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Infrared characterization of biocidal nylon

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Abstract

Attenuated total reflectance Fourier transform infrared spectrometry has been employed to assess the degree of chlorination of hydantoin moieties which are covalently linked to the surface of the polyamide, Nylon 66. The *N*-chlorinated hydantoin functional groups are active in producing biocidal activity against pathogenic microorganisms upon direct contact with the surface molecules of the fabric. Chlorination of the treated Nylon 66 causes a blue shift of the hydantoin amide bands which can be conveniently monitored as a quality control procedure in the production of the biocidal fabric. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

During the past decade, work in these laboratories has focused on the synthesis, testing, and development of effective new *N*-halamine biocidal polymers. These polymers could be utilized in a variety of applications, such as in water treatment, coatings on medical devices, and elastomers [1–3]. Recently, the technology has been extended elsewhere to the use of the biocidal *N*-halamines in derivatizing cellulose for rendering fibers and fabric materials odor-free and antimicrobial for potential medical applications [4–6]. More recently, *N*-halamine moieties have been attached through covalent bonding to the amide nitrogens of Nylon 66; this was accomplished by chemical treatment of the polymer molecules on the surface of the nylon fibers, and the material was shown to have regenerable antimicrobial properties [7].

Polymers derivatized with *N*-halamine moieties are generally insoluble in water and organic solvents and thus can be difficult to characterize. We have found that an effective means of determining when the polymers have achieved optimum biocidal activity, i.e. when they are properly chlorinated or brominated, is to observe the shift of the carbonyl stretching bands to higher frequency in the infrared spectrum induced by the halogenation reaction process. For example, poly-5-methyl-5-(4′-vinylphenyl)hydantoin, which is the precursor to a very effective biocidal water treatment polymer, exhibits distinctive carbonyl stretching bands in its infrared spectrum at about 1724 and 1777 cm^{-1}. Upon chlorination of an alkaline, aqueous suspension of this polymer to produce the biocidal polymer poly-1,3-dichloro-5-methyl-5-(4′-vinylphenyl)hydantoin, the two bands shift to about 1750 and 1805 cm^{-1}, respectively. The observation of the frequency shift is a rapid, convenient, and inexpensive means of quality control in assaying this biocidal polymer. Confirmation can be obtained by elemental analyses, but this is considerably more time consuming and expensive for multiple analyses as compared to infrared spectroscopy (especially if infrared equipment is already in hand). The purpose of this Communication is to demonstrate that biocidal nylon containing *N*-chloramine moieties, or any fibers for that matter containing such moieties, can be characterized by FTIR. Of course, transmission FTIR for a KBr pellet of polymer, as employed above for the poly-styrenehydantoin, is not applicable for nylon fibers. Thus, attenuated total reflectance (ATR) FTIR was used in this study.

The use of infrared techniques to characterize the surfaces of polymers and polymer films is not new and has become increasingly popular in recent years (for a few examples, see Refs. [8–20]). However, the use described herein, i.e. to predict when a material such as derivatized nylon becomes fully halogenated, and hence optimally biocidal, is to our knowledge, novel and should be of interest to those working in the biocidal polymer field.

2. Experimental

2.1. Treatment process

The chemical treatment process for converting nylon into

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a biocidal material has been described in detail [7]. Briefly, Nylon 66 fabric material was soaked in10% formaldehyde solution under basic conditions (0.5N NaOH) at 80°C for 2 h. The fabric was then washed with distilled water until a neutral pH was obtained. The fabric now containing a hydroxymethyl functional group at the amide nitrogen of Nylon 66 was placed in a treatment bath containing 10 g of 3-hydroxymethyl-5,5-dimethylhydantoin (provided by Lonza, Fairlawn, NJ), 1.2 g of $MgCl_2$, 0.4 g Triton X-100 wetting agent, and 200 ml of distilled water held at pH 2.5 and 80°C for 30 min. The treated Nylon 66 now containing the hydantoin functional group on the surface of the material was then cured in an oven at 130°C for 15 min. After curing, it was washed with detergent at 50°C for 30 min. To instill biocidal activity, the treated material was soaked in dilute bleach (0.75% active chlorine) at ambient temperature for 3 h and then dried in air.

2.2. Titration analyses of chlorine on the fabric

Strips of the fabric were dipped in 100 ml of distilled water in a beaker, and about 1 mg of potassium iodide was then added. The mixture was held for 5 h under nitrogen atmosphere to ensure complete reaction of potassium iodide with the combined chlorine moiety and minimal air oxidation. Then the solution containing the fabric was analyzed by the standard iodometric titration method. The equation used to calculate the concentration of chlorine (in mg) on the surface of one side of fabric is

$$W_{\mathrm{Cl}} = \frac{V \times N \times 35.45}{S \times 4}$$

where W_{Cl} is the milligrams of chlorine on one side of 6.45 cm^2 of fabric, V the volume of titrant (ml), N the normality of sodium thiosulfate titrant, and S the sample surface area (cm^2).

Each analysis was run in triplicate, and the three titration results were always within 5% precision.

2.3. ATR-FTIR

Spectra were recorded with a Mattson RS-1 FTIR spectrometer with a Harrick twin parallel mirror reflection variable angle ATR accessory. Germanium ATR crystals (single pass parallelepiped, 50 mm × 10 mm × 2 mm) were used as internal reflection elements. The nylon fabric was held against one side of the crystal. The background spectra were recorded with the Ge crystal contacting nitrogen gas in the absence of fabric. All of the IR data were collected at a spectral resolution of 4 cm^{-1} with 500 coadded sample scans using a high D^* MCT-A detector with N_2 purge of the sample compartment.

3. Results and discussion

The ATR-FTIR spectra of samples of the nylon material after the various treatment steps are shown in Figs. 1 and 2. Spectrum a in each of the figures represents untreated Nylon 66. The prominent infrared bands of nylon and other polyamides have been well characterized [21–25]. The band at 3301 cm^{-1} in Fig. 1a may be assigned to the N–H stretching vibrational mode, ν_{NH}, while those at 1635 and 1539 cm^{-1} in Fig. 2a correspond to the amide I and amide II bands, respectively. The two amide bands result from electronic coupling of the $\nu_{\mathrm{C=O}}$ and $\nu_{\mathrm{C\text{-}N}}$ modes and the mechanical coupling of the $\nu_{\mathrm{C\text{-}N}}$ and the in-plane δ_{NH} modes [24].

The spectra shown in Figs. 1b and 2b were recorded after the Nylon 66 was reacted with formaldehyde in basic solution. The ν_{NH} band near 3300 cm^{-1} has vanished indicating that the proton on N has been replaced by CH_2OH. The OH stretching mode band above 3500 cm^{-1} was not resolved due to overlap of that band with the analogous one for adsorbed water. In the low frequency region, the amide I band at 1635 cm^{-1} is now significantly broadened due to overlap with bands due to the OH bending modes of CH_2OH and adsorbed water. Low intensity structure in the

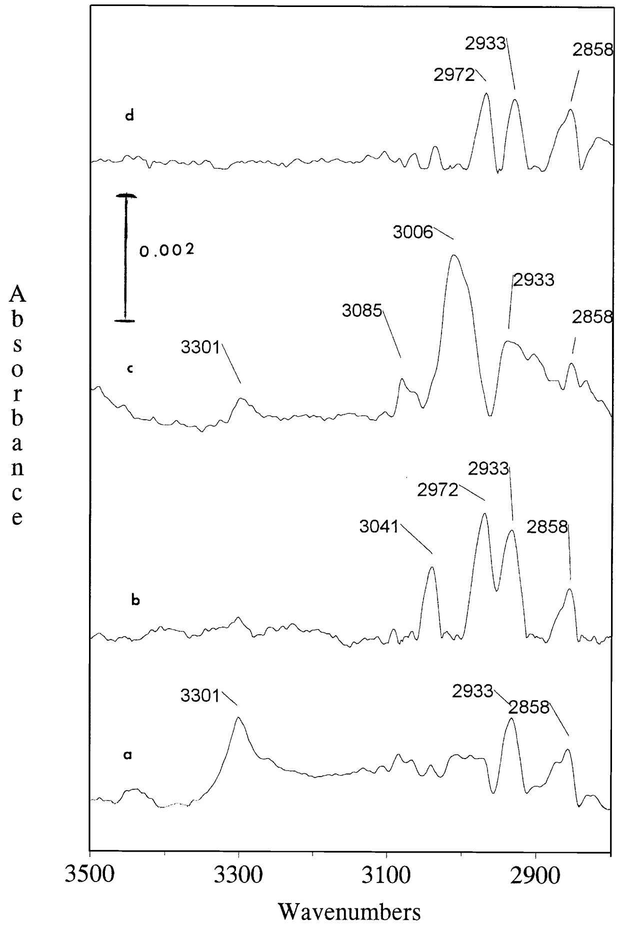

Fig. 1. The high frequency region of the ATR-FTIR spectra for Nylon 66 fabric: (a) untreated; (b) after treatment with formaldehyde in basic solution; (c) after treatment of the Nylon 66 hydroxymethyl derivative with 3-hydroxymethyl-5,5-dimethylhydantoin; (d) after chlorination of the hydantoin derivative of Nylon 66.

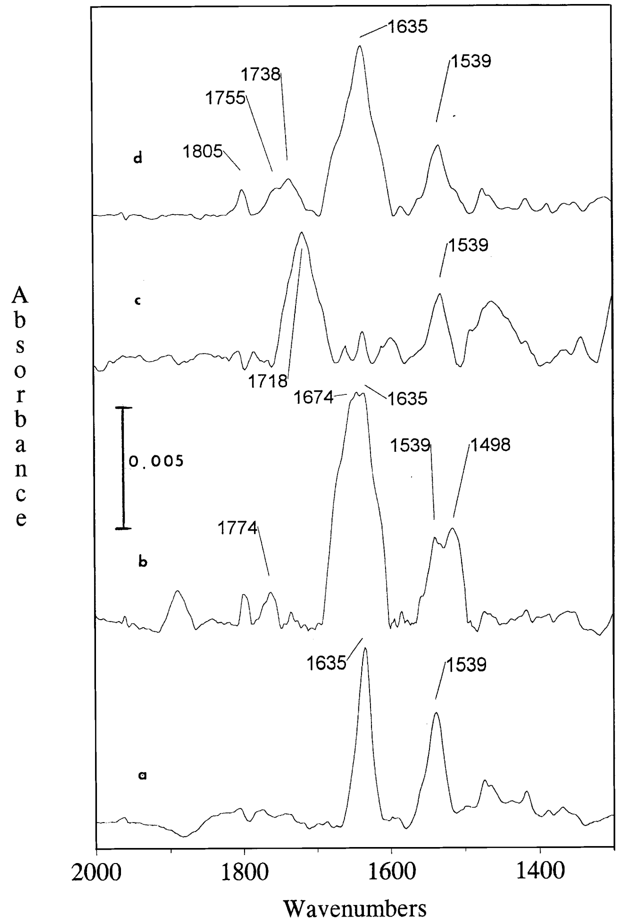

Fig. 2. The low frequency region of the ATR-FTIR spectra for Nylon 66 fabric: (a) untreated; (b) after treatment with formaldehyde in basic solution; (c) after treatment of the Nylon 66 hydroxymethyl derivative with 3-hydroxymethyl-5,5-dimethylhydantoin; (d) after chlorination of the hydantoin derivative of Nylon 66.

1700 cm^{-1} region is probably due to a small amount of formaldehyde impurity; the bands at 1498 and near 1900 cm^{-1} remain unassigned.

Following the coupling reaction between the hydroxymethyl derivative of Nylon 66 and the hydroxymethylhydantoin, the spectra shown in Figs. 1c and 2c were recorded. The small band at 3301 cm^{-1} corresponds to ν_{NH} for the amide N on the hydantoin ring, indicating a successful coupling reaction. The broad, intense band centered at 1718 cm^{-1} corresponds to the complex vibrational coupling of the modes for the two inequivalent carbonyl stretches and the amide and imide C–N modes of the hydantoin moiety. It is notable that the nylon bands are less intense in this spectrum. This is probably just an artifact due to the positioning of a new sample in the ATR cell; ATR spectroscopy samples approximately 1 μm outside the crystal, which makes absolute intensity measurements tenuous. All four spectra are drawn to the same absorbance scale.

The spectra in Figs. 1d and 2d were obtained following chlorination of the hydantoin moiety attached to the Nylon 66. The band near 3300 cm^{-1} has again disappeared, indicating successful chlorination of the hydantoin ring. The low-intensity, unresolved doublet with components at 1755 and 1738 cm^{-1} can be assigned to the coupled C=O/C–N modes which shift to higher frequency upon chlorination. The blue shift of the hydantoin band caused by chlorination was thus about 28 cm^{-1} (comparing the center of the unresolved doublet in 2d with that in 2c). This is the same (4 cm^{-1} resolution) as the corresponding shift (27 cm^{-1}) observed for the polystyrenehydantoin doublet mentioned in Section 1, lending support to the treated nylon band assignments. The origin of the weak band at 1805 cm^{-1} is not clear, but since it is present in spectrum 2b also, it cannot be, in this case, assigned to the hydantoin moiety.

The spectra in Figs. 1d and 2d were recorded for a freshly chlorinated Nylon 66 sample. The analytical titration analysis for a replicate sample indicated that the fabric contained 0.011 mg Cl cm^{-2}. After 2.5 months storage, a sample chlorinated at the same time contained 0.008 mg/cm^2 of Cl (a decline of 27%). The blue shift in the infrared doublet for the latter sample was only 23 cm^{-1}. So it would appear that the blue shift in the infrared doublet can be used as a qualitative indication, at least, of the degree of chlorination of the Nylon 66, and hence, of the biocidal efficacy generated in the material.

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References

[1] Sun G, Wheatley WB, Worley SD. Ind Engng Chem Res 1994;33:168.
[2] Worley SD, Sun G. Trends Polym Sci 1996;4:364.
[3] Eknoian MW, Putman JH, Worley SD. Ind Engng Chem Res 1998;37:2873.
[4] Bickert JR, Xu X, Sun G, Williams JF. Int Conf Safe Protec Fab'98 1998:1.
[5] Sun G, Xu X. Tex Chem Col 1998;6:26.
[6] Sun G, Xu X. Tex Chem Col 1999;31:21.
[7] Lin J, Winkelman C, Worley SD, Broughton RM, Williams JF, Bickert J. J Appl Polym Sci, in press.
[8] Lee S, Tien Y, Hsu C. Plasmas Polym 1999;4:229.
[9] Zhang D, Dougal S, Yeganeh MS. Polym Prepr 1999;40:226.
[10] Gonon L, Vasseur OJ, Gardette J. Appl Spectrosc 1999;53:157.
[11] Geng S, Friedrich J, Gahde J, Guo L. J Appl Polym Sci 1999;71:1231.
[12] Liu Q, De Wijn JR, De Groot K, Van Blitterswijk CA. Biomaterials 1998;19:1067.
[13] Chen J, Gardella JA. Appl Spectrosc 1998;52:361.
[14] Bouma RHB, Nauta WJ, Arnauts JEF, Van den Boomgaard T, Steuten JM, Strathmann H. J Appl Polym Sci 1997;65:2679.
[15] Tsubokawa N, Satoh M. J Appl Polym Sci 1997;65:2165.
[16] Poncin-Epaillard F, Vallon S, Drevillon B. Macromol Chem Phys 1997;198:2439.
[17] Muller M, Schmitt FJ. Macromol Symp 1997;119:269.
[18] Premnath V. Macromolecules 1995;28:7584.

[19] Zhang J, Kato K, Uyama Y, Ikada Y. J Polym Sci A: Polym Chem 1995;33:2629.
[20] Ren Y, Shoichet MS, McCarthy TJ, Hsu SL. Macromolecules 1995;28:358.
[21] Fraser RDB, Price WC. Nature 1952;170:490.
[22] Miyazawa T, Shimanouchi T, Mizushima S. J Chem Phys 1958;29:611.
[23] Beer M, Kessler HB, Sutherland GBBM. J Chem Phys 1958;29:1097.
[24] Cannon CG. Spectrochim Acta 1960;16:302.
[25] Garcia D, Starkweather HW. J Polym Sci: Polym Phys 1985;23:537.