APPLICATIONS OF FIBROUS SUBSTRATES CONTAINING INSOLUBILIZED PHASE Change POLYMERS

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ABSTRACT

Incorporation of polyethylene glycols into fibrous substrates produces several improved functional properties when they are insolubilized by crosslinking with a methylolamide resin or by polyacetal formation by their reaction with glyoxal. The range of molecular weights of polyols that may be insolubilized is broad (Mw of 600-20,000) as are the curing conditions (0.25-10 min at 80-200°C). Most representative fiber types and blends (natural and synthetic) and all types of fabric constructions (woven, nonwoven and knit) have been modified by incorporation of the bound polyls. The most novel property is the thermal adaptability of the modified substrates to many climatic conditions. This adaptability is due to the high latent heat of the crosslinked polyols that function as phase change materials, the hydrophilic nature of the crosslinked polymer and its enhanced thermal conductivity. Other enhanced properties imparted to fabrics include flex and flat abrasion, antimicrobial activity, reduced static charge, resistance to oily softs, resiliency, wind resistance and reduced lint loss. Applications commercialized in the U. S. and Japan include sportswear and skiwear. Several examples of ecletic sets of properties useful for specific end uses are given. In addition, other uses are biomedical, horticultural, aerospace, indoor insulation, automotive interiors and components and packaging material.

INTRODUCTION

Unique sets of properties imparted to fibrous substrates or materials containing crosslinked polyethylene glycols has been described in our publications on the insolubilization of polyols by crosslinking with DMDHEU or dimethyldihydroxyethyleneurea with acid catalysts [1,2,3,4] and more recently by their reaction with glyoxal to form polyacetals by tosylate intermediates [5]. Multifunctional property improvements vary to some extent with the nature, construction and porosity of the fibrous substrate, the curing conditions employed, the type of crosslinking agent employed, molecular weight of the polyol, and various additives in the solutions used to effect polymerization or insolubilization. Moreover, certain applications require an improved set of product attributes different from those required in other applications. Commercial products and applications in which there are current industrial interest are evaluated with regard to desirable property improvements imparted by this process. Structural aspects of the crosslinked or insolubilize polyols that are responsible for property enhancement are discussed. The interactive nature of processing and polymerization conditions with the nature of the fiber assembly and geometry are also explored. Future developments and improvements based on these concepts and processes are presented.

MULTIFUNCTIONAL PROPERTIES IMPARTED

Water-soluble polyols may be insolubilized onto fibrous materials by reacting with the tetrafunctional resin DMDHEU or with glyoxal by a sulfonate intermediate. Representative structural units of the modified polyols are shown in Figure 1. The existence of a fiber-polymer matrix results in many improved functional properties compared to the untreated substrate or fabric. Each of these attributes is due to one or more aspects of the modified polyols bound to the fiber and are noted in Table I. Thermal adaptability is the most novel of all the properties imparted to fibers and is probably due to three simultaneous phenomena. First, the insolubilized polyethylene glycols (as a network polymer in either reaction system) function as PCM's (phase change materials) with high latent heats of fusion and crystallization, thus buffering temperature changes in hot and cold weather. Secondly, these modified polymers are also very hydrophilic and provide enhanced thermal comfort.
due to their water sorption properties and the amount of energy stored during the evaporation and condensation of excess water. Thirdly, there is also evidence from our infrared thermography studies that the crosslinked polymer in the fiber matrix changes the thermal conductivity of the fiber surface. This latter effect has also been observed by scientists engaged in aerospace research [6]. The increased moisture content, sorption and capacity of the modified fabrics are also due to the hydrophilic nature of the crosslinked polymer. The marked increase in wear life (usually observed by increases in flex abrasion) and in sizable reduction of lint loss or particle release and fiber entanglement (pilling) on the surface is attributable to the elastomeric nature of the insoluble polyols. Such an elastomeric nature gives the coated fibers the ability to absorb mechanical stresses and deformations and prolongs failure that would more readily occur in the unmodified fibers. Enhancement of the soil release and antistatic behavior of fabrics containing the bound polyols was expected, since the incorporation of various types of polyethylene oxides to fabrics is well-documented and was observed as early as 1957. Durable press properties have been observed (conditioned wrinkle recovery angles as high as 325° in all cotton fabrics). The mechanism of resiliency probably differs conventional crosslinking of cellulosic fibers with resins in that this effect can be achieved at very low curing temperatures and involves grafting and homopolymerization of the polyol to provide such resiliency. Although the rationale for enhanced wind resistance was not explained, it may be due to removal of moisture from the air as it passes through the fabric; further study of this effect is in progress. The antimicrobial activity may be due one or two factors: (a) the slow release of an active antimicrobial agent (such as formaldehyde) under certain conditions and/or (b) the hydrophilic nature of the coated fiber that dessicates the microorganisms and thus deprives them of moisture needed to sustain growth. The mechanism of antimicrobial activity is also being studied in more detail.

TABLE I. Multifunctional Properties Imparted to Fibrous Substrates Containing Insolubilized Polyols

<table>
<thead>
<tr>
<th>Attributes of modified substrates</th>
<th>Cause(s) of attributes</th>
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<tbody>
<tr>
<td>Thermal adaptability and thermal comfort</td>
<td>Latent heat of polyethylene glycols</td>
</tr>
<tr>
<td>Water sorption, capacity and content</td>
<td>Moisture content and water transport properties</td>
</tr>
<tr>
<td>Resistance to wear, lint loss and pilling [7]</td>
<td>Thermal conductivity of polymeric coating</td>
</tr>
<tr>
<td>Reduction of static charge and improved soil release [8]</td>
<td>Hydrophilic nature of crosslinked polymer</td>
</tr>
<tr>
<td>Resiliency or anti-wrinkling [9]</td>
<td>Flexibility of polymeric gel or elastomer</td>
</tr>
<tr>
<td>Enhanced wind resistance [10]</td>
<td>Nonionic and hydrophilic nature of polymer</td>
</tr>
<tr>
<td></td>
<td>Possible removal of moisture from air by hydrophilic polymer</td>
</tr>
<tr>
<td></td>
<td>Hydrophilicity of polymer or slow release of antimicrobial agent</td>
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</tbody>
</table>
INFLUENCE OF FIBER TYPE AND FABRIC CONSTRUCTION

Due to the nature of the reactions used for insolubilizing the polyols (condensation reaction of hydroxyl end groups of the polymer with a tetrafunctional N-methylol cyclic urea and use of the dialdehyde glyoxal), certain types of functional groups on fibers will also react with these resins or functional groups. Grafting of the polymer onto cellulosic fibers as well as some reaction of resin with the cellulosic fibers occurs even at low curing temperatures (120°C or less). This has been verified by using scanning electron microscopy to detect the insolubility of modified cellulose fabrics in solvents such as cupriethylenediamine [12]. The reaction of cellulosic fibers with glyoxal under a variety of conditions is also well documented. When the curing temperature is higher, the cellulose reacts as readily as the polyol does with the crosslinking resin and glyoxal, and the resultant fabric has much poorer mechanical properties than fabrics cured under milder conditions. Wool, polyamide and polyurethane fibers contain some primary amino (-NH₂) groups on the surface of the fibers. Thus, there is also the possibility of grafting the polymer onto these fibers as well as reaction of the amino groups with the crosslinking resin and reaction of these groups with the dialdehyde glyoxal to form imine bonds. However, durability of the polymer coating or the polymer in the fiber matrix is not as good for wool as it is for polyamide and polyurethane substrates. This is due to the poor physical bonding of the polymer to the scales of the wool fiber.

Other types of fibers, such as polyester and acrylic, have fewer functional groups available (such as -OH) that make grafting and/or direct reaction with the resin or glyoxal less likely than with cellulosic, proteinaceous and fibers containing amino- groups. However, durability of the polymer on these types of fibers is good. Thus, bonding may occur in these types of fibers by some ionic interactions and possibly even hydrophobic type bonds between the polymer and fiber surfaces. Chemically inert fibers such as polypropylene and glass have some durability of the crosslinked polymer in the fiber matrix. This may be due to the presence of a few hydroxyl groups on the fiber surface and/or hydrophobic bonding between the polymer and the fiber surface. In addition to the nature of the reactive groups of the fiber, the nature of the fiber surface will also affect the adhesion, type of bonding and durability of the crosslinked polymer in the fiber/polymer matrix.

The physical nature of the fabric or fibrous assembly also has some influence on the amount of polymer incorporated into the matrix, its distribution in the matrix and some of the physical properties of the modified fabric or surface. These effects are primarily independent of fiber type and related to the porosity, air permeability and construction of the fabric. For example, the amount of polymer bound in a loosely woven cotton and loosely woven polypropylene would be about the same. Moreover, the distribution of the polymer in each type of fabric would be similar. In this instance, the open fabric structure would result in more polymer being bound between fibers and very little polymer on the fabric surface. For tightly woven fabrics, polymer attachment is more difficult, and more polymer tends to be present on the fabric surface than between fibers. More surface deposition of polymer also results in a stiffer fabric or material than in fabrics where surface deposition is minimal. For knits, these effects are the same as those observed in wovens. Since knit constructions tend to be more open and porous, modified knits usually have a good hand after treatment. Nonwovens are very porous and open structures (relative to most wovens and knits) and thus have the best surface aesthetics of all three major types of fabric constructions when they contain the crosslinked and bound polymers.

Since the modified fabrics contain a crosslinked polymer, their dimensional stability to laundering, that is, their ability to retain their original dimensions, is excellent. This is particularly useful for knit fabrics, since these types of constructions have poor dimensional stability in the unmodified state. In contrast, the ability of the modified fabrics to retain their dimensions in the wet state varies markedly with the fabric construction. Nonwoven fabrics containing the crosslinked polymer have very good wet dimensional stability. With most nonwovens, there is 0-2% shrinkage in the wet state. With wovens, this wet shrinkage can be between 7-15% in area. With certain types of knits, the wet shrinkage is dramatic (ranges of 25-40% in area), while with other knits, wet shrinkage may be 15% in one direction, but expand 15% in another direction, giving an overall area change of zero. Again, this phenomenon is independent of fiber type. All types of fabric constructions, even those with high wet shrinkage, return to their original dimensions on drying, and have outstanding dry dimensional stability. The wet shrinkage in certain constructions has been viewed by some as a negative
attribute in early stages of the development of textile products. However, some scientists and engineers are now exploring how this dramatic difference in fabric dimensions in the wet and dry state can be used to produce novel mechanical effects useful in irrigation and other applications as self-adaptive structures with a shape memory that responds to changes in humidity and water content.

EFFECT OF SOLUTION COMPOSITION

The amount of polyols bound to fibrous surfaces and the resultant properties imparted are not only dependent on the fiber type and fabric construction but are also dependent on the molecular weight of the polyethylene glycol (M, 600 to 20,000), the composition of resin and acid catalyst employed for the DMDHEU reaction. For the insolubilized polyacetal derived from the polyl, it is dependent on both the concentration of glyoxal and the concentration and type of sulfonic acid used to form sulfonate intermediates as well as the molecular weight of the polyl. Unreacted, lower molecular weight polyols, such as those with M, of 600 and 1,000, are fairly amorphous and have low melting (Tm) and crystallization (Tc) temperatures and moderate enthalpies of fusion (Hf) and crystallization (Hc). As the molecular weight increases, the polyols become more crystalline and have higher Hf and Hc, and correspondingly higher Tm and Tc. Enthalpies are optimum at M, of 6,000-10,000, and the melting and crystallization temperatures tend to level off at these molecular weights. The same trend in the thermal properties is observed when these polyols are either crosslinked with the tetrafunctional resin DMDHEU or react with glycols to form insoluble polyacetals. However, their latent heat values and melting and crystallization points are lower than those of the unmodified polymers. The magnitude of their heat absorption (Hf) and heat release (Hc) generally increases with increasing molecular weight. This magnitude is more dependent on the curing conditions than on the fiber type and fabric construction. As these polymers are crosslinked, the amorphous regions are the first to react, and thus higher molecular weight polyols have more crystalline material remaining to provide better latent heat properties than lower molecular weight, amorphous p polyols. Figure 2 shows thermal scans of modified fabrics containing insolubilized polyols derived from reaction with PEG-1,000/DMDHEU and from PEG-3,350/glyoxal/methanesulfonic acid. In each instance, the area under the curve is the latent heat of fusion absorbed with increasing temperature. The maximum heat absorption occurs at Tm. When such modified fabrics are cooled, comparable heat release occurs at lower temperatures with maximum heat release occurring at Tc.

Polyethylene glycols may be reacted with unalkylated DMDHEU resins (e.g., the structure shown in Figure 1 (a) in which all four reactive groups are hydroxyl or may be reacted with DMDHEU resins in which the two -N-CH2OH groups are partially alkylated and/or glycolated. Several catalysts are effective (such as p-toluene sulfonic acid, a mixed system with MgCl2.6H2O/citric acid or NaHSO4) for network polymerization of both types of resins at the same level of reactivity, but there are at least two major advantages to using the alkylated DMDHEU resin. The first advantage is that there are much lower levels of free formaldehyde in the solution containing the alkylated DMDHEU than those containing the unalkylated DMDHEU. Nevertheless, most fabrics treated with either resin system have negligible amounts of formaldehyde release (0-70 ppm) after washing and drying. The second major advantage is that the resultant fabrics are usually much softer when the alkylated DMDHEU is used as a crosslinking agent than when the unalkylated DMDHEU is used. This phenomenon is probably due to less crosslinking (slower reaction rate) of alkylated groups relative to unalkylated groups in the resin. However, there are some instances where certain types of fabrics are equally supple when either resin may be used to crosslink a polyl of the same molecular weight. A good example is the treatment of knit 90/10 cotton/Lycra (elastomeric polyurethane) fabrics with PEG-1,000/DMDHEU. Scanning electron microscopy indicates that there is little surface deposition of polymer for both resins used to treat this fabric. Each of the resultant fabrics was softer than the corresponding untreated control fabric.

For reaction of the polyols with glyoxal to form insolubilized polyol bound to the fibers, stoichiometric amounts of sulfonic acids are required. Since methanesulfonic acid is half the molecular weight of p-toluene sulfonic acid, it may be effectively used at concentrations as low as 6% to form sulfonate end groups of the polyols that subsequently react with glyoxal. This system has the advantage of being totally formaldehyde-free, but adhesion
anism of the polyacetal to the fibrous surface and prolonged durability to laundering appears not to be as good as that of polymer derived from reaction with DMDHEU resins. Studies are in progress to modify fiber surfaces and use other techniques to improve such durability.

EFFECT OF CURING CONDITIONS

The polyethylene glycols were initially insolubilized on various types of fibers by a conventional pad-dry-cure process [1]. This process usually consisted of immersing the fabrics in solutions containing approximately 60% solids (polyol + resin), removing excess solution through squeeze rolls, drying 5-7 minutes at 85°C, then curing for 2-3 minutes at 140-160°C. Although modified fabrics prepared by this process had acceptable thermal properties, cellulosic fabrics such as cotton had substantial strength losses that were similar to those usually obtained when cotton was treated with any durable press agent. Moreover, all types of treated fabrics were much stiffer than the corresponding untreated fabrics. It was later determined that using such conventional process conditions resulted in overcuring that reduced desirable thermal properties by reaction of the resin with crystalline regions of the polyols. Moreover, at high cure temperatures the hydroxyl groups in the cotton fabric react at the same rate with the DMDHEU as the hydroxyl end groups of the polyol react with DMDHEU. This leads to a rigid system in which the cellulosic fibers lose at least half their tensile strength.

When the mildest curing conditions (time/temperature) were employed in a single step to bind and insolubilize polyols to fibers, most functional improvements were superior to those obtained by the above two-step conventional dry-cure process. The most comprehensive change and improvement were in the heats of fusion and crystallization of the crosslinked polymer and corresponding higher temperatures of $T_m$ and $T_c$ of the bound polymer. In many instances, fabrics cured by a single step method had superior thermal properties to those cured by the conventional two-step method even when the former fabrics had less polymer incorporated than the latter fabrics. A representative example is curing of 55/45 pulp/polyester nonwoven fabric treated with PEG-1,000/DMDHEU. The fabric cured in a single step for 1.5 min. at 90°C had a weight gain of only 46%, but had a $T_m$ of 35°C, a $T_c$ of 10°C and corresponding $H_f$ of 22 J/g and $H_c$ of 21 J/g. The same fabric cured in a single step for 3 min. at 90°C had a weight gain of 87%. However, even under these conditions it was overcure, since it had a $T_m$ of 12°C, a $T_c$ of -10°C and corresponding $H_f$ of 16 J/g and $H_c$ of 15 J/g.

Cotton fabric treated with PEG-1,000/DMDHEU, then cured by a conventional two-step process, had breaking strength and flex abrasion losses of about 50% compared to the control. This treated fabric was also about three times stiffer than untreated fabric. In contrast, cotton fabric treated with an identical solution, then cured for 5 min/85°C lost only 20% of its breaking strength and had an 800% increase in its flex life compared to untreated cotton fabric. Moreover, the treated cotton fabric was about 40% softer than the untreated fabric. Thus, it is usually beneficial to use the minimum curing conditions to insolubilize the polymer inside the fiber matrix.

Insolubilization of the polyols via formation of polyacetals also is sensitive to optimum curing conditions for a particular formulation and molecular weight of polyol. Preliminary results [5] indicate that somewhat higher curing temperatures (usually above 125°C) are required to insolubilize the polyols by this route than are required to insolubilize them by reaction with DMDHEU resins in the presence of acid catalysts.

APPLICATIONS SUITABLE FOR MULTIPROPERTY IMPROVEMENTS

The diversity of improved properties imparted to fabrics and fibrous substrates make the modified materials suitable for many applications. Nevertheless, there are certain sets of properties that are more useful for each application. Table II illustrates a few examples of applications and the sets of functional properties appropriate for that application.
TABLE II. Relationship between Application and Functional Properties Imparted to Fibrous Substrates Containing Crosslinked Polyols

<table>
<thead>
<tr>
<th>Application</th>
<th>Group of Desirable Functional Properties</th>
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<tbody>
<tr>
<td>Sportswear and skiwear</td>
<td>Thermal adaptability, wind resistance, water sorption, softness and dimensional stability</td>
</tr>
<tr>
<td>Garments for biomedical and computer clean rooms</td>
<td>Thermal adaptability, resistance to static charge, antimicrobial activity, lint loss, water sorption</td>
</tr>
<tr>
<td>Shoe components and socks</td>
<td>Thermal adaptability, durability to wear, water sorption and antimicrobial activity</td>
</tr>
<tr>
<td>Automotive interiors</td>
<td>Thermal adaptability, resistance to static charge, oily soil release, wear resistance</td>
</tr>
<tr>
<td>Industrial and consumer wipes</td>
<td>Sorption of water and oil, liquid capacity, antimicrobial activity, wet dimensional stability</td>
</tr>
<tr>
<td>Work uniforms</td>
<td>Thermal adaptability, resistance to static charge, pilling and oily soil release, anti-wrinkling, durability to wear and prolonged laundering</td>
</tr>
<tr>
<td>Indoor insulation</td>
<td>Thermal adaptability, ability to remove humidity from air, dimensional stability, antimicrobial effects</td>
</tr>
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Pulp/polyester nonwoven fabrics used for surgical scrub suits afford a representative example of property improvements that are specific and relevant to this end use. When these fabrics are treated with PEG-1,000/DMDHEU and subsequently cured, thermal adaptability is imparted (heat absorption in the range of 25-35°C). The modified fabric absorbs at least twice the amount of water in the liquid and gaseous state, has a 100 fold decrease in static charge, 300% improvement in its flex life, and has significantly less particles released than from the corresponding untreated nonwoven fabric. Numerous other examples of eclectic sets of properties suitable for a specific application could be cited, and currently form the basis for many commercial products from current and prospective licensees. In addition to the applications or end uses in Table II, other possible end uses include blankets and bedding materials, geotextiles, horticultural and agricultural applications and defense/aerospace applications such as space suits and military uniforms and apparel. Some applications are to replace existing materials while other applications are more novel and may lead to the development of products that did not previously exist.
FUTURE TRENDS AND OPPORTUNITIES

Predicting future commercial developments from present scientific trends and interest in any area of science is quite difficult. However, there appear to be several fundamental concepts and practical opportunities in the application of polymers to fibers to improve many functional properties by a single process. It would be worthwhile to investigate further the structural aspects of polymers that cause them to function as phase change materials. A fundamental comparison of the few compounds, polymers and other compositions with high latent heats of fusion and crystallization should also be interesting and rewarding.

Another area of opportunity is to synthesize new polymers or modify existing polymers that impart multifunctional property improvement when they are bound to a fibrous substrate. Combinations of properties should lead to the development and commercialization of materials that could function in physically and chemically hazardous environments for both civilian and military uses. Opportunities exist for use of these new materials in the biomedical and health care areas as well as for pollution control and improvement of the environment.

A third area of opportunity is modification of fiber surfaces by high energy sources such as plasma, glow discharge and excimer lasers. This research has intensified in the past decade [11], and has led to improvement in the adhesion, wettability and dyeability of fibrous surfaces. In conjunction with the attachment of tailor-made polymers to fibrous surfaces, these studies should produce new types of fibrous composites, protective clothing and materials suitable for many new and existing applications.

A final area of opportunity is the emerging science and technology of intelligent materials and self-adaptive structures. Application of polymers to fibers that impart a thermal, mechanical or other type of memory should lead to modified materials that retain or change their shape or structure when exposed to external stimuli such as heat, light, electric current and/or moisture. These concepts, in conjunction with existing knowledge of modified fibrous materials, should lead to new products and technologies in electronic, health care, aerospace and consumer applications.

REFERENCES


Figure 1. Reaction of end groups of difunctional polyols with (a) tetrafunctional resin DMDHEU to form network or crosslinked structure and (b) dihydrate of glyoxal + sulfonic acid to form polyacetals.
Figure 2. Thermal scans (heating mode) of (a) 55/45 pulp/polyester nonwoven fabric treated with PEG-1000/DMDHEU, cured to wt. gain of 50% and (b) 100% cotton woven fabric treated with PEG-3350/glyoxal methanesulfonic acid to wt. gain of 32%.