occurred rapidly after drying or removal of water from the substrate. Fabrics were washed in hot tap water (60 ° C) containing 1% by weight of a commercially available phosphate-based detergent (Tide *), rinsed in additional tap water (25 ° C), then tumble or oven dried to constant weight. Solutions contained 50% PEG, 11–13% DMDHEU/3.3–3.9% mixed acid catalyst (5/1 molar ratio of $MgCl_2 \cdot 6H_2O$/citric acid); 5% NaCl was also used as an additive in the PEG 1000 solution to obtain optimum binding of the polyol to all substrates.

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* Use of a company or product name by the U.S. Department of Agriculture does not imply approval or recommendation of the product to the exclusion of others which may also be available.

Thermal analysis by differential scanning calorimetry

Poly(ethylene glycol)s and substrates containing the crosslinked polyols were placed in hermetically sealed pans suitable for evaluating non-volatile substances. Determinations of T_m, T_c, H_f and H_c (respectively, temperatures of melting and crystallization and enthalpies of fusion and crystallization) were made on a Mettler TA 4000 DSC System with a low temperature cell accessory over heating ranges of -40 to $+70\,^{\circ}$C and cooling ranges of $+70$ to $-40\,^{\circ}$C for the modified substrates and over heating and cooling ranges of -20 to $+100\,^{\circ}$C and $+100$ to $-20\,^{\circ}$C for the uncrosslinked polyethylene glycols. Substrates and polymers were both evaluated at heating and cooling rates of $10\,^{\circ}$C min^{-1}. The instrument was temperature-calibrated with cyclohexane and indium and calorifically calibrated with sapphire.

RESULTS AND DISCUSSION

When a network polymer between the linear, low molecular weight poly(ethylene glycol)s and DMDHEU was formed, some of the heat of fusion and crystallization of the uncrosslinked polymer was retained, and the corresponding T_m and T_c occurred at lower temperatures (Tables 1 and 2) than in the uncrosslinked polymer. For comparison with fibrous substrates containing bound polyols, the heating and cooling curves of the PEG 1000 and PEG 1450 are shown in Figs. 1 and 2, respectively. The magnitude

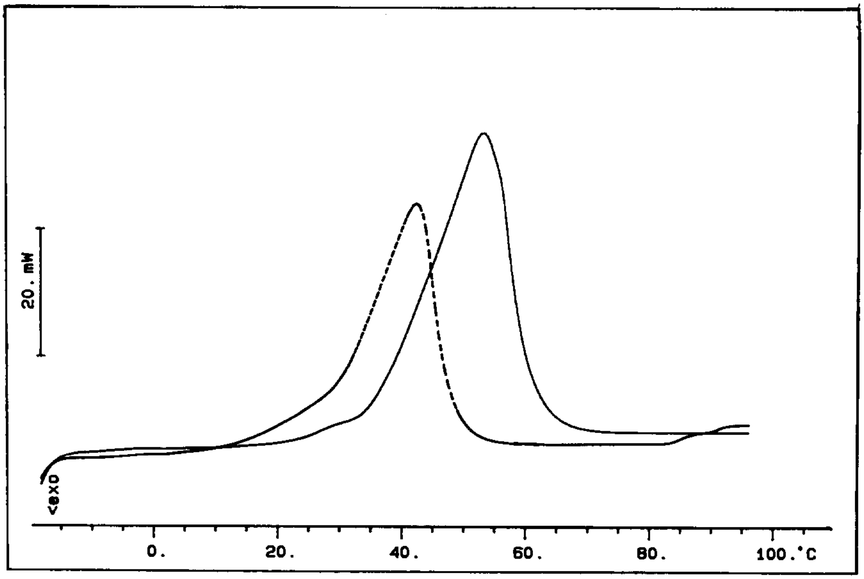

Fig. 1. DSC heating scans ($10\,^{\circ}$C min^{-1}) of PEG 1000 (— — —) and PEG 1450 (———).

TABLE 1

Thermal analysis of fibrous substrates treated with PEG 1000/DMDHEU

Fiber type and construction [a]	Cure time (min)	Cure temp. (°C)	Weight gain (%)	T_m (°C)	H_f (cal g^{-1})	T_c (°C)	H_c (cal g^{-1})
None [b]	–	–	–	38	30.9	+20	30.0
100% cotton woven	4.0	80	25	26	1.3	+9	1.8
	6.0	80	51	22	2.8	+7	3.4
	5.0	85	48	19	3.2	−5	3.4
	3.0	90	46	18	2.9	−4	3.2
	5.0	100	52	15	2.9	−8	3.0
75/25 C/PET thermally bonded nonwoven	3.0	90	43	31	2.5	−2	2.5
	3.0	100	68	23	1.7	−2	1.7
	5.0	100	91	18	5.5	−10	5.3
55/45 pulp/PET hydroentangled nonwoven	1.5	90	46	35	5.2	+10	5.1
	3.0	90	87	12	3.8	−10	3.7
	1.5	100	75	19	4.4	−2	5.3
	5.0	100	71	22	4.0	+5	4.8
35/65 C/PET woven	5.0	80	29	32	2.6	+9	2.8
	6.0	80	39	19	2.4	+5	2.9
	5.0	85	33	18	2.4	−3	2.8
	3.0	90	28	29	2.4	+7	2.2
	5.0	100	38	12	2.4	−15	1.7
100% polypropylene melt-blown nonwoven	1.5	90	127	25	6.8	−1	7.4
	3.0	90	166	20	7.2	−4	6.8
	0.8	100	28	25	4.1	+2	4.1
	1.5	100	182	21	7.1	−5	6.8
	5.0	100	199	9	6.2	−14	3.6
100% polypropylene woven	3.0	90	32	18	3.1	−10	3.1
	3.0	100	49	19	3.6	−1	3.8
	5.0	100	66	15	3.7	−7	4.0

[a] C/PET, cotton/polyester, pulp/PET, pulp/polyester.

[b] PEG 1000.

of the thermal storage and release values of these two polyols was 30–35 cal g^{-1}. Their crystallization temperatures were almost identical (20–22 °C), but PEG 1450 melted 10 °C higher then PEG 1000.

It was recently discovered that nonwoven substrates treated with PEGs/DMDHEU, and then cured under mild conditions, afforded selective crosslinking in the amorphous regions, and thus produced modified substrates with much higher melting and crystallization temperatures and corresponding enthalpy contents [5] than those cured at higher temperatures (generally above 100 °C). The thermal characteristics of fibrous substrates containing crosslinked PEG 1000 (Table 1) varied markedly for woven as well as nonwoven fabrics cured under various conditions with the polyol and resin. Irrespective of fiber type and construction, most fabrics had the highest T_m and T_c values at minimum time/temperature curing conditions

TABLE 2

Thermal analysis of fibrous substrates treated with PEG 1450/DMDHEU

Fiber type and construction [a]	Cure time (min)	Cure temp. (°C)	Weight gain (%)	T_m (°C)	H_f (cal g^{-1})	T_c (°C)	H_c (cal g^{-1})
None [b]	–	–	–	48	35.6	22	34.6
100% cotton woven	3.0	80	24	35	3.5	12	3.2
	4.0	80	46	33	4.4	10	3.9
	3.0	90	56	33	3.2	18	4.7
	2.0	100	40	37	2.5	18	5.2
75/25 C/PET thermally bonded nonwoven	3.0	90	77	38	6.6	12	6.4
	1.5	100	26	37	5.1	12	4.7
	3.0	100	96	35	7.3	8	6.8
	5.0	100	101	22	5.2	2	7.4
55/45 pulp/PET hydroentangled nonwoven	1.5	90	27	35	2.9	16	3.2
	3.0	90	75	34	5.8	12	6.1
	1.5	100	62	36	5.3	16	5.4
	5.0	100	87	22	6.7	8	6.6
35/65 C/PET woven	3.0	80	19	35	2.6	11	2.5
	4.0	80	31	33	3.3	9	3.1
	3.0	90	39	22	3.6	5	3.6
	2.0	100	33	23	2.7	15	4.1
100% polypropylene melt-blown nonwoven	1.5	90	128	41	10.4	19	9.2
	3.0	90	170	39	10.0	16	7.5
	0.8	100	65	43	9.1	20	7.7
	1.5	100	154	36	9.4	17	8.9
	5.0	100	166	37	9.4	14	8.8
100% polypropylene woven	3.0	90	35	22	2.5	3	3.3
	3.0	100	59	37	4.0	11	4.3
	5.0	100	66	25/33	5.0	10	5.4

[a] As in Table 1.
[b] PEG 1450.

required to insolubilize the polyol on the fiber. The higher melting and crystallization temperatures also produced correspondingly higher heat contents (enthalpies) on heating and cooling under these conditions than for fabrics cured at longer times and higher temperatures. Nonwoven fabrics (irrespective of fiber type) had more pronounced differences in their thermal behavior than did woven fabrics when each was cured under corresponding combinations of time and temperature. A few thermal scans are shown to illustrate and amplify these trends (Figs. 3–11).

When the nonwoven pulp–polyester fabric was cured at 90 °C for 1.5 and for 3 min with the PEG 1000/DMDHEU, dramatic differences were observed, not only in the amount of bound polymer (46 vs. 87% wt. gains, respectively), but also in the thermal storage and release properties of the modified substrates. Figure 3 shows the heating scans of the two treated

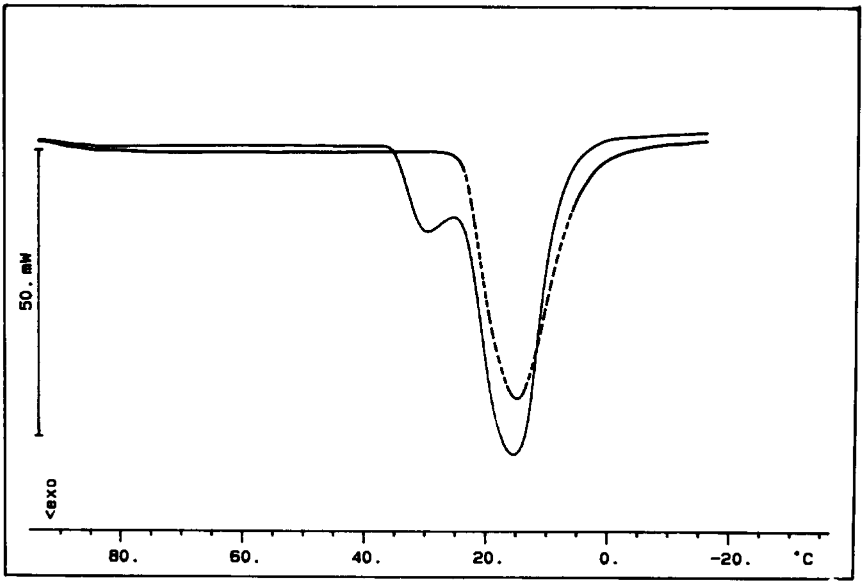

Fig. 2. DSC cooling scans (10 °C min^{-1}) of PEG 1000 (— — —) and PEG 1450 (———).

fabrics, in which the fabric cured for the shorter time had a greater H_f (5.2 cal g^{-1}) than the fabric cured longer (3.8 cal g^{-1}). The T_m for the first fabric was also substantially higher (35 °C) than for the second fabric (12 °C). Both the magnitude of the heat absorption and differences in maximum melting

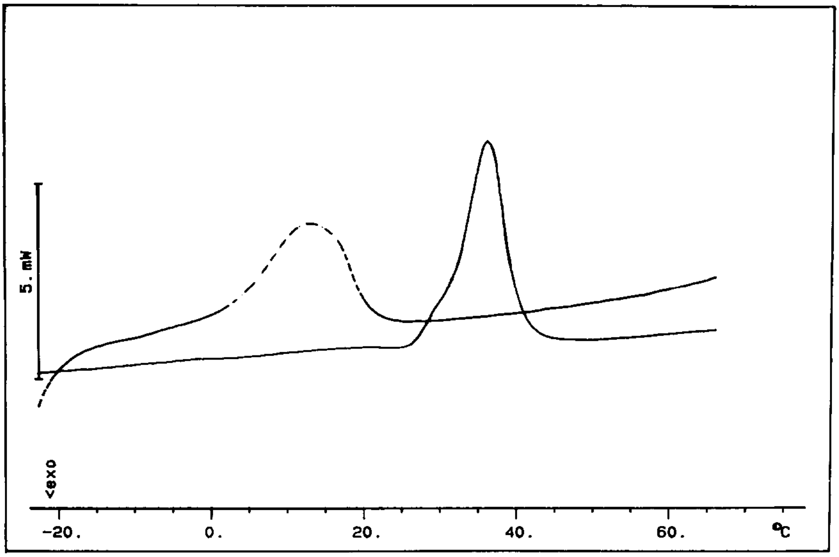

Fig. 3. DSC heating scans (10 °C min^{-1}) of 55/45 pulp/PET nonwoven treated with PEG 1000/DMDHEU and cured 1.5 min/90 °C (———) and 3 min/90 °C (— — —).

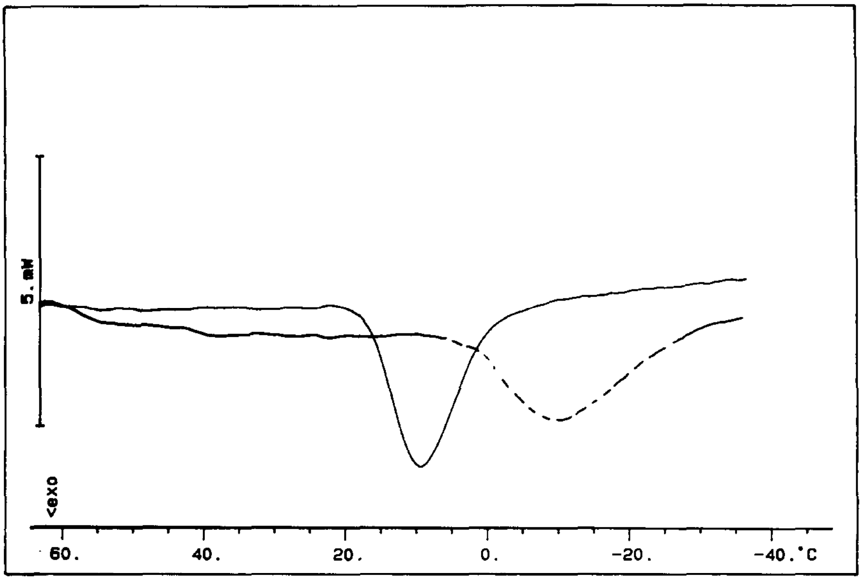

Fig. 4. DSC cooling scans (10 °C min^{-1}) of 55/45 pulp/PET nonwoven treated with PEG 1000/DMDHEU and cured 1.5 min/90 °C (———) and 3 min/90 °C (— — —).

or softening temperatures are consistent with more crystalline material being present in the polymer bound to the fabric that was cured for the least time. It is reasonable to assume that crosslinking of the amorphous regions occurs

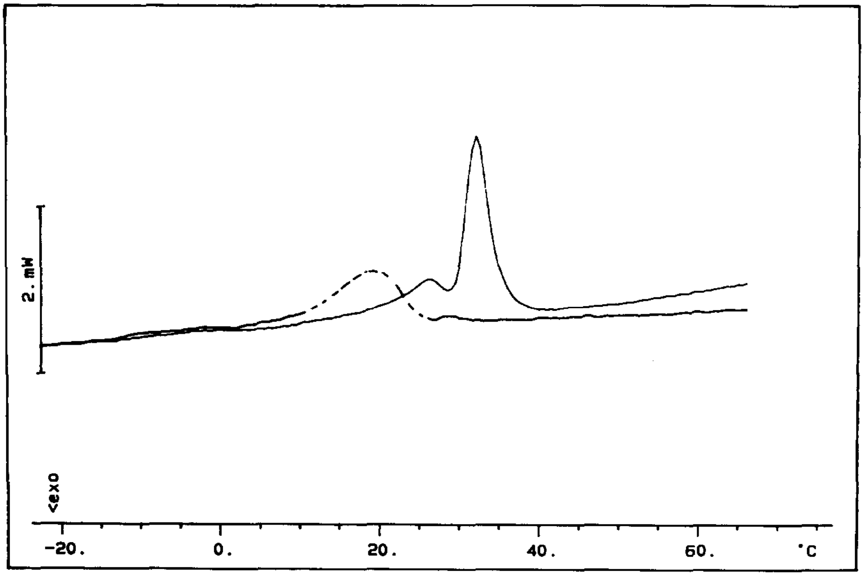

Fig. 5. DSC heating scans (10 °C min^{-1}) of 35/65 woven C/PET treated with PEG 1000/DMDHEU and cured 5 min/80 °C (———) and 5 min/85 °C (— — —).

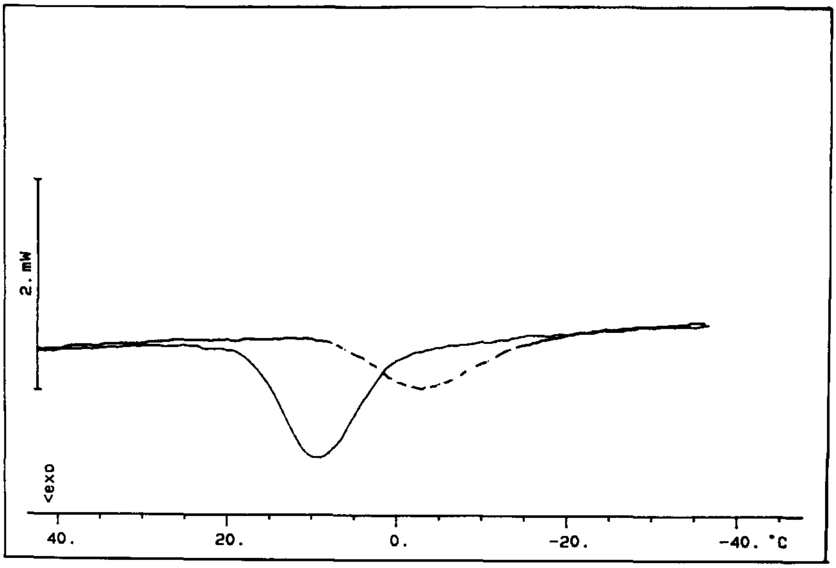

Fig. 6. DSC cooling scans (10 °C min^{-1}) of 35/65 woven C/PET treated with PEG 1000/DMDHEU and cured 5 min/80 °C (———) and 5 min/85 °C (— — —).

first in this semi-crystalline polymer. The same trend was observed in the cooling scans of these two fabrics (Fig. 4). The fabric cured for the shorter time had a crystallization temperature of +10 °C, compared with −10 °C for the fabric cured for the longer time. The heat of crystallization was also higher for the first fabric even though there was less bound polymer on this substrate.

A similar trend was observed when the substrate was a woven fabric. A 35/65 cotton/polyester fabric cured for 5 min at 80 °C and at 85 °C had comparable weight increases and thermal storage and release values. However, the maximum melting and minimum crystallization temperatures differed (Figs. 5 and 6). The fabric cured at 80 °C had T_m and T_c at +32 °C and +9 °C, while the fabric cured at 85 °C had T_m and T_c at +18 °C and −3 °C). If the same fabric was cured for 5 min at 100 °C (not shown), the melting and crystallization temperatures were further lowered and some decrease in thermal storage and release values also occurred.

Perhaps the most dramatic effect of difference in curing conditions for the PEG 1000/DMDHEU was observed with the melt-blown polypropylene fabric. As shown in Fig. 7, curing for 1.5 min at 90 °C produced a fabric with a thermal release value approximately twice that of a fabric cured for 5 min at 100 °C (7.4 vs. 3.6 cal g^{-1}, respectively). This result was obtained with much less bound polymer on the first fabric (125% weight gain) than on the second fabric (199% weight gain), again indicating that crosslinking amorphous regions first under mild conditions is preferable for binding the polymer to give optimum thermal characteristics to the modified substrate.

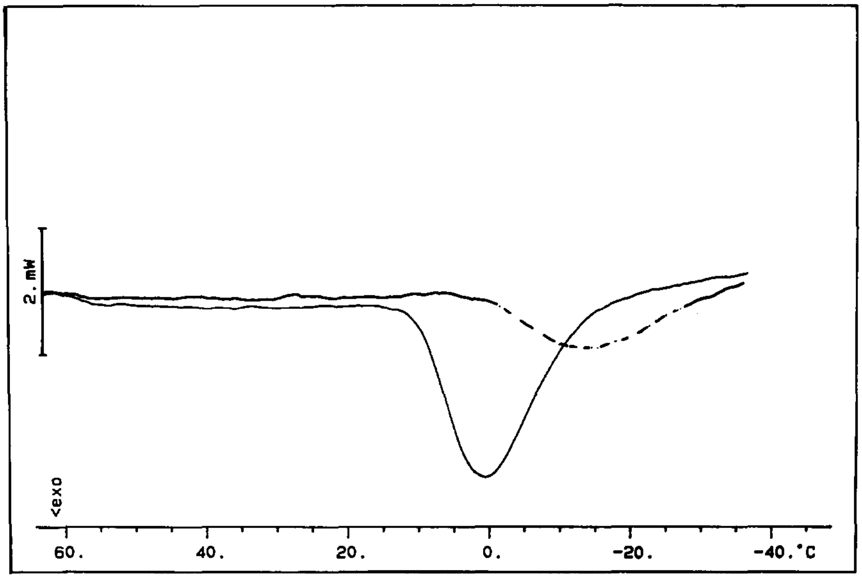

Fig. 7. DSC cooling scans (10 °C min^{-1}) of 100% melt-blown polypropylene nonwoven treated with PEG 1000/DMDHEU and cured 1.5 min/90 °C (———) and 5 min/100 °C (— — —).

Corresponding differences in crystallization temperatures were also observed. The T_c for the fabric cured for 1.5 min at 90 °C was −1 °C, but −14 °C for the fabric cured for 5 min at 100 °C.

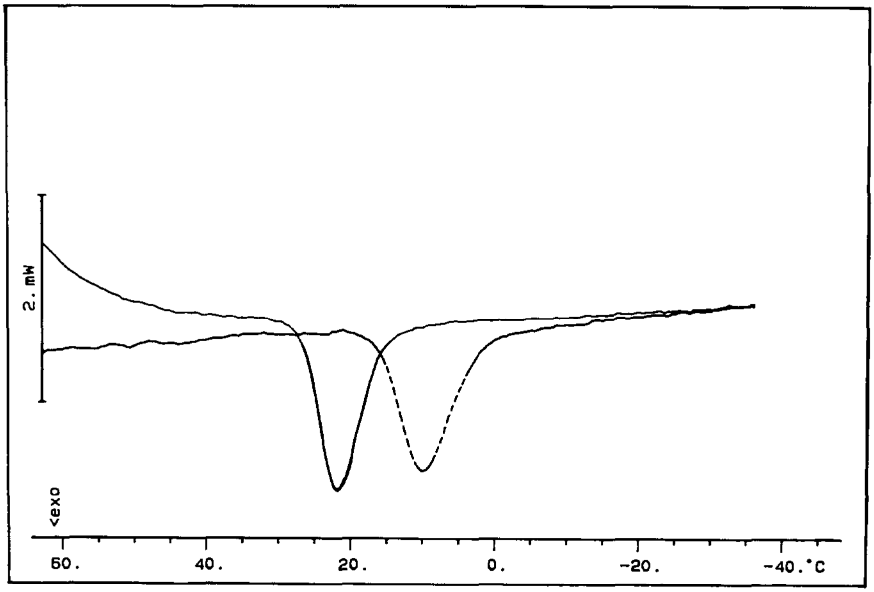

Fig. 8. DSC cooling scans (10 °C min^{-1}) of 100% woven cotton treated with PEG 1450/DMDHEU and cured 2 min/100 °C (———) and 4 min/80 °C (— — —).

Similar trends in melting and crystallization temperatures and in heat contents were observed for various woven and nonwoven fabrics treated with PEG 1450/DMDHEU and cured at different time/temperature combinations. The results for all fabrics are shown in Table 2. There was less differentiation in melting and crystallization temperatures as a function of curing conditions for fabrics treated with the PEG 1450/DMDHEU than for the fabrics treated with the PEG 1000/DMDHEU. This could be attributable to the more crystalline nature of PEG 1450 relative to PEG 1000. This aspect would require fewer crosslinks between molecules of PEG 1450 to achieve insolubilization, and thus produce more crystalline and higher melting structures. A few selected thermal scans from fabrics listed in Table 2 illustrate these trends.

It was possible to insolubilize the PEG 1450 on all-cotton fabric using a variety of curing conditions to obtain comparable thermal storage and release values and generally high T_m and T_c values. However, some curing conditions were preferable to others. For example, the cooling scans in Fig. 8 show that woven cotton fabric cured at 100 °C for 2 min had a higher crystallization temperature (18 °C) than the same fabric cured at 80 °C for 4 min (10 °C). The magnitude of the heat release for the former fabric (5.2 cal g^{-1}) was also greater than for the latter fabric (3.9 cal g^{-1}), even though the first fabric had slightly less polymer bound to it.

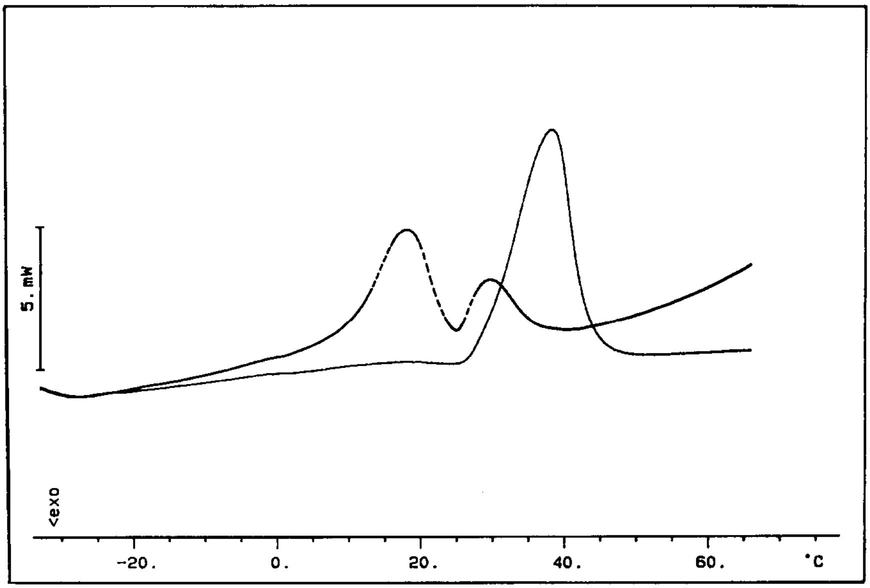

Fig. 9. DSC heating scans (10 °C min^{-1}) of 75/25 C/PET nonwoven treated with PEG 1450/DMDHEU and cured 3 min/90 °C (———) and 5 min/100 °C (— — —).

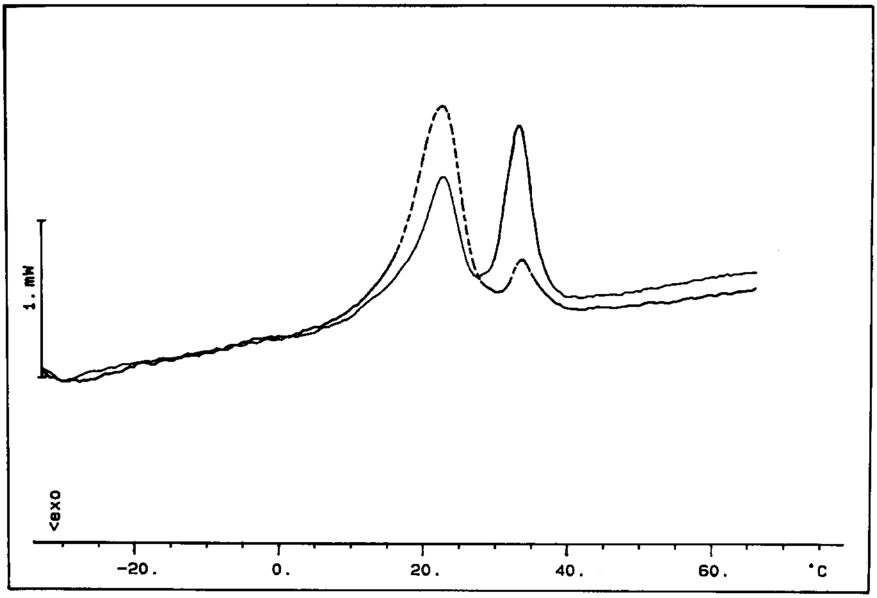

Fig. 10. DSC heating scans (10 °C min^{-1}) of 35/65 woven C/PET treated with PEG 1450/DMDHEU and cured 4 min/80 °C (———) and 3 min/90 °C (— — —).

The 75/25 thermally bonded cotton/polyester nonwoven was also amenable to binding crosslinked PEG 1450 under a variety of conditions to obtain desirable thermal characteristics. However, curing conditions of 5 min at 100 °C produced a fabric with only slightly more weight gain (101%) than a fabric cured for only 3 min at 90 °C (77%). Moreover, as illustrated in Fig. 9, the former fabric had a T_m of only 22°C compared with a T_m of 38°C for the fabric cured under milder conditions. Corresponding enthalpy of fusion values were also higher (6.6 vs 5.2 cal g^{-1}) for the fabric cured under the milder conditions.

With the 35/65 cotton–polyester woven fabric, it was preferable to use lower temperature/longer time combinations rather than higher temperature/shorter time combinations to obtain bound polyol with the highest heat contents and melting and crystallization temperatures. For example, Fig. 10 shows that this fabric cured for 4 min at 80 °C had two peaks, with the one of greater magnitude at 33°C, while the fabric cured for 3 min at 90 °C also had two peaks, with the one of greater magnitude at a lower temperature (22 °C). The presence of two peaks is indicative of the crosslinking of polyols of different molecular weight in the M_n distribution of this polymer, which usually varies about 10%. In this particular case, the magnitude of the thermal storage or heat content (enthalpy of fusion) was similar for the two fabrics cured under different conditions, even though their melting temperatures were different.

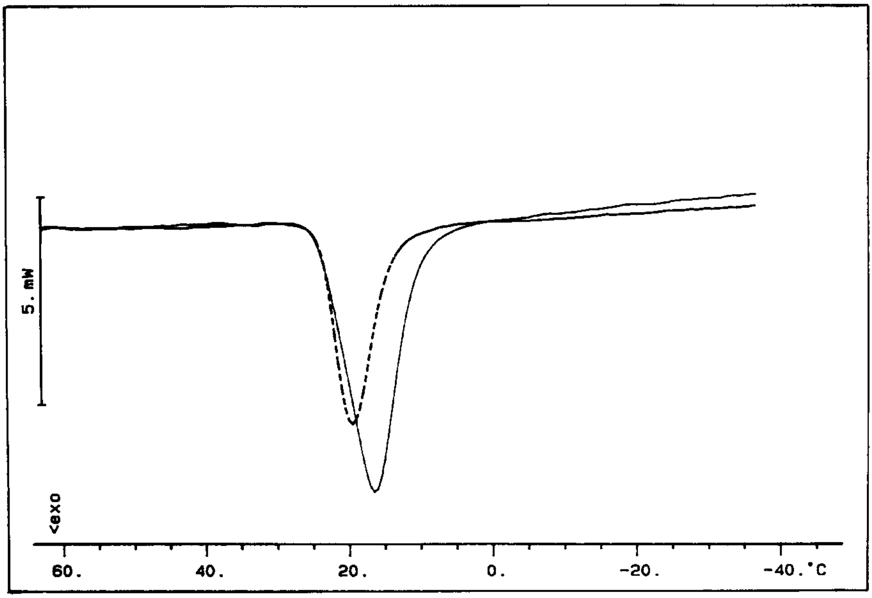

Fig. 11. DSC cooling scans (10 °C min^{-1}) of 100% melt-blown polypropylene nonwoven treated with PEG 1450/DMDHEU and cured 0.8 min/100 °C (———) and 1.5 min/100 °C (— — —).

The melt-blown nonwoven polypropylene provides a final example of how curing conditions affect the thermal characteristics of the crosslinked PEG 1450 bound to a substrate. The cooling scans in Fig. 11 show that, when the nonwoven polypropylene was cured for only 0.8 min at 100 °C, a substantial exotherm was observed at 20 °C (7.7 cal g^{-1}). If the same fabric was cured for 1.5 min at 100 °C, the observed exotherm at 17 °C was only slightly greater in magnitude or heat content (8.9 cal g^{-1}) than that of the first fabric, even though the weight gain of the latter fabric was more than twice that of the former.

CONCLUSIONS

Fabrics comprised of diverse fiber types and construction were treated with PEG 1000/DMDHEU and with PEG 1450/DMDHEU, then cured under a variety of conditions. Thermal analyses indicate that selection of curing conditions (time/temperature combinations) markedly influences the heat content of the crosslinked polyols bound to the fibrous substrates and their melting (T_m) and crystallization (T_c) temperatures. Under appropriate curing conditions (usually the lowest curing temperature and shortest time), the bound polymer has the highest thermal storage and release contents and melting and crystallization temperatures. Nonwoven fabrics, presumably due to more uniform curing and rapid loss of water, generally had better thermal characteristics than woven fabrics for comparable amounts of polymer bound to the fibers. This trend was not as prevalent for the PEG 1450 as it was for the PEG 1000, owing to differences in initial crystallinity of the parent polymer and the fewer crosslinks required by the higher molecular weight polymer to achieve insolubilization. This information will be useful for predicting the behavior of thermally adaptable fabrics containing crosslinked polyols, and for enhancing their thermal properties.

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REFERENCES

1 T.L. Vigo and C.E. Frost, in B. Miller (Ed.), Thermal Analysis: Proceedings of the Seventh International Conference on Thermal Analysis, Vol. II, Wiley, New York, 1982, pp. 1286–1295.
2 T.L. Vigo and C.E. Frost, J. Coated Fabr., 12 (1983) 243.
3 T.L. Vigo and J.S. Bruno, J. Appl. Polym. Sci., 37 (1989) 371.
4 T.L. Vigo and J.S. Bruno, in I. Glasman (Ed.), Textile Technology International 1989, Sterling Press, London, 1989, pp. 274–278.
5 T.L. Vigo and J.S. Bruno, Multipurpose nonwovens containing crosslinked polyols affixed by a low temperature cure, accepted for Proc. AATCC Natl. Tech. Conf., Philadelphia, PA, Oct. 3–6, 1989.