

Physical Properties of Wool Fibers Modified with Isocyanate Compounds

Giuliano Freddi,¹ Riccardo Innocenti,² Takayuki Arai,³ Hideki Shiozaki,⁴ Masuhiro Tsukada³

¹Stazione Sperimentale per la Seta, via Giuseppe Colombo, 83, 20133 Milano, Italy

²CNR-Istituto per lo Studio delle Macromolecole, Sezione di Biella, Corso G. Pella, 16, 13900 Biella, Italy

³National Institute of Agrobiological Sciences, Oowashi 1-2, Tsukuba, Ibaraki 305-8634, Japan

⁴Institute of Silk Science, 3-25-1, Hyakunincho, Shinjuku-Ku, Tokyo, 169-0073, Japan

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ABSTRACT: Wool fibers were chemically modified with various kinds of isocyanates and diisocyanates. The reactivity of these modifying agents was examined as a function of the reaction solvent, temperature, time, and isocyanate chemistry. The use of dimethyl sulfoxide as the solvent, aliphatic mono and bifunctional isocyanates, such as dodecyl isocyanates and hexamethylene diisocyanate, and a temperature of 75°C resulted in higher weight gains. The moisture content of wool fibers tended to decrease with increasing the weight gain, the extent of which depended on the isocyanate used. Monofunctional isocyanates caused a sharp drop of tensile strength and an increase of elongation at break, while bifunctional isocyanates preserved the intrinsic tensile properties of wool. The FTIR spectra showed changes in the amide I, II, and III ranges, in the CO stretching range

at 1750–1700 cm^{-1} , and in the CH stretching and bending regions at 3000–2800 and 1500–1350 cm^{-1} , respectively, attributable to the incorporation of the modifying agent. DSC measurements highlighted remarkable changes in the thermal behavior of acylated wool fibers. The bimodal melting endotherm at 230–240°C shifted to lower temperature, and the relative intensity of the constituent peaks changed as a function of the weight gain. Foreign deposits adhering to the surface of chemically modified wool fibers were detected by SEM analysis. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1390–1396, 2003

Key words: fibers; proteins; crosslinking differential scanning calorimetry (DSC); FTIR

INTRODUCTION

The range of modifying agents applicable onto protein fibers is quite wide. We recently focused the attention on dibasic acid anhydrides and isocyanates.^{1–5} These are acylating agents whose target reactive sites are the nucleophiles present in several amino acid side chains, including amino, guanidyl, imidazole, hydroxyl, phenolic, carboxyl, and free sulphydryl groups.^{6,7} The yield of the reaction is strongly influenced by a number of experimental parameters, including properties of the solvent, chemistry of the acylating agent, accessibility and reactivity of nucleophiles into the fibers, reaction temperature, and time. It has been shown, for example, that the reaction of anhydrides and isocyanates proceeds much faster in dipolar aprotic solvents, such as dimethyl sulfoxide, thanks to the strong swelling power of the solvent.⁸ The studies on the reactivity of different acylating agents and nucleophiles in wool have been extensively reviewed by Maclaren and Milligan.⁶ The higher the temperature and the longer the time, the higher the

yield of the reaction, although fiber properties could be severely affected by the harsh treatment conditions or by an excessive loading of the modifying agent.

Chemical modification of wool has been the subject of extensive studies during the 1960s and 1970s.⁶ Afterward, this field of research has been abandoned, probably because most of the chemical treatments considered technologically exploitable did not result in any real industrial application. However, these studies have recently gained new interest, owing to the increasing requirements of the textile market for innovative articles not only for clothing but also for technical applications, which may help in extending the use and consumption of natural protein fibers. We recently developed a new technique for the preparation of protein fibers with increased absorption and binding capacity of metal cations (Cu^{2+} , Co^{2+} , Ag^+) by incorporating ethylenediaminetetraacetic dianhydride into the fibers.^{2–4} These technical fibers could be applied as sorbents for removing and recycling metals from water, or as textiles with enhanced barrier properties against micro-organisms. The acylation of silk and wool with anhydride compounds possessing a long hydrocarbon chain as the pendant group led to the production of effective water repellent fibers.¹ Interestingly, the optimum effect was reached at relatively low weight gain (3–6% w/w).

Correspondence to: G. Freddi.

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The use of isocyanates for the chemical modification of wool has been reported to induce interesting changes in fiber properties.^{6,9,10} Monofunctional isocyanates were effective in improving the chemical resistance of wool towards attack by acids, alkalis, and oxidizing agents, and in reducing the felting shrinkage. Bifunctional isocyanates had almost the same effect, but shrink resistance was much more enhanced. Improved settability could be conferred on wool by using isocyanate compounds with aromatic or long hydrocarbon side groups. The effect was due to the increase of hydrophobic interactions within the fiber matrix, which led to stabilization of set.

In a recent study we reported the chemical modification of silk with different isocyanates.³ The kinetics of acylation was studied as a function of different variables, such as solvent, temperature, time, and isocyanate chemistry. Then, various fiber properties were examined. The resistance to degradation by acid and alkali was enhanced, tensile strength remained almost unchanged, while elongation at break tended to decrease. Moreover, optical properties and thermal stability were not influenced by the reaction, suggesting that the fine structure of silk remained unchanged regardless of chemical modification. The present study deals with the reaction of different isocyanate compounds with wool fibers. Because the development of new modification techniques applicable to wool requires a detailed investigation of the reaction conditions and mechanism, mono- and bifunctional molecules were used and various experimental variables were investigated. Moreover, the chemical and physical properties of modified wool fibers are discussed to identify optimum reaction conditions for a substantial modification of the functional properties of wool.

EXPERIMENTAL

Materials

Reagent grade phenyl isocyanate (Catalog No.165-01743), hexamethylene diisocyanate (082-02822) and dodecyl isocyanate (586-47491) were purchased from Wako Pure Chemical Industries, Ltd. (Tokyo, Japan). Allyl isocyanate (24,327-2) and 1,3-phenylene diisocyanate (30,823-4) were purchased from Sigma-Aldrich K.K. (Japan). Wool fibers were treated with isocyanate or diisocyanate according to the procedure described by Kuwamura and Negishi.¹¹ The fibers were first immersed for 10 min in 60% dehydrated methanol at room temperature and then immersed successively for three times in methanol. The fibers were then placed in dehydrated dimethyl sulfoxide (DMSO). Immediately after removing the fibers from DMSO, they were treated with isocyanate or diisocyanate compounds in DMSO at 60–75°C for various

TABLE I
Weight Gain of Wool Fibers Modified with Phenyl Isocyanate (5% w/v) or Hexamethylene Diisocyanate (3% w/v) in DMSO for 3 h at Different Temperatures

Isocyanate compound	Weight gain (%)	
	60°C	75°C
Phenyl isocyanate	3.1	5.3
Hexamethylene diisocyanate	19.9	36.4

periods of time. The reaction system was connected to a reflux condenser and held in a thermostatic bath. The material-to-liquor ratio was 1 : 30. At the end of the reaction, the treated samples were first washed twice with DMSO at 55°C and then placed in acetone at 55°C for 2 h to remove any unreacted isocyanate or diisocyanate, and finally washed with water.

Measurements

The weight gain was calculated from the increase in weight of the original wool fibers before and after the reaction. Moisture regain was determined on dried samples kept at 20°C and 65% R.H. for 7 days and expressed as grams of moisture/100 g wool fiber. The tensile properties of untreated and modified wool fibers were measured with a Tensilon UTM-II (Orientec Co., Ltd., Saitama, Japan), using the standard technique at 20°C and 65% R.H. at a gauge length of 100 mm and strain rate of 40 mm/min. Results are the average of 20 measurements. FTIR spectroscopy analyses were performed with a Nicolet-150P spectrometer (Nicolet Instruments, Madison, WI), equipped with an ATR diamond cell (SPECAC). Heat-flow differential scanning calorimetry (DSC) measurements were performed with a Mettler Toledo DSC 821 System (Greifensee, Switzerland) at a heating rate of 10°C/min. The open aluminium cell was swept with N₂ gas during the analysis. Results are the average of duplicate analyses (reproducibility of ΔH measurements was $\pm 1\%$). Surface morphology was examined with a Stereoscan 440 (LEO Electronic Microscopy Ltd., Cambridge, UK) scanning electron microscope at 10 kV acceleration voltage, after gold coating.

RESULTS AND DISCUSSION

Chemical reactivity

The chemical modification of wool with isocyanates was performed in DMSO as the solvent medium. DMSO is a dipolar aprotic solvent frequently used for the reaction of isocyanates, as well as acid anhydrides, with protein fibers.^{1,3,6} It has the ability to induce a remarkable extent of fiber swelling (about 145% at 95°C for wool fiber),¹² and to promote penetration and diffusion of reactants into the fiber matrix. In fact, in a

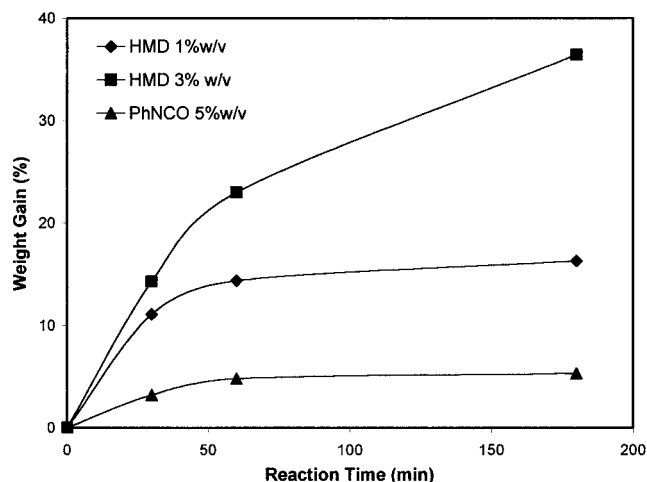


Figure 1 Weight gain vs. reaction time of wool fibers acylated with phenyl isocyanate and hexamethylene diisocyanate at 75°C, in DMSO.

preliminary test in which wool was acylated with phenyl isocyanate in DMSO and DMF, the former solvent gave a twofold yield of reaction (data not shown).

To study the effect of temperature on the reaction of wool with isocyanates, samples were incubated at 60 and 75°C in DMSO, the other experimental variables being constant. The results listed in Table I show that the higher the temperature, the higher the yield, expressed in terms of weight increase of the original sample. Two isocyanate molecules, one mono- and the other bifunctional, phenyl isocyanate (PhNCO) and hexamethylene diisocyanate (HMD), respectively, were used. The latter displayed the highest weight gain in the reaction with wool. This result probably reflects the difference in the physicochemical properties of the two reactants, that is, the presence of a bulkier aromatic group, as well as the different number of cyanate groups.

PhNCO and HMD were then used to study the kinetics of acylation at a fixed temperature of 75°C, over various reaction times. Figure 1 shows that the rate of reaction of the aromatic monofunctional isocyanate compound was very low, even though the

concentration in the reaction system was higher. On the other hand, HMD displayed a significantly higher reactivity. The curve at 1% w/v HMD showed a sharp initial rise, followed by a plateau that was probably due to the consumption of the reactant in the reaction system. In fact, with increasing the concentration of the diisocyanate to 3% w/v, the weight gain continued to increase with the reaction time, attaining about 36% after 3 h, one of the highest values reached in this study.

The difference in reactivity between PhNCO and HMD aroused the interest of testing different kinds of isocyanate compounds. Table II shows the results obtained with a variety of mono- and bifunctional isocyanates, listing both experimental and theoretical weight gain values. The latter were calculated on the basis of the assumption that isocyanates react completely with basic and hydroxyl amino acid residues of keratins,^{6,13} whose concentration accounts for about 0.28 mmol/g (carboxyl groups may react as well, but at a much lower rate).^{13,14} Aliphatic isocyanates displayed higher reactivity than aromatic ones, regardless of the presence of one or two cyanate groups. HMD reached about 70% of the theoretical saturation value. Considering that it is a bifunctional reagent, we should admit the possibility that a single molecule may bind two reactive sites.⁶ Self-condensation is also possible.¹⁰ Allyl and dodecyl isocyanate showed slightly lower levels of acylation, totalling 62 and 54%, respectively. These results suggest that the presence of a hydrocarbon chain promotes diffusion of the isocyanate compounds into the swollen wool fiber towards the reactive sites. On the other hand, the bulky phenyl group seems to play an adverse effect for both chemical and steric reasons, limiting the yield of reaction. This result is somewhat contrasting with that reported for silk, another protein fiber, which reacted with PhNCO at a higher extent, reaching the theoretical saturation value.³ However, wool is completely different from silk, as far as structure and morphology of the fiber is concerned. The presence of segregated cellular compartments might have hindered diffusion of the reagents with the bulkier aromatic side groups.

TABLE II
Theoretical and Experimental Weight Gain of Wool Fibers Modified with Different Isocyanates and Diisocyanates (5% w/v) in DMSO at 75°C for 3 h

Isocyanate Compound	MW (g/mol)	Weight Gain (%)	
		Theoretical	Experimental
Phenyl isocyanate	119.12	33.4	5.3
1,3-Phenylene diisocyanate	160.13	44.8	3.4
Allyl isocyanate	83.09	23.3	14.4
Dodecyl isocyanate	211.35	59.2	31.7
Hexamethylene diisocyanate ^a	168.20	47.1	33.1

^a Concentration: 3% w/v.

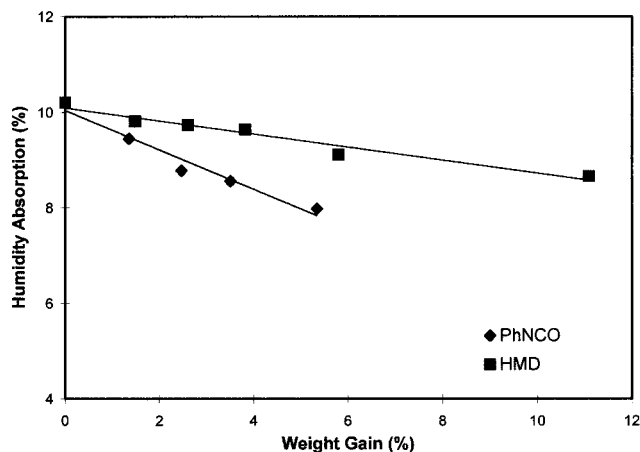


Figure 2 Moisture regain vs. weight gain of wool fibers acylated with phenyl isocyanate and hexamethylene diisocyanate.

Moisture content and tensile properties

The introduction of bulky hydrophobic groups into the fiber substrate is expected to lower the affinity for the water molecules by altering the balance of the electrostatic charges, replacing existing hydrogen bonds and introducing additional hydrophobic interactions.^{1,6,7} Accordingly, the results shown in Figure 2 indicate that the amount of water bound to wool fibers under standard conditions of temperature and humidity decreased with increasing weight gain. The effect was stronger with PhNCO than with HMD, but in both cases the trend clearly indicated a gradual decrease of the capacity of wool to absorb and bind moisture.

Tensile properties of wool fibers modified with PhNCO and HMD were measured in the dry state, and the results were plotted as a function of the weight gain. Breaking load of wool modified with HMD (Fig. 3) showed a certain extent of variability at low weight gain, and then attained a plateau, while that of wool modified with PhNCO dropped sharply. A variable degree of fiber yellowing was noticed after reaction of wool with PhNCO. Similar results were obtained with silk as well, suggesting that this reactant is able to induce irreversible weakening of the fiber structure, with negative effects on tensile properties.³

The behavior of elongation at break is shown in Figure 4. The reaction of wool fibers with PhNCO resulted in higher values of elongation at break. Similar results were obtained with another monofunctional isocyanate compound, dodecyl isocyanate (data not shown). On the other hand, by reaction with HMD the values of elongation at break increased slightly at very low weight gain, and then attained a stable value close to that of untreated wool. As a bifunctional reagent, HMD is able to crosslink adjacent reactive

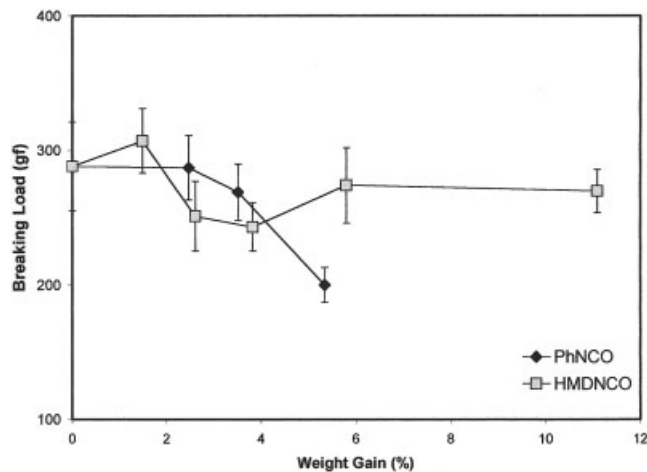


Figure 3 Breaking load vs. weight gain of wool fibers acylated with phenyl isocyanate and hexamethylene diisocyanate.

sites in the wool fiber matrix.^{3,6,10} Hence, the results suggest that with increasing weight gain the number of crosslinks increased and the wool fiber became less extensible than that reacted with monofunctional isocyanates.⁶

FTIR spectroscopy

The reaction of wool with various modifying agents entails the incorporation of new chemical groups into the fiber matrix. These can be detected by infrared spectroscopy as new absorption bands, or may overlap existing bands typical of the fibrous substrate, causing more or less drastic changes in their intensity.

Figure 5 shows the FTIR spectra of wool fibers acylated with HMD in the 2000–800 cm^{-1} range. As the weight gain increased, the IR pattern displayed significant changes: a new absorption band appeared as a

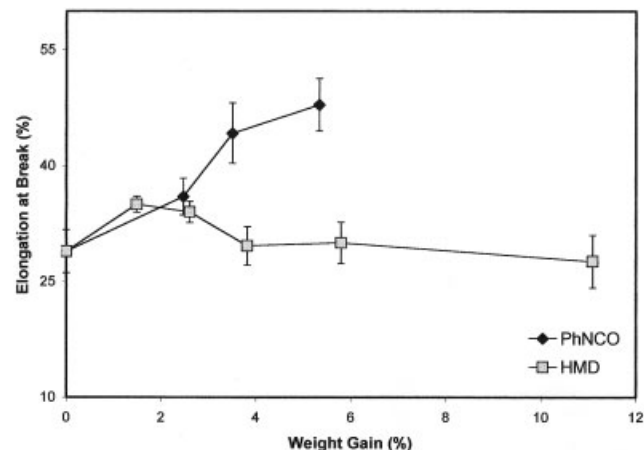


Figure 4 Elongation at break vs. weight gain of wool fibers acylated with phenyl isocyanate and hexamethylene diisocyanate.

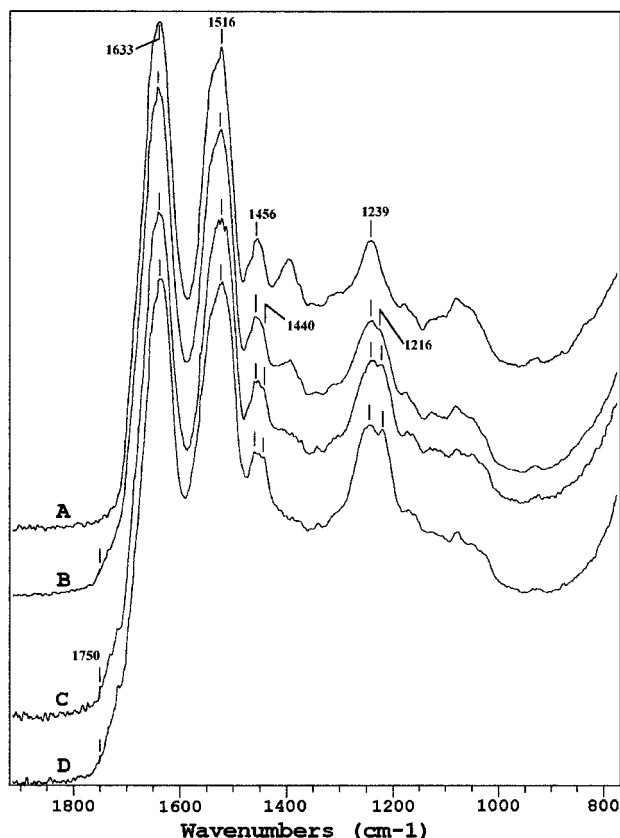


Figure 5 FTIR spectra of wool fibers untreated (a) and acylated with hexamethylene diisocyanate. Weight gain: (b) 5.8%; (c) 11%; (d) 36%.

shoulder of the intense amide I band at higher wavenumbers ($>1700\text{ cm}^{-1}$); amide II at 1516 cm^{-1} gradually increased in intensity and tended to become broader; the band at 1456 cm^{-1} became more intense, and a shoulder appeared at lower wavenumbers (ca. 1440 cm^{-1}); in the amide III range a new band emerged at 1216 cm^{-1} . Moreover, the intensity of two absorption bands at 2931 cm^{-1} and 2856 cm^{-1} (not shown) increased significantly with increasing the weight gain.

The reaction of an isocyanate compound with the hydroxyl or amine reactive sites of wool can be outlined as follows:



where "W" is the wool keratin backbone, and "R" is the side chain group of the isocyanate. As a consequence, spectral changes are expected to occur in various vibrational modes, such as: CN stretching and NH bending (amide II and III ranges), and CO stretching (amide I and the $1750\text{--}1700\text{ cm}^{-1}$ range). Moreover, the aliphatic nature of the isocyanate "R" group

may influence the CH stretching and bending regions at $3000\text{--}2800\text{ cm}^{-1}$ and $1500\text{--}1350\text{ cm}^{-1}$, respectively. These hypotheses are consistent with the experimental results. In particular, the disubstituted urea-like group (2) with two NH bonds can be considered responsible for the main changes in the amide II range.¹⁵ Because NH bending is a significant component not only of amide II, but also of a number of modes in the $1400\text{--}1200\text{ cm}^{-1}$ range, including amide III, it may be responsible for other minor spectral changes detected in this highly mixed vibrational region. The new bands at 1216 and $1750\text{--}1700\text{ cm}^{-1}$ may arise from the CN and CO stretching contribution of the newly formed group (1), respectively.¹⁵ Obviously, the changes in the CH stretching and bending regions are attributed to the contribution of the hydrocarbon chain of HMD. All these accumulated spectroscopic results give evidence of the effective reaction of isocyanates with wool.

Differential scanning calorimetry

The thermal properties of wool acylated with isocyanates were studied by differential scanning calorimetry. Figure 6 shows the DSC thermograms of different wool samples, including untreated, DMSO-treated, and HMD-acylated fibers with increasing weight gain. Untreated wool fibers showed a broad endotherm starting at above 200°C , attributed to melting and degradation of the different morphological components forming the highly complex hierarchical structure of wool.¹⁶ It was characterized by the presence of the typical bimodal melting endotherm with two peaks at 236 and 239°C . The treatment of wool with DMSO alone slightly changed the relative intensity of the peaks in the doublet, while the peak temperature remained unchanged. Wool fibers acylated with HMD

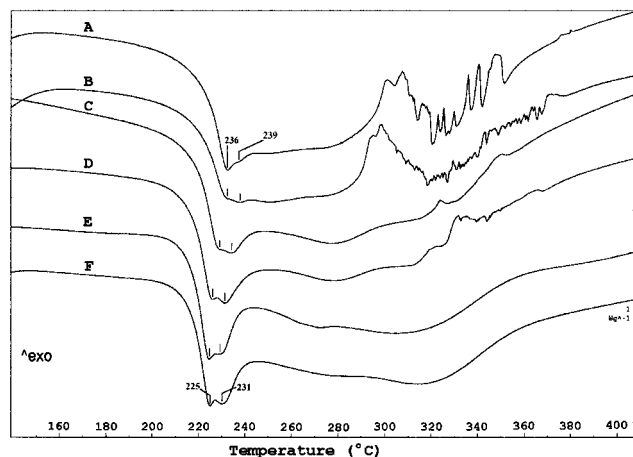


Figure 6 DSC curves of wool fibers untreated (a), treated with DMSO at 75°C for 30 min (b), and acylated with hexamethylene diisocyanate. Weight gain: (c) 2.8%; (d) 5.8%; (e) 11%; (f) 36%.

TABLE III
Enthalpy (ΔH) of the Bimodal Melting Endotherm
(range: 200–240°C) of Wool Fibers Untreated, Treated
with DMSO, and Acylated with HMD with Different
Weight Gains

Samples	ΔH (J/g)
Untreated	15.61
DMSO-treated	11.30
HMD-2.6%	23.64
HMD-5.8%	30.35
HMD-11.1%	35.30
HMD-36.0%	34.72

showed a lower temperature shift of the bimodal melting endotherm, whose peak temperatures stabilized at 225 and 231°C at above 6% weight gain. With increasing weight gain, the intensity of the low-temperature peak increased, the enthalpy (ΔH) of the melting process showed a tendency to increase (Table III), and the melting/decomposition endotherm became broader in the high temperature range (>250°C).

The complex melting/decomposition endotherm of wool, which spans over a wide temperature range, is considered the sum of various thermal transitions.^{16–20} Those occurring at high temperature (>250°C) can be ascribed to overlapping thermal degradation phenomena of keratins. The bimodal melting endotherm falling in the range of 230–240°C has been extensively investigated. The *helix/matrix* and *ortho/para* hypotheses were proposed to explain its origin (this nomenclature was recently used by Wortmann and Deutz¹⁷). In the *helix/matrix* hypothesis the low-temperature peak is ascribed to melting of the α -helices in the intermediate filaments, and the high-temperature peak to degradation of the matrix in which filaments are embedded.^{18,19} On the other hand, the *ortho/para* hypothesis assigns the low- and high-temperature peaks to differential melting of the α -helical material in the *ortho*- and *para*-cortical cells, respectively.^{17,20} The latter theory was recently supported by the demonstration that isolated *ortho*- and *para*-cortical cells show distinct melting point values.¹⁷ The two types of cells are also known to exhibit different accessibility and reactivity towards solvents and chemicals, leading to the well-known phenomena of bilateral staining²¹ and differential supercontraction.¹⁷

The treatment with the solvent alone and the reaction with HMD strongly influenced the thermal behavior of wool. Wool is a heterogeneous material characterized by a highly complex hierarchical structure of the fiber, which makes it difficult to relate the overall observed thermal changes to an individual keratin fraction. However, on the basis of the above reported assignment of the major thermal transitions, it can be suggested that the lower temperature shift of the peak doublet resulting from acylation was probably caused

by disordering and weakening of the existing intermolecular interactions within the intermediate filaments of *ortho*- and *para*-cortical cells, as well as between the filaments and the matrix, which enhanced the thermal motion of the system. Other thermal changes, such as the apparent increase of the enthalpy of the melting process, as well as the high-temperature broadening of the melting/decomposition endotherm could be ascribed to the ability of the bifunctional isocyanate compound to form crosslinks, which resulted in a partial strengthening and stabilization of the system.

Surface morphology

The surface morphology of wool fibers was examined by scanning electron microscopy to highlight eventual

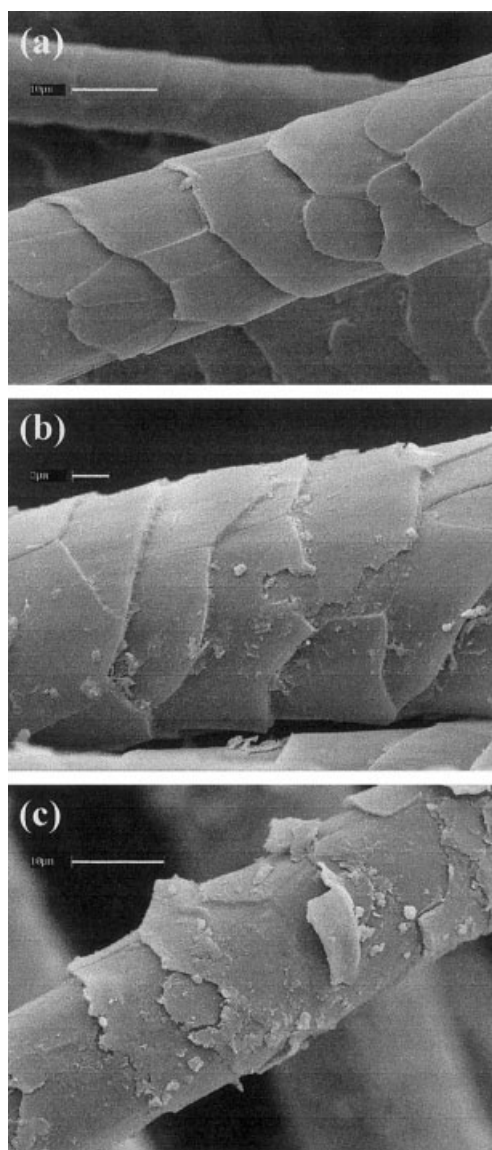


Figure 7 SEM photographs of wool fibers untreated (a), and acylated with hexamethylene diisocyanate (5.8% w.g.) (b), and phenyl isocyanate (5.3% w.g.).

changes induced by reaction with isocyanates (Fig. 7). Foreign deposits, completely absent in untreated wool, appeared onto the surface of acylated fibers [Fig.7(b)], the amount of which tended to increase with increasing weight gain. The deposit preferentially accumulated at the scale edge. The latter showed evidence of initial degradation, as indicated by the loss of small scale fragments in their distal part. More extensive signs of degradation appeared onto the surface of wool fibers acylated with PhNCO, as indicated by the separation of larger parts of the scales from the fiber axis [Fig. 7(c)].

CONCLUSIONS

Different isocyanates are bound by wool fibers at a different rate and extent, depending on the reaction conditions and chemical structure of the acylating agent. Aliphatic mono- and bifunctional isocyanates displayed higher reactivity than aromatic ones. The latter had some drawbacks, because they induced a marked degradation of wool attributable to oxidative phenomena occurring during the reaction. Evidence of the effective incorporation of the acylating agent into the fiber matrix was obtained by means of FTIR measurements, which showed changes of selected absorption bands attributable to functional groups of the reactant.

The effect of the reaction on the fine structural properties of wool fibers was elucidated by DSC measurements. The thermal response indicated that different morphological compartments of the fibers were involved in the reaction (intermediate filaments and matrix in *ortho*- and *para*-cortical cells) and that

crosslinking played a role in determining the thermal behavior of acylated wool fibers.

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