

Surface Tailoring of Biomedical Polymers: An FTIR Study

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ABSTRACT: A multistep, surface-tailoring process of polymeric materials was developed with two consecutive plasma treatments and followed by derivatization reactions. In the first step, tetrafluoroethylene was plasma-polymerized, generating a highly crosslinked perfluoric surface layer. The next step introduced amine groups into the plasma polymer through exposure of the surface to plasma of ammonia. The reactive amine moieties were then used as anchoring sites for further derivatization. Finally, poly(ethylene glycol) chains were grafted onto the surface via a hexamethylene diisocyanate spacer. This method, aimed at the chemical modification of polymers for biomedical applications, was first demonstrated with poly(ethylene terephthalate) (PET) as a substrate in a previously published study (Cohn, D.; Stern, T. *Macromolecules* 2000, 33, 137). The aim of this study was to demonstrate the applicability of the method described previously to different polymers: poly(lactic acid), poly(ethylene) (PE), polystyrene (PST), poly(methyl methacrylate), a polybutadiene-based polyurethane (PEUOXAB-20), and Lycra. Fourier transform infrared (FTIR) spectroscopy was used to characterize the surface-modified substrates and the various control treatments. The results obtained were consistent with the derivatization scheme and in full agreement with the FTIR and ESCA results previously obtained for PET. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2203–2209, 2001

Key words: surface modification; plasma; biostability; biocompatibility; vascular grafts

INTRODUCTION

This study was part of a research program aimed at the chemical modification of polymers for biomedical applications. In two previous articles, the chemical derivatization of polyurethanes through chemically active sites situated along the polymer chain was described.^{1,2} In those studies, along with the desired properties, a significant undesired change in the mechanical properties was observed, caused by the interference of the grafted molecules with the microphase separation of the polymers.

The sequential use of plasma treatments and chemical derivatization procedures offers the pos-

sibility of a versatile, surface-confined tailoring of a polymer substrate. In a separate study,³ this working concept was exemplified on poly(ethylene terephthalate) (PET) by the performance of two consecutive plasma treatments, first with tetrafluoroethylene (TFE) and second with ammonia, followed by the grafting of poly(ethylene glycol) (PEG) molecules via a hexamethylene diisocyanate (HDI) bridge. The purpose of the first plasma treatment was to enhance the substrate's biodurability through the creation of an inert perfluoro protective layer, whereas the second plasma treatment resulted in an amine-rich surface. With the aim of minimizing the thrombogenicity of the material, these amine groups performed as anchoring sites for the grafting of the PEG chains via the HDI spacer.

This article presents research conducted to demonstrate the applicability of the method de-

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scribed previously to different polymers: poly(lactic acid) (PLA), poly(ethylene) (PE), polystyrene (PST), poly(methyl methacrylate) (PMMA), a polybutadiene-based polyurethane (PEUOXAB-20),² and Lycra. This article reports in detail only the experiments conducted on Lycra. Stability and biological evaluations were performed and will be published separately.

EXPERIMENTAL

We performed plasma treatments by placing a thin layer of each polymer, coated on KBr grains [with the purpose of increasing the sensitivity of the Fourier transform infrared (FTIR) analysis], into glass petri dishes, which were introduced into a cylindrical Pyrex plasma chamber connected to a radio frequency generator (13.56 MHz; HFS 501 S) and a matching unit (MN 500, RF Plasma Products, Inc.). The TFE, purchased from PCR, and ammonia plasma treatments were performed at 50 W and 0.65 mbar for periods of 10 and 7 min, respectively.

The coating of KBr grains (Fluka) with a very thin layer of polymer was performed via the addition of 10 mL of a 0.02% polymer solution in the appropriate solvent to 5 g of ground and dried KBr powder. Accordingly, PLA, PE, PST, PMMA (Aldrich), PEUOXAB-20 (synthesized²), and Lycra (DuPont) were dissolved in chloroform, xylene, CCl₄, chloroform, and dimethyl formamide (Frutarom), respectively. The solvent was then evaporated while the mixture was rotated under vacuum; the removal of the solvent was achieved in a vacuum oven at 50°C overnight. We then performed plasma treatments by placing glass petri dishes that contained a thin layer of the polymer-coated KBr grains (a total of about 400 mg) in the plasma reaction chamber.

The reaction between the amine groups present on the fluorinated surface and HDI (supplied by Aldrich) was carried out by the immersion of the samples in 3 mL of HDI at room temperature for 45 min. The polymer was then thoroughly rinsed in dry dioxane (Frutarom). The remaining free isocyanate groups were then reacted with dry PEG chains (PEG1000; Aldrich) at 70°C for 1 h with dibutyl tin dilaurate (DBTDL; Aldrich) as a catalyst (15 mg of DBTDL/g of PEG). After the reaction, the coated grains were rinsed with a 2:1 mixture of ethanol and acetone (Frutarom) and dried.

FTIR analyses of each of the surface treatments were performed with KBr pellets (ca. 200 mg) containing 40 mg of the coated KBr grains with a Nicolet 510 FTIR spectrometer.

RESULTS AND DISCUSSION

The very thin polymer coating on the KBr grains (see the Experimental section) significantly increased the surface area, which enabled a relatively enhanced sensitivity of the FTIR measurements of the different surface-modification procedures. A schematic representation of the consecutive surface-derivatization procedures is presented in Figure 1.

Figure 2 illustrates the FTIR spectra of Lycra before and after the two consecutive plasma treatments. The original polymer, being a poly(ether urethane urea), exhibited the main characteristic absorption bands at 1110, 1720, and 1640 cm⁻¹, which belonged to the ether, urethane, and urea groups, respectively. The appearance of the strong absorption band at 1250 cm⁻¹ in the TFE-treated polymer indicated the abundant presence of CF₂ and CF₃ groups after the TFE treatment. The changes in the FTIR spectrum caused by the ammonia plasma treatment were relatively difficult to see because of superimposing peaks. Nevertheless, an increase in the absorption bands at 1250–1300 and 1600 cm⁻¹ was observed; it belonged to vibrations of the primary amine groups introduced to the surface by the second plasma treatment.

The reaction of HDI molecules with the surface-bound amine moieties was reflected in the FTIR spectrum (Fig. 3) by the strong appearance of the N=C=O peak at 2270 cm⁻¹ (the HDI molecules reacted only through one of their two isocyanate groups) and the increase in the 1640 cm⁻¹ band due to the newly formed urea bonds. After the subsequent reaction between the remaining free isocyanate groups at the surface and the OH-terminal groups of the PEG1000 molecules, the disappearance of the N=C=O peak at 2270 cm⁻¹ was apparent. Concomitantly, a strong increase in the peak at 1720 cm⁻¹, caused by the newly formed urethane linkages, and the prominent peak at 1110 cm⁻¹, which belonged to the additional ether groups that originated in the grafted PEG, was easily noticed.

Alternatively, this last reaction was performed with Jeffamine ED-600 (an amine-terminated PEG; molecular weight = 600) instead of PEG1000. Fig-

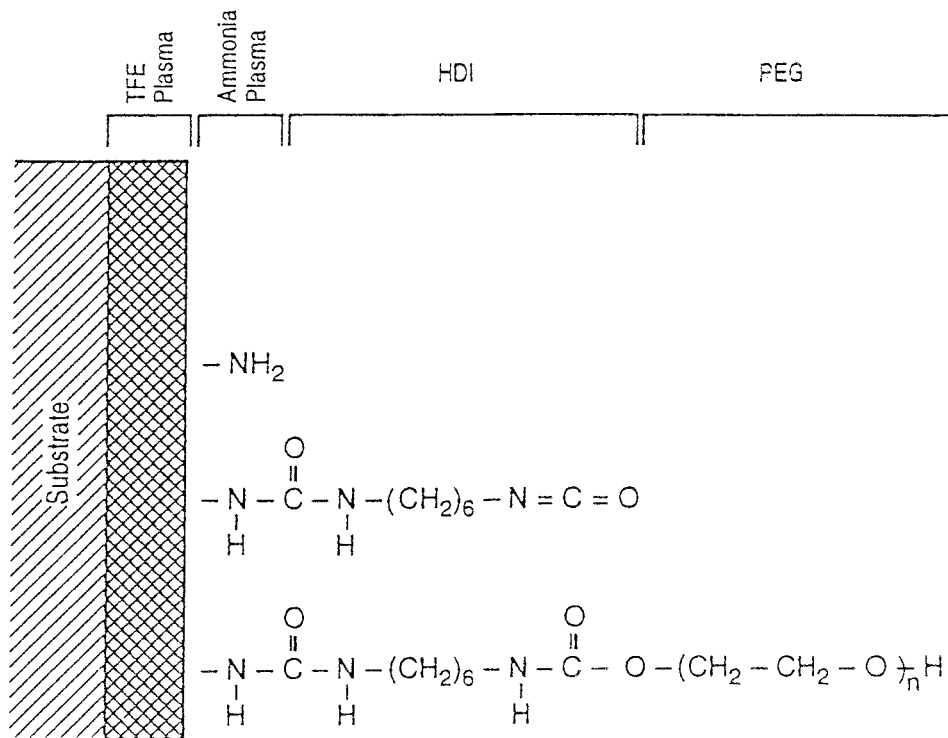


Figure 1 Schematic representation of the surface-modification procedure.

Figure 4 presents the FTIR spectra of the derivatization steps performed with ED-600 and PEG1000. Both spectra look essentially the same, including

the almost complete disappearance of the N=C=O peak at 2270 cm⁻¹ and the appearance of the very strong ether peak at 1110 cm⁻¹. The difference,

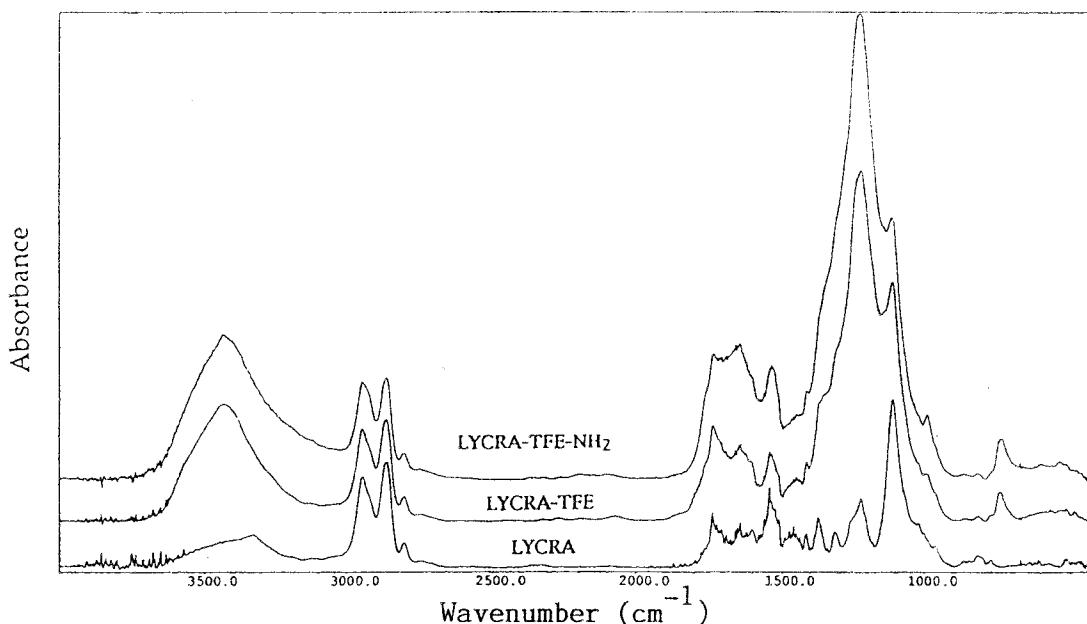


Figure 2 FTIR spectra of the TFE and ammonia-treated Lycra compared with the original polymer.

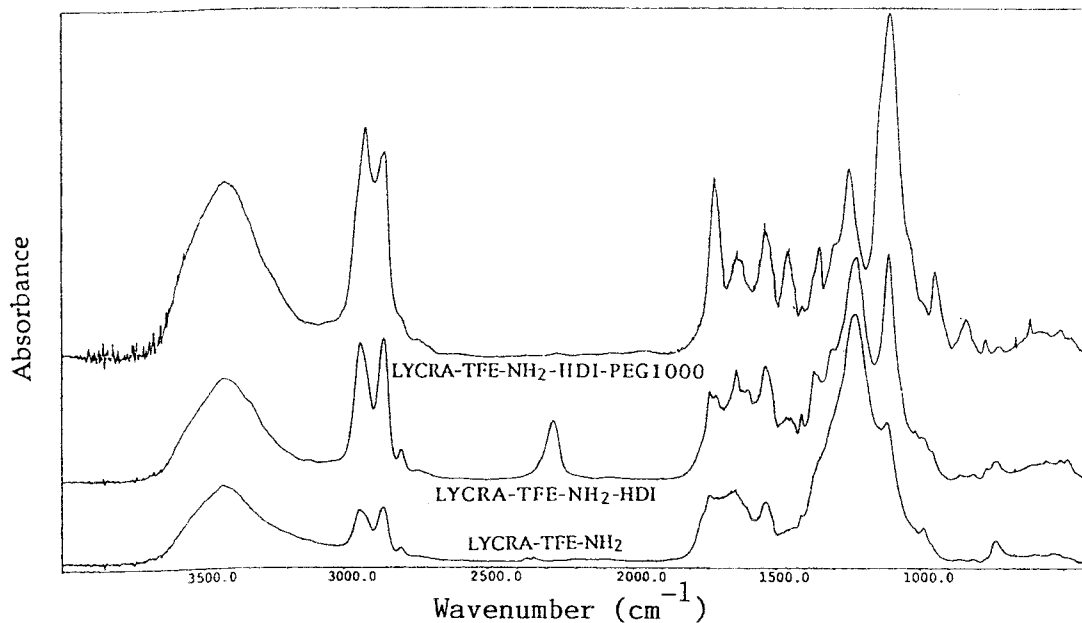


Figure 3 FTIR spectra of Lycra after two consecutive plasma treatments and after two chemical derivatization reactions.

however, is in the strong urea linkage absorption band at 1640 cm^{-1} , formed by the reaction between the NH_2 and $\text{N}=\text{C}=\text{O}$ groups, when Jeffamine reacted, in comparison with the relatively strong urethane band at 1720 cm^{-1} , present upon reaction with PEG.

These results, obtained for Lycra, are in complete agreement with the FTIR results obtained

when PET was used as a substrate³ and are also supported by X-ray photoelectron microscopy studies that were performed.³

To support the results described previously and to assess the substrate independence, we carried out the same surface-modification process on a series of polymers (see the Introduction and Experimental sections). The results

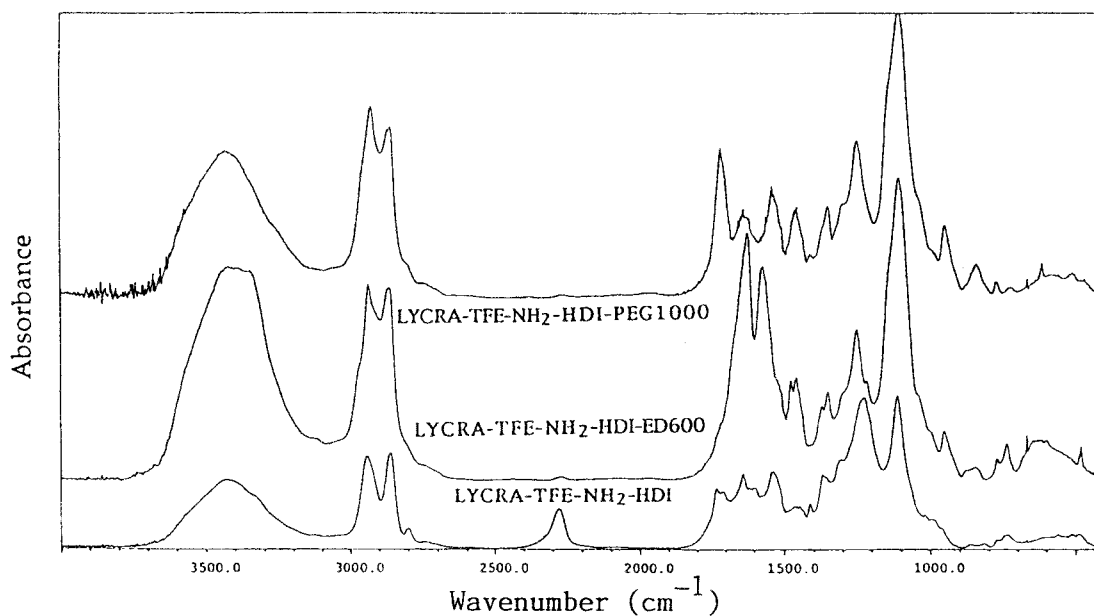


Figure 4 Comparison of three-step and four-step surface-modified Lycra with PEG1000 and, alternatively, with Jeffamine ED-600 in the fourth step.

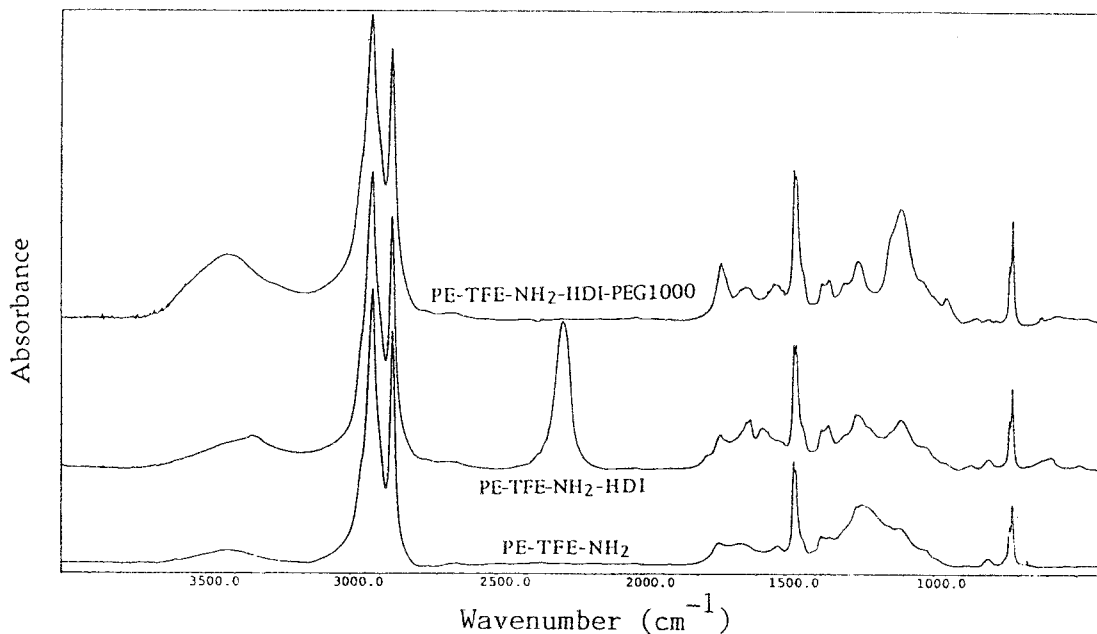


Figure 5 FTIR spectra of polyethylene after two consecutive plasma treatments and after two chemical derivatization reactions.

obtained for all these polymers were very similar to those obtained for Lycra and PET.³ Figures 5 and 6 show the FTIR spectra of the last three modification steps performed on low-density polyethylene and PLA, respectively. In both cases, the appearance of the N=C=O and urea

peaks in the third step and the disappearance of the N=C=O and the appearance of the urethane and ether peaks in the fourth step were observed.

To further prove the covalent nature of the derivatization scheme, we carried out two differ-

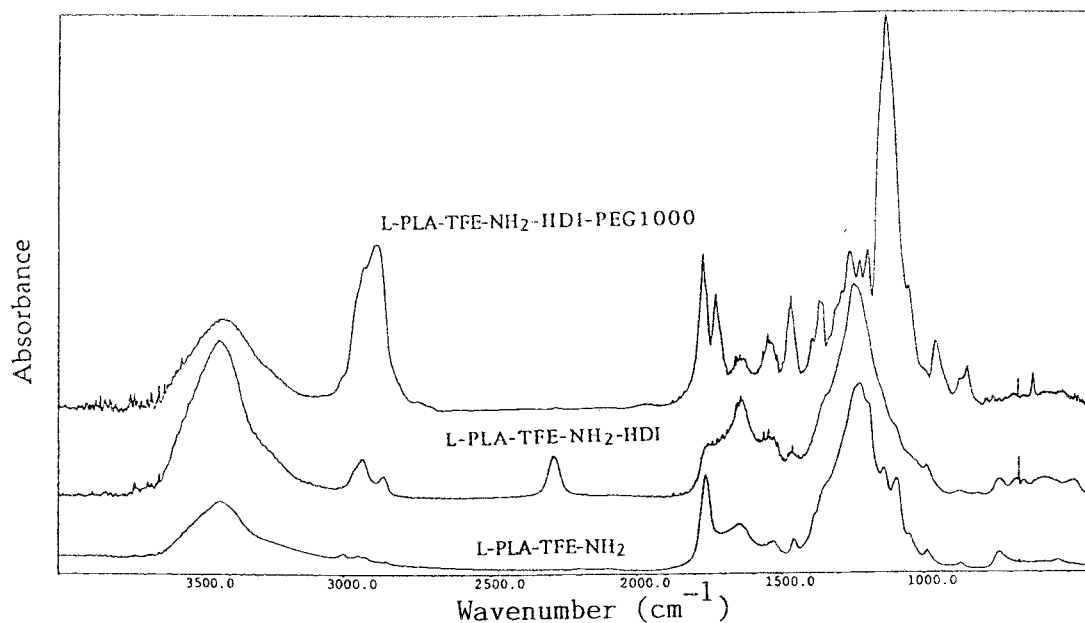


Figure 6 FTIR spectra of *L*-PLA after two consecutive plasma treatments and after two chemical derivatization reactions.

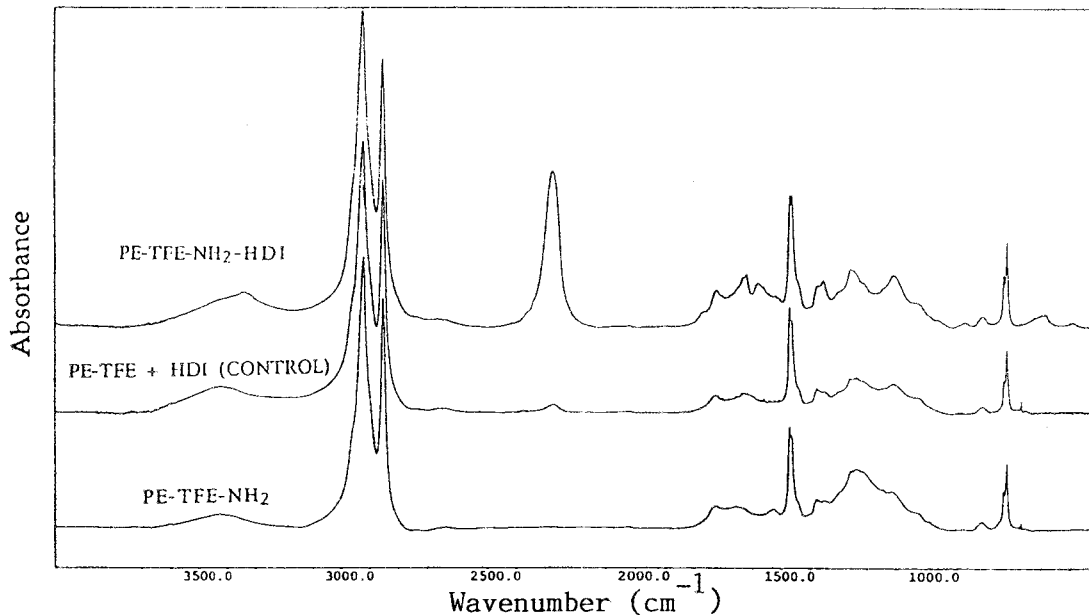


Figure 7 FTIR spectrum of a third-step control sample compared with the spectra of the original reaction and the first two steps.

ent control experiments, exemplified here for PE and PLA.

The purpose of the first control treatment, shown here for PE, was both to further verify the occurrence of the N=C=O/amine reaction and, although indirectly, to prove the presence of the

plasma-generated amine groups at the surface. The control experiment was carried out under the same conditions as the original reaction, except that the ammonia plasma stage was omitted and, therefore, no surface amine groups were present. The FTIR spectrum of the control sample (Fig. 7)

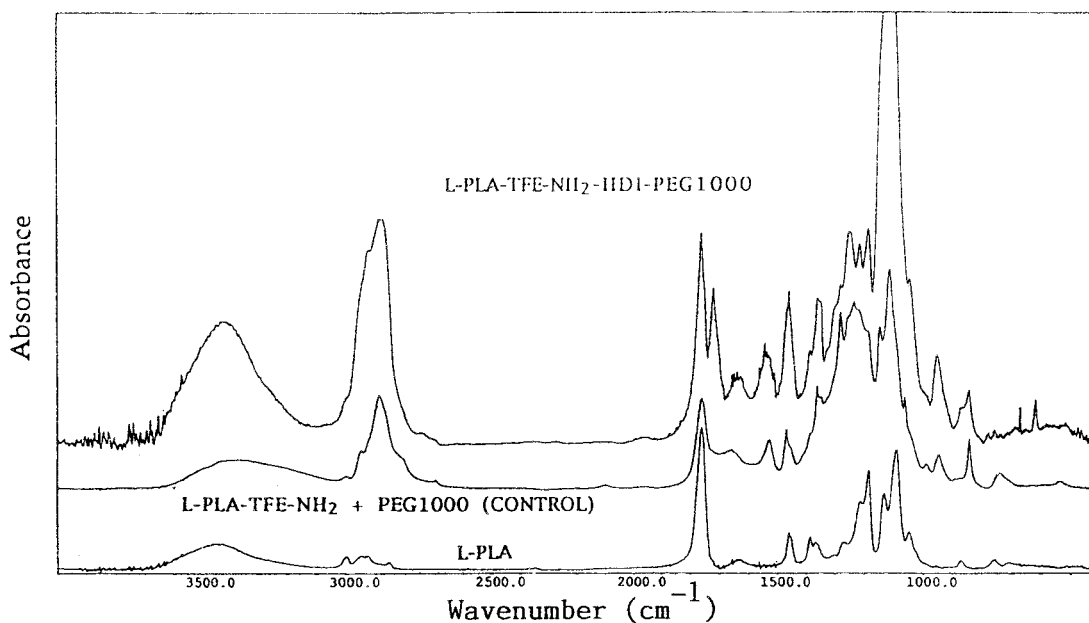


Figure 8 FTIR spectrum of a fourth-step control sample compared with the spectra of the original reaction and the original polymer.

showed the almost complete absence of the N=C=O absorption band at 2270 cm^{-1} and also the absence of the urea linkage absorption band at 1640 cm^{-1} . Hence, as expected, no reaction occurred without the presence of the bonded amine groups, and there was very little physical adsorption of HDI molecules.

The second control experiment was carried out to further verify the occurrence of the last reaction between the remaining free N=C=O group of the bonded HDI and PEG1000. For that purpose, the reaction was carried out under the same conditions as before, only without the prior performance of the third-step amine/N=C=O reaction. This experiment is shown here as performed on PLA. The characteristic peaks of the ether group and the urethane linkage are both absent in the FTIR spectrum of the control treatment as presented in Figure 8, which is contrasted by the prominent presence of these peaks in the spectrum of the original reaction (Fig. 7). Here as well, there was very little, if any, physical adsorption of PEG without the actual occurrence of the reaction.

CONCLUSIONS

A four-step surface-modification process was performed on Lycra; it included two sequential plasma treatments and two subsequent chemical derivatization reactions. Both the occurrence of the chemical reactions and the actual presence of the different layers at the substrate surface were verified by FTIR spectroscopy, the results of which were in complete agreement with the FTIR and ESCA results obtained in previous experiments on PET. The control experiments supported these findings.

The same surface-modification sequence was performed on a series of different polymeric substrates, which demonstrated the substrate-independent nature of the method.

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