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Thermal properties of insolubilized polyacetals derived from non-formaldehyde crosslinking agents ☆

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Abstract

Crosslinked polyols when applied to woven or non-woven fabrics impart high heats of fusion, lower thermal conductivity and several other physical properties. Previous publications have demonstrated that polyethylene glocols could be crosslinked onto a substrate with tetrafunctional cyclic urea compounds. A new formaldehyde free crosslinking system has been discovered using stoichiometric amounts of sulfonic acids and glyokal to form polyacetals with the same polyols. These polyacetals exhibit the same multifunctional properties and are also durable to laundering.

Keywords: Glyoxal; Heat of fusion; PEG; Polyacetal; Cross link

1. Introduction

Crosslinked polyethylene glycols bound to fabrics or fibrous substrates of diverse textile construction (woven, non-woven and/or knit) impart high heats of fusion, lower thermal conductivities and improved mechanical and other functional properties [1,2]. Previous publications have demonstrated that polyethylene glycols could be crosslinked onto fibrous substrates with tetrafunctional cyclic urea compounds, such as dimethyloldihydroxyethyleneurea (DMDHEU), via acid catalysis. However, a new formaldehyde-free crosslinking system has been discovered from the reaction of stoichiometric amounts of sulfonic acids, glyoxal and polyethylene glycols (M_w, 600–20m) to form polyacetals on fibrous materials [3]. These polyac-

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etals exhibit the same multifunctional properties on fabrics as the crosslinked polyols derived from DMDHEU or other formaldehyde-containing crosslinking agents. The thermal properties of the resultant fabrics derived from polyols of different number average molecular weight are described in this report.

2. Materials

Polyethylene glycols (PEG) with M_n of 600, 1000 and 1450 were of commercial grade and obtained from Dow Chemical [a]; PEG with M_n of 20m was practical grade and glyoxal was a 40% aqueous solution, both obtained from Fluka Co. [a] *p*-Toluenesulfonic acid monohydrate (ptsa) was obtained from J.T. Baker Co. [a] The fibrous substrate containing the polyacetal was woven 65/35 cotton/polyester fabric (100 g m^{-2}).

3. Experimental

The fabric was padded through aqueous solutions of PEG, glyoxal and sulfonic acid (varying wt/wt proportions described in the body of this paper) to a wet pickup of 90% of the original weight of the fabric (wof). They were cured in a forced draft oven between 120 and 140°C for 1–5 min to form an insoluble polyacetal coating on the fabric. All fabrics were afterwashed at 60°C in hot tap water with detergent, then tumble dried. The moisture contents of all the fabrics were determined on a Mettler PM 200 Drying Unit before and after each treatment in order to obtain the weight on a dry basis. The efficiency of the reaction was calculated by dividing the weight gain (dry basis) of the fabric by the amount (% solids) of reactants applied to the fabric during the padding operation. The quantity of reactants applied was calculated from the wet pickup by the fabrics. Ten milligrams of the treated fabrics were hermetically sealed in 0.5-cm-diameter aluminum pans and tested in a Mettler TA 4000 DSC System for melting (T_m) and crystallization (T_c) temperatures, and heats of fusion (H_f) and crystallization (H_c). Evaluations were made at heating and cooling rates of 10°C min^{-1}. The calorimeter was temperature-calibrated with cyclohexane and indium and enthalpy-calibrated with sapphire.

4. Results and discussion

The formation of simple acetals from carbonyl groups and alcohols is readily catalyzed by trace amounts of acids, particularly *p*-toluenesulfonic acid. However, the formation of novel, water-insoluble polyacetals from glyoxal and polyethylene glycols requires stoichiometric amounts of sulfonic acids (such as methanesulfonic

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[a] Names of companies or commercial products are given solely to provide specific information; their mention does not imply recommendation or endorsement by the U.S. Department of Agriculture over others not mentioned.

acid or *p*-toluenesulfonic acid). A proposed mechanism consistent with the formation of such polyacetals is the in situ formation of disulfonates of the polyols and subsequent nucleophilic displacement of sulfonate groups by the tetrahydrate of glyoxal. Another feasible mechanism is the initial formation of sulfonate hemiacetals or acetals of glyoxal and subsequent reaction of these intermediates with polyethylene glycols to form polyacetals [3]. A variety of concentrations of the polyol, glyoxal and sulfonic acids are suitable for producing bound polyacetal on the fabric and imparting desirable thermal properties. Most of the following data and discussion are derived from results with PEG-1450. In the first series of evaluations, concentrations of the polyol and glyoxal were held constant and the concentration of the sulfonic acid was varied. Thus, 65/35 cotton/polyester fabrics were padded with a solution containing 45% PEG 1450, 14% glyoxal and various amounts of ptsa to a wet pick up of 90% weight of fabric (wof), then dried and cured in one step at 135°C for 2 min as shown in Table 1.

As the concentration of ptsa increased in the pad bath; the add-on based on the weight of the fabric (wof) and the efficiency of the reaction increased. The heat of fusion leveled off with a concentration of about 10% ptsa. However, the heat of crystallization continued to increase with increasing concentration of the sulfonic acid. Melting and crystallization temperatures leveled off (30 and 17°C, respectively) at 10% ptsa concentrations. In the second series of evaluations (Table 2), the PEG-1450 concentration was held constant at 45%, ptsa concentration at 20% and the glyoxal concentration was varied from 4 to 14% with a dry/cure time of 2 min at 135°C. As the amount of glyoxal increased, both the weight gain of the fabrics

Table 1
45% PEG 1450 + 14% glyoxal vs. ptsa concentration [a]

ptsa/%	Weight gain/%	H_f	T_m	H_c	T_c	Eff./%
20	29.2	8.4	31.6	15.8	17.4	48
15	26.1	9.3	29.7	10.0	17.3	45
10	21.9	8.3	26.2	9.5	9.8	41
5	7.2	2.5	28.7	2.5	6.3	13

[a] H_f and H_c in J g^{-1}; T_m and T_c in °C; Eff. is % efficiency of the reaction (% yield).

Table 2
45% PEG 1450 + 20% ptsa vs. glyoxal concentration [a]

Glyoxal/%	Weight gain/%	H_f	T_m	H_c	T_c	Eff./%
14	35.1	11.9	19.8	11.3	2.7	70
10	34.0	11.3	17.8	11.4	1.3	68
8	28.4	11.2	17.8	11.1	3.3	59
4	7.0	4.1	21.4	4.1	5.2	16

[a] H_f and H_c in J g^{-1}; T_m and T_c in °C; Eff. is % efficiency of the reaction (% yield).

Table 3
45% PEG 1450 + 14% glyoxal + 20% ptsa vs. cure temperature [a]

Cure temp./°C	Weight gain/%	H_f	T_m	H_c	T_c	Eff./%
140	44.3	14.1	35.6	18.5	5.4	62.0
135	58.4	14.0	35.7	17.2	12.3	77.2
130	51.4	13.2	35.2	12.4	7.3	75.0
125	46.9	13.6	35.7	11.5	8.8	70.5

[a] H_f and H_c in J g^{-1}; T_m and T_c in °C; Eff. is % efficiency of the reaction (% yield).

Table 4
Effect of varying polyol molecular weight in pad bath [a,b]

PEG	Weight gain/%	H_f	T_m	H_c	T_c	Eff./%
600	45.3	3.2	4.2	–	–	79
1000	66.0	24.8	15.8	7.3	−4.8	99
1450	35.5	21.8	17.7	14.0	4.3	61
20m	18.2	16.9	47.2	13.7	32.4	42

[a] H_f and H_c in J g^{-1}; T_m and T_c in °C; Eff. is % efficiency of the reaction (% yield). [b] Cured at 135°C for 2 min.

and the reaction efficiency increased. However, the heats of fusion leveled off at about 8% glyoxal in the treatment bath.

In the third series, concentrations of all reactants were held constant (45% PEG 1450, 14% Glyoxal, 20% ptsa) but the cure temperature (at 2 min) was varied in five degree increments from 125 to 140°C. The optimum cure temperature was 135°C. At that temperature, the efficiency of the reaction increased to 77% and the heat of fusion was 14.0 J g^{-1} (Table 3).

When different molecular weights of PEG are allowed to react with glyoxal and a sulfonic acid, the resultant insoluble polyacetal has a different T_m and T_c depending on the PEG used. As noted in Table 4, the lower the molecular weight of the polyol, the lower the respective melting and crystallization temperatures.

The amount of weight gain, heat of fusion and efficiency of the reaction does not increase with the increase in molecular weight of the PEG but was optimum with PEG 1000. However, melting and crystallization temperatures did generally increase with increasing molecular weight as noted by the very high values for polyacetal derived from PEG-20m.

5. Conclusions

Polyacetals can be insolubilized on fibrous substrates by reaction of stoichiometric amounts of polyols and sulfonic acids in the presence of glyoxal, an inexpensive formaldehyde-free agent. Proposed mechanisms for polyacetal formation are in situ formation of polyol disulfonates followed by reaction with glyoxal tetrahydrate or formation of sulfonate hemiacetals or acetals of glyoxal followed by reaction with polyethylene glycols. The modified substrates have unique thermal storage and release properties. Insolubilization of polyacetals on fibers is dependent on the relative proportions of reactants (glyoxal, polyol and sulfonic acid), curing conditions, and on the molecular weight of the precursor polyethylene glycols.

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