

## TEMPERATURE-ADAPTABLE FIBERS CONTAINING SUBSTANCES WITH SOLID-SOLID TRANSITIONS

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### ABSTRACT

Incorporation of 50% aqueous solutions of compounds (exhibiting high  $\Delta H$  values due to solid–solid transitions prior to melting or crystallization) into hollow fibers or treatment of conventional fibers with these solutions, produced after drying and conditioning, modified fibers with 2–4 times the heat content ( $Q$ ) of the corresponding untreated fibers in a given temperature interval. Of the compounds evaluated, 2,2-dimethyl-1,3-propanediol and 2-hydroxymethyl-2-methyl-1,3-propanediol produced the most reliable and reproducible thermal effects in the modified fibers that lasted through 50 heating and cooling cycles. Of the treated fibers, hollow rayon was the most effective, followed by cotton, then hollow polypropylene relative to the corresponding untreated fibers. As monitored by differential scanning calorimetry, these modified fibers had thermal storage and release values useful at temperatures as high as 72–102°C on heating and as low as 37–7°C on cooling, with generally little variability in their  $Q$  values within the same fiber or between different batches of the same fiber. Other compounds of this type were not effective for use with the fibers due to sublimation/high vapor pressure characteristics (2,2-dimethyl-1-propanol and pentaerythritol) or because of their anomalous and inconsistent thermal behavior (2-amino-2-methyl-1,3-propanediol).

### INTRODUCTION

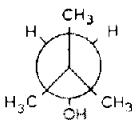
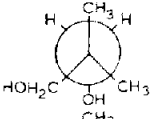
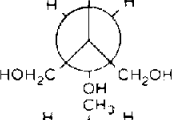
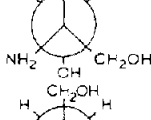
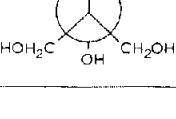
Recent studies in our laboratory have demonstrated that the incorporation of inorganic salt hydrates and polyethylene glycols of varying molecular weight into hollow textile fibers produced temperature-adaptable materials having 2–4 times the thermal storage and release characteristics of untreated fibers after repeated heating and cooling [1,2]. These substances varied in their ability to sustain such thermal effects, and all may be classified as phase change materials, i.e., substances that exhibit high enthalpy changes on fusion or melting and on crystallization or cooling, i.e., a change of state from solid to liquid and the reverse.

However, it has also been noted in the literature that certain compounds and polymers undergo solid–solid transitions that occur before fusion or melting and are characterized by very large changes in enthalpy and entropy,

in many instances an order of magnitude greater than that of fusion [3-5]. This dramatic thermal change has been attributed to reorientational disorder and these substances have been commonly denoted as "plastic crystals". However, Wunderlich and Grebowicz [5] recently suggested that such thermal changes may also be explained by conformational disorder, such phenomena are characteristic of what is called a "condis crystal". Five compounds (all soluble to some extent in water, having tetragonal symmetry, and structural analogs of pentaerythritol) were selected because of their high  $\Delta H$  and  $\Delta S$  values for incorporation into hollow fibers and treatment of conventional textile structures. These are shown in Table 1. The treated fibers were then evaluated by thermal analysis to ascertain if they were comparable or superior to previously prepared temperature-adaptable fibers with regard to marked increases in their thermal storage and release ability at appropriate temperature intervals.

TABLE 1

Experimentally determined transition and fusion data for selected substances<sup>a</sup>

| Substance                                | Structure <sup>b</sup>  | Transition |                                   |                   | Fusion     |                                   |                   |
|--|---|------------|-----------------------------------|-------------------|------------|-----------------------------------|-------------------|
|  |   | Temp. (°C) | $\Delta H$ (cal g <sup>-1</sup> ) | $\Delta S$ (e.u.) | Temp. (°C) | $\Delta H$ (cal g <sup>-1</sup> ) | $\Delta S$ (e.u.) |
| 2,2-Dimethyl-1-propanol                  |  | -31.0      | 12.1                              | 4.4               | 51-54      | 11.0                              | 3.0               |
| 2,2-Dimethyl-1,3-propanediol             |  | 40-43      | 31.3                              | 10.3              | 125-126    | 10.8                              | 2.8               |
| 2-Hydroxymethyl-2-methyl-1,3-propanediol |  | 81         | 46.1                              | 15.6              | 197        | 10.7                              | 2.7               |
| 2-Amino-2-methyl-1,3-propanediol         |  | 78-80      | 57.3                              | 17.2              | 110-112    | 6.8                               | 1.9               |
| Pentaerythritol                          |  | 182-183    | 72.0                              | 21.5              | 258        | 8.9                               | 2.3               |

<sup>a</sup> From ref. 4.<sup>b</sup> Represented by Newman projections, but not necessarily in the most preferred conformation.

## EXPERIMENTAL

### *Materials*

The following textiles were used: (a) hollow filament polypropylene fibers ( $0.66 \text{ mg m}^{-1}$ ) with a single cavity cross-section (total and internal diameters of 90 and  $36 \mu\text{m}$ ; Hercules \*); (b) hollow filament rayon tow ( $0.19 \text{ mg m}^{-1}$ ) with a single cavity cross-section (total and internal diameters of 25 and  $20 \mu\text{m}$ ; Courtaulds); and (c) mercerized cotton sewing thread (three-ply yarn with a staple length of 25–32 mm and a denier of  $31.8 \text{ mg m}^{-1}$ ; Belding Lily).

The chemicals used as desiccants in the solid state ( $\text{CaSO}_4$ ) and used as saturated salt solutions to provide a certain relative humidity ( $\text{KNO}_2$ ) were reagent-grade (Fisher Chemical Co.). Substances with solid–solid transitions used in the study were: (1) 2,2-dimethyl-1-propanol (reagent grade, m.p.  $52^\circ\text{C}$ , Aldrich Chemical Co.); (b) 2,2-dimethyl-1,3-propanediol (practical grade, m.p.  $126^\circ\text{C}$ , Eastman Kodak Co.); (c) 2-hydroxymethyl-2-methyl-1,3-propanediol (technical grade, m.p.  $181^\circ\text{C}$ , Aldrich Chemical Co.); (d) 2-amino-2-methyl-1,3-propanediol (reagent grade, m.p., after two recrystallizations from ethanol,  $108^\circ\text{C}$ , Eastman Kodak Co.); (e) pentaerythritol (reagent grade, m.p.  $252^\circ\text{C}$ , Eastman Kodak Co.). The melting points listed above represent the onset temperatures and were determined by differential scanning calorimetry using sealed pans as previously described in the literature [4]. Aqueous solutions of these substances were made from the compounds as received for application to fibers. More detailed information on the structure, and literature data on thermal analysis of these compounds in the solid state, is given in Table 1.

### *Treatment of fibrous materials*

The hollow fibers, rayon and polypropylene, were cut to 125-mm lengths, aligned in fiber bundles, then filled with 50% aqueous solutions of the plastic crystals by an aspiration technique [1], with the exception of pentaerythritol which was incorporated into the fibers as a 30% aqueous solution. After the fibers were filled, they were placed horizontally and cooled at  $-15^\circ\text{C}$  or lower, then dried to constant weight in a desiccator for 24 h over anhydrous  $\text{CaSO}_4$  at ambient temperature and atmospheric pressure, then subsequently conditioned in a desiccator at  $20^\circ\text{C}/45\% \text{ RH}$  (over a saturated solution of  $\text{KNO}_2$ ) prior to thermal analysis. The cotton thread was immersed in each of the above aqueous solutions, then centrifuged for 5 min at  $320g$  in a

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laboratory-type centrifuge (2080 rpm for this centrifuge), cooled, dried and conditioned in the same manner as the hollow fibers.

### *Thermal analysis*

Treated and untreated fibers, solids and aqueous solutions were analyzed for their solid–solid thermal transitions by placing them in pans recommended for non-volatile substances. For melting determinations of the solids, hermetically sealed pans were used. Variation of the thermal energy with time ( $dH/dt$ ) was measured on a Perkin-Elmer differential scanning calorimeter (DSC-2B) equipped with a Thermal Analysis Data Station (Model 3600) at various temperature intervals dictated by the material evaluated. The instrument was temperature-calibrated with cyclohexane and indium (for solid–solid transitions and melting, respectively) and calorifically-calibrated with a 0.0282 g sapphire disc. The instrument was set to run at heating and cooling rates of  $20^{\circ}\text{C min}^{-1}$ , a chart speed of  $20 \text{ mm min}^{-1}$ , a DSC range of  $10 \text{ mcal s}^{-1}$ , recorder ranges of 10–50 mv, and a positive pressure (137.9 kPa) of dry  $\text{N}_2$  through the sample holder block. All analyses were run manually on heat mode until the desired upper temperature was reached, run onto auto-cool mode until the temperature reached the desired lower limit, then recycled each time for the desired number of heating and cooling cycles (1–50); the samples were also concurrently monitored with the specific heat software program for the data station in the temperature ranges of interest for heating and cooling, and the thermal scans for selected cycles stored for specific heat capacity,  $C_p$ , and heat content.  $Q$ , computations and graphic display. The total heat content at various temperature intervals,  $Q$ , was determined by comparison with a sapphire standard, and computed manually with a K&E compensating planimeter for both heating and cooling cycles by measuring the area under the curve. Manual calculations of  $Q$  for the sapphire standard and samples were computed as previously described [2]. Also,  $Q$  was computed with a computer program using TADS (Thermal Analysis Data Station). The percent error between manual and computerized  $Q$  values was low and did not exceed 2.5%. Aluminum pans of equal weight were selected to make the calculations more precise.

## RESULTS AND DISCUSSION

The five compounds chosen for treatment of or incorporation into fibers varied greatly in their ability to increase the thermal storage and release characteristics of modified fibers after prolonged thermal cycling (defined as at least 50 heating and cooling cycles). Two of the five compounds, 2,2-dimethyl-1-propanol and pentaerythritol, whose solid–solid transition temperatures represent the low and high extremes of the compounds evaluated,

were not acceptable for treating fibers because of their unusually high vapor pressure which caused these substances to sublime from the fibers. After ten heating and cooling cycles, hollow rayon fibers containing 2,2-dimethyl-1-propanol had heat contents practically indistinguishable from that of the untreated hollow rayon fiber. Although rayon fibers containing pentaerythritol had 2.5–3.0 times the heat content of the untreated rayon fiber after ten thermal cycles (ca. 26–30 cal g<sup>-1</sup> over a 30°C temperature interval), their thermal effectiveness was completely lost after 50 heating and cooling cycles.

The amino compound, 2-amino-2-methyl-1,3-propanediol, exhibited anomalous thermal behavior, both in the solid state and when incorporated into the fibers. When the solid or treated fiber (e.g., rayon) was thermally scanned from 17 to 102°C (heating and cooling), little or no solid–solid endothermic transitions occurred on heating and only a small exotherm occurred on cooling (92–52°C). If, however, the solid or treated fibers were thermally scanned from –3 to 102°C, a significant endotherm occurred at 82°C on the initial heating cycle; after ten heating and cooling cycles an exotherm (on heating) was also noted at 27–32°C. Regardless of which thermal scan range was employed, the exotherm on cooling was generally unaffected and moderate in magnitude compared to other materials of this type. Recrystallization of the solid twice from ethanol and a thermal scan in the range –3–102°C produced similar results, although the number of cycles varied in which this unusual exotherm followed by an endotherm (on heating) was observed. Although the rayon hollow fibers treated with the amino compound still had a substantially high heat content after 50 thermal cycles on heating (48–49 cal g<sup>-1</sup> in the range 72–102°C), their cooling behavior was much poorer (only 22 cal g<sup>-1</sup> in the range 92–52°C) for the same number of thermal cycles. The appearance of an exotherm on heating, and the dependence of the thermal effectiveness of the treated fibers on the purity and temperature ranges make this particular substance unreliable for fiber treatment until further studies can ascertain what factors (such as the formation of metastable crystalline forms or various impurities) influence its thermal behavior.

In contrast to the above three compounds, 2,2-dimethyl-1,3-propanediol (DMP) exhibited reliable and reproducible thermal storage and release characteristics on prolonged thermal cycling when it was incorporated into hollow rayon and polypropylene fibers or used to treat cotton yarn. The solid and a 50% aqueous solution of this compound also gave reliable thermal scans, with heat contents of all samples varying by less than 5% with different replications of the same treatment or substance. These results are shown in Table 2 and Figs. 1–3 (for treated hollow rayon fibers, cotton yarn and hollow polypropylene fibers, respectively). All treated fibers exhibited thermal storage characteristics (endotherm on heating) at 32–62°C and thermal release characteristics (exotherm on cooling) at 37–7°C.

TABLE 2

Calorimetric data on untreated fibers and those treated with 50% aqueous solutions of 2,2-dimethyl-1,3-propanediol (DMP)

| Substance <sup>a</sup>                          | $Q$ (on heating) <sup>b</sup><br>(cal g <sup>-1</sup> ) | $Q$ (on cooling) <sup>c</sup><br>(cal g <sup>-1</sup> ) | No. heating and<br>cooling cycles |
|---|---|---|-----------------------------------|
| Untreated rayon                                 | 9.3   | 8.7   | 1                                 |
|   | 8.8   | 8.1   | 10                                |
| 50% aq. DMP in rayon <sup>d</sup>               | 30.5  | 27.2  | 1                                 |
|   | 30.2  | 27.0  | 10                                |
|   | 29.5  | 26.4  | 50                                |
| Untreated cotton                                | 9.6   | 8.8   | 1                                 |
|   | 9.1   | 8.5   | 10                                |
| Cotton treated with<br>50% aq. DMP <sup>d</sup> | 24.4  | 21.6  | 1                                 |
|   | 23.9  | 21.4  | 10                                |
|   | 23.4  | 21.9  | 50                                |
| Untreated polypropylene                         | 13.4  | 11.9  | 1                                 |
|   | 13.3  | 12.0  | 10                                |
| 50% aq. DMP in polypropylene <sup>d</sup>       | 25.6  | 23.3  | 1                                 |
|   | 26.2  | 23.2  | 10                                |
|   | 25.5  | 22.5  | 50                                |
| 50% aq. DMP                                     | 45.8  | 40.4  | 1                                 |
|   | 45.5  | 40.3  | 10                                |
| Solid DMP                                       | 47.1  | 41.4  | 1                                 |
|   | 46.1  | 40.9  | 10                                |

<sup>a</sup> All substances (fibers, solids, solutions) dried to constant weight and conditioned prior to thermal analysis. All  $Q$  values are an average of two replications that generally varied by 5% or less between thermal scans.

<sup>b</sup> Heat content computed from area between +32 and +62°C.

<sup>c</sup> Heat content computed from area between +37 and +7°C.

<sup>d</sup> After drying and conditioning, fiber/compound wt:wt ratio was 1:2.8 for rayon, 1:0.94 for cotton and 1:1 for polypropylene.

Although the heat contents ( $Q$  values) varied only by 23–31 cal g<sup>-1</sup> for all fiber types on heating and on cooling, rayon, followed by cotton, then polypropylene fibers treated with the DMP were the most thermally effective compared to the corresponding untreated fiber. As noted in Fig. 1 and Table 2, hollow rayon fibers containing the DMP had approximately 3.5 times the heat content of untreated hollow rayon fibers at the same temperature intervals (both heating and cooling), with no significant changes on prolonged thermal cycling (less than 1 cal g<sup>-1</sup> from 10–50 cycles). Similar results were observed with the treated cotton samples (Fig. 2 and Table 2).

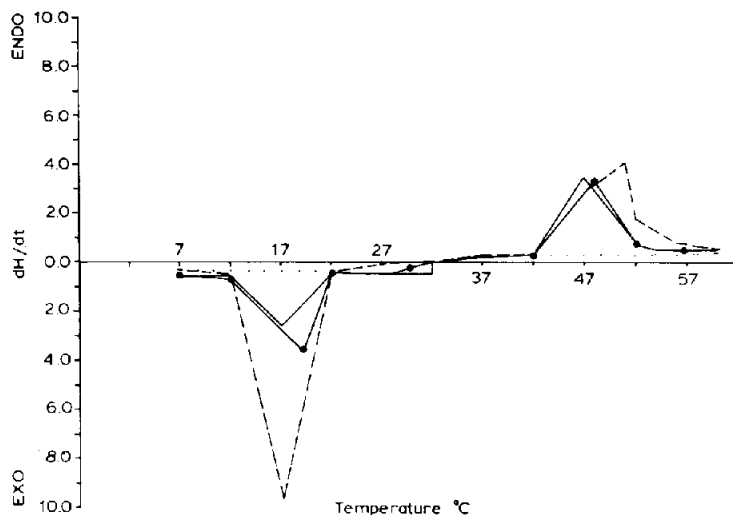


Fig. 1.  $dH/dt$  vs. temperature for hollow rayon fibers (a) unmodified, 1 heating and cooling cycle ( $\cdots$ ); (b) filled with DMP, ( $\text{—}$ ) 1 and ( $\bullet\text{—}\bullet$ ) 50 heating and cooling cycles; (c) neat DMP, 10 heating and cooling cycles ( $\text{- - - -}$ ).

However, the treated cotton had about 2.5 times the heat content of the untreated cotton. With polypropylene (Fig. 3 and Table 2), the same stability was noted after prolonged thermal cycling, but these treated fibers had about twice the heat content of untreated polypropylene fibers.

The incorporation of 50% aqueous solutions of 2-hydroxymethyl-2-

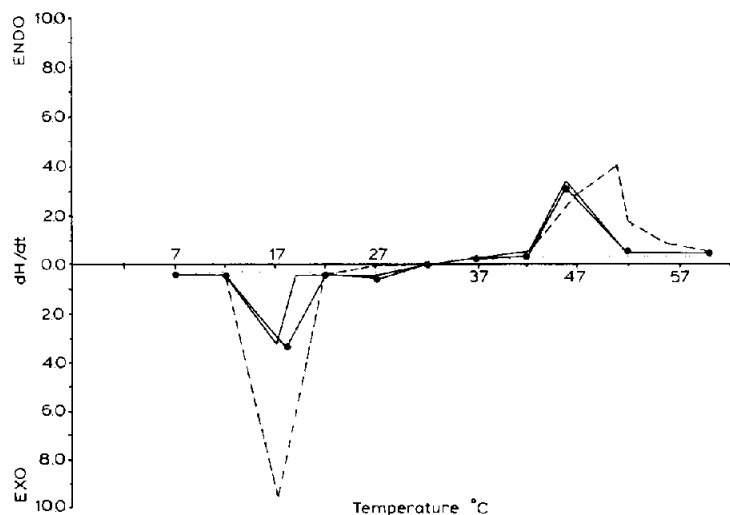


Fig. 2.  $dH/dt$  vs. temperature for cotton yarn (a) unmodified, 1 heating and cooling cycle ( $\cdots$ ); (b) treated with DMP, ( $\text{—}$ ) 1 and ( $\bullet\text{—}\bullet$ ) 50 heating and cooling cycles; (c) neat DMP, 10 heating and cooling cycles ( $\text{- - - -}$ ).

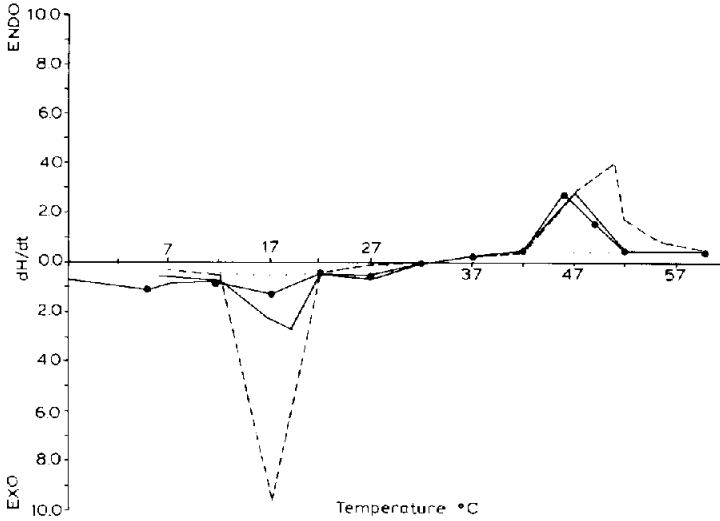


Fig. 3.  $dH/dt$  vs. temperature for hollow polypropylene fibers (a) unmodified, 1 heating and cooling cycle (.....); (b) filled with DMP, (—) 1 and (●—●) 50 heating and cooling cycles; (c) neat DMP, 10 heating and cooling cycles (-----).

methyl-1,3-propanediol (HMP) into hollow polypropylene fibers, and treatment of cotton fibers with this solution, produced modified fibers with good thermal stability after 50 heating and cooling cycles and with little variation in heat content from one sample to another (Table 3 and Figs. 4 and 5). The modified fibers exhibited their thermal storage characteristics in the range

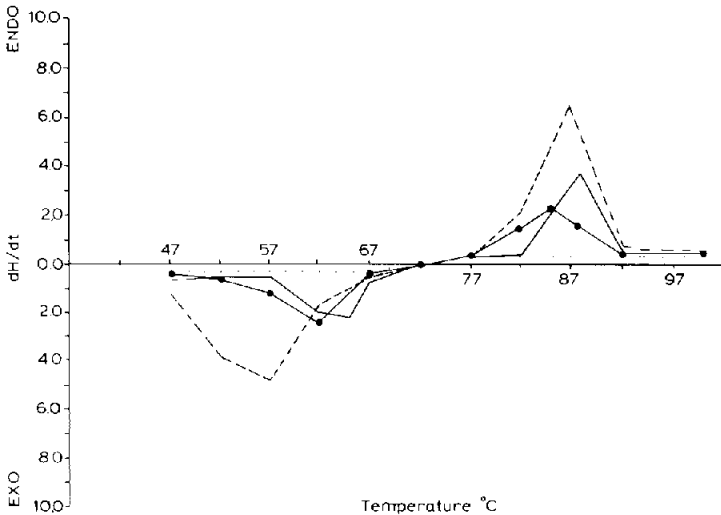


Fig. 4.  $dH/dt$  vs. temperature for cotton yarn (a) unmodified, 1 heating and cooling cycle (.....); (b) treated with HMP, (—) 1 and (●—●) 50 heating and cooling cycles; (c) neat HMP, 10 heating and cooling cycles (-----).



TABLE 3

Calorimetric data on untreated fibers and those treated with 50% aqueous solutions of 2-hydroxymethyl-2-methyl-1,3-propanediol (HMP)

| Substance <sup>a</sup>                          | $Q$ (on heating) <sup>b</sup><br>(cal g <sup>-1</sup> ) | $Q$ (on cooling) <sup>c</sup><br>(cal g <sup>-1</sup> ) | No. heating and<br>cooling cycles |
|---|---|---|-----------------------------------|
| Untreated rayon                                 | 12.5  | 8.8   | 1                                 |
|   | 9.7   | 8.8   | 10                                |
| 50% aq. HMP in rayon <sup>d</sup>               | 38.9  | 33.5  | 1                                 |
|   | 37.3  | 33.4  | 10                                |
|   | 36.8  | 33.0  | 50                                |
| Untreated cotton                                | 10.0  | 8.9   | 1                                 |
|   | 10.0  | 8.9   | 10                                |
| Cotton treated with<br>50% aq. HMP <sup>d</sup> | 27.5  | 23.4  | 1                                 |
|   | 26.2  | 24.0  | 10                                |
|   | 25.3  | 23.2  | 50                                |
| Untreated polypropylene                         | 15.7  | 13.9  | 1                                 |
|   | 15.3  | 13.9  | 10                                |
| 50% aq. HMP in polypropylene <sup>d</sup>       | 32.7  | 28.8  | 1                                 |
|   | 31.9  | 28.8  | 10                                |
|   | 31.7  | 28.4  | 50                                |
| 50% aq. HMP                                     | 39.2  | 37.8  | 1                                 |
|   | 47.2  | 37.9  | 10                                |
| Solid HMP                                       | 55.2  | 48.6  | 1                                 |
|   | 54.2  | 48.3  | 10                                |

<sup>a</sup> See footnote <sup>a</sup>, Table 2. All  $Q$  values are an average of two replications that varied by 5% or less between thermal scans (except 50% aqueous solution that had considerable variation and of the filled rayon fiber with four replications and great variability).

<sup>b</sup> Heat content computed from area between +72 and +102°C.

<sup>c</sup> Heat content computed from area between +77 and +47°C.

<sup>d</sup> After drying and conditioning, fiber/compound wt:wt ratio was 1:5.3 for rayon, 1:0.7 for cotton and 1:0.8 for polypropylene.

72–102°C (endotherm on heating) and thermal release characteristics in the range 77–47°C (exotherm on cooling). The modified polypropylene fibers had approximately twice the heat content of the untreated polypropylene fibers in these temperature intervals, while the treated cotton fibers had about 2.5 times the heat content of the untreated cotton at comparable intervals.

When the HMP was incorporated into hollow rayon fibers, marked variability was observed in the initial heat content of the treated fiber from one sample to another (Table 4). This variability was also observed in the

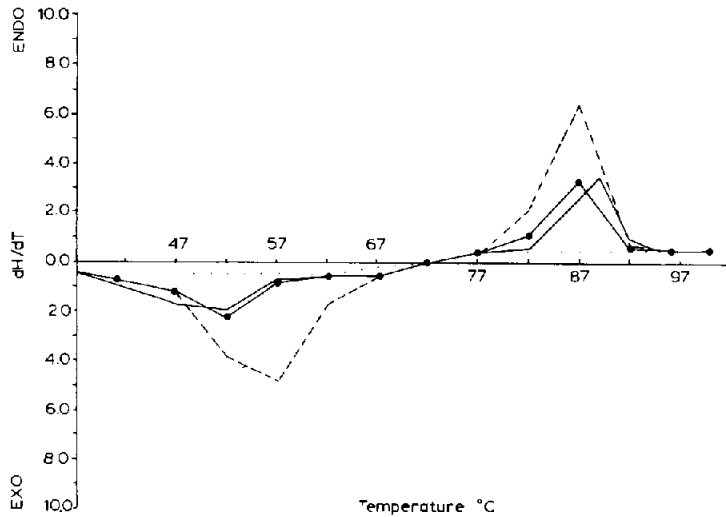


Fig. 5.  $dH/dt$  vs. temperature for hollow polypropylene fibers (a) unmodified, 1 heating and cooling cycle ( $\cdots\cdots$ ); (b) filled with HMP, (—) 1 and (●—●) 50 heating and cooling cycles; (c) neat HMP, 10 heating and cooling cycles (-----).

50% aqueous solution after one cycle, but appeared to moderate somewhat after ten heating and cooling cycles. In previous investigations [1,2], such variability was attributed to the uneven distribution of the substance in the hollow fiber and/or the pressure of excess water that inhibited the thermal transition, or made it erratic and unpredictable. In this instance, it appears that the hydrophilic nature of the rayon fiber makes it difficult to remove

TABLE 4

Variability of  $Q$  of hollow rayon fibers containing 2-hydroxymethyl-2-methyl-1,3-propanediol (HMP)

| Substance <sup>a</sup> | Sample | Replication No. | Fiber/PCM Ratio (wt:wt) | Heating (cal g <sup>-1</sup> ) |      |      | Cooling (cal g <sup>-1</sup> ) |      |      |
|------------------------|--------|-----------------|-------------------------|--------------------------------|------|------|--------------------------------|------|------|
|                        |        |                 |                         | Cycle 1                        | 10   | 50   | Cycle 1                        | 10   | 50   |
| 50% aq. soln.          | 1      | 1               | —                       | 28.2                           | 43.3 | —    | 37.8                           | 38.1 | —    |
|                        |        | 2               | —                       | 50.2                           | 51.0 | —    | 45.4                           | 37.7 | —    |
| 50% aq. HMP in rayon   | 1      | 1               | 1:5.3                   | 30.8                           | 28.4 | 28.0 | 25.3                           | 25.3 | 24.9 |
|                        |        | 2               | 1:5.3                   | 47.1                           | 46.2 | 45.7 | 41.7                           | 41.5 | 41.2 |
|                        | 2      | 1               | 1:5.3                   | 35.2                           | 32.9 | 32.3 | 26.7                           | 27.5 | 27.6 |
|                        |        | 2               | 1:5.3                   | 49.6                           | 48.0 | 47.6 | 28.6                           | 41.8 | 35.5 |
|                        | 3      | 1               | 1:2.6                   | 26.7                           | 24.7 | 24.1 | 22.8                           | 22.5 | 22.0 |
|                        |        | 2               | 1:2.6                   | 36.0                           | 34.0 | 33.2 | 30.8                           | 30.6 | 29.7 |

<sup>a</sup> All substances dried to constant weight and conditioned prior to thermal analysis.

enough water to obtain a reliable and reproducible solid–solid thermal transition on heating and cooling, since the aqueous solution itself had some variability. Thus, a tentative value of about 35–40 cal g<sup>-1</sup> of the treated rayon fiber is a reasonable assignment, but more data are needed to determine the conditions under which rayon fibers treated with the HMP will give reliable and reproducible heat contents.

## CONCLUSIONS

Five compounds known to have high enthalpy values due to solid–solid thermal transitions (transitions that occur prior to melting or crystallization) were used to modify the thermal storage and release characteristics of textile fibers, both hollow and conventional. Only two of the five substances, 2,2-dimethyl-1,3-propanediol and 2-hydroxymethyl-2-methyl-1,3-propanediol, imparted significantly higher and reproducible heat contents to the modified fibers after prolonged thermal cycling (50 heating and cooling cycles). In most instances at a given temperature interval, modified rayon had about 3.5–4.0 times the heat content of the untreated rayon, treated cotton had 2.5 times the heat content of untreated cotton, and modified polypropylene had twice the heat content of the corresponding untreated fiber. Modification of these fibers allow the production of temperature-adaptable materials useful in the range 5–100°C (heating and cooling), and offer additional choices for the application of these modified fibers in environments and situations where such thermal storage and release characteristics are desirable (e.g., insulation, protective clothing, protection of plants and animals from extreme climatic conditions).

## ACKNOWLEDGEMENT

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