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Synthesis of cross-linked polyurethane elastomers with fluorescein linkages

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Abstract The reaction of polyurethane prepolymers with fluorescein (free acid) and glycerin or castor oil-cross-linker has been performed in *N*,*N*-dimethylformamide and in such way a cross-linked elastomer material has been obtained. Polyurethane prepolymers were prepared by reaction of the poly(1,4-butane)diols (Terathane 1400) with aliphatic 1,6 hexamethylene diisocyanate. The above polymerization reactions lead to the formation of novel aromatic–aliphatic polyurethane elastomers having fluorescein moieties in the main chain. The resulting novel cross-linked polyurethanes have excellent mechanical properties, especially in the castor oil polyurethane elastomer formulations and show light-violet fluorescence property and could be used as photoactive polymers for labeling materials. These polyurethanes were characterized through IR, TGA, DSC, and mechanical analyses. Some aspects of the fluorescent emission in fluorescein-polyurethane elastomers were studied.

Introduction

Polyurethane (PU) is one of the most versatile and useful engineering materials. By proper selection of reactants, the resulting PU can be used as rigid crystalline plastic, flexible elastomer, coatings, adhesives, leather, thermoplastic elastomers, and composites [1–3]. Polymers with fluorescent properties have been investigated and were found to include chromophore in the backbone or as a pendant group. They are used as fluorescent labels and photo-harvesters [4–6]. Fluorescent labeling has been used to study specific interactions between macromolecules in polyelectrolytes, water soluble polymers, homopolymers, block and random copolymers [6–12].

Linear polyurethanes were prepared using fluorescein as chain extender. These materials are soluble in most organic solvents and give film with excellent transparency. These polymers show intense yellow luminescence in solution and as films [13–15].

In the last decades, bio-renewable feedstocks for PU manufacturing have become an increasing interest for both economic and environmental reasons [3, 16]. The castor oil has been used widely to develop new materials for many different applications, because it is the major oil composed essentially of the triglycerides of a hydroxy acid, ricinoleic acid [17].

The natural polymers having more than two hydroxyl groups per molecule were used as chain extenders or as cross-linker. They improve the physico-mechanical properties of polyurethane obtained [18].

In this article we wish to report the polyaddition reactions of fluorescein, a diol tautomer, and glycerin or castor oil as a cross-linker with a polyurethane prepolymer, with and without catalyst, for the formation of photoactive polyurethanes elastomers.

These photosensitive polymers have unique ability of forming high quality films, and by this reason, have made them suitable for applications in the field of coating materials, including textiles and synthetic leather.

Experimental

Materials

All chemicals used in this study were used as received from the suppliers. Polyether and chain extenders were dried

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under a vacuum until the content of water was below 0.03%. 1,6-hexamethylene diisocyanate (HDI) was obtained from Fluka. The polyetherdiol was poly(1,4-butane)diol (Terathane 1400). This polymer was obtained from Fluka. The polyetherdiol average molecular weight is 1400 g/mol. The chain extenders: fluorescein was obtained from Fluka, and glycerin (Gly), castor oil (CO) were obtained from Aldrich and were used as received. Dimethylformamide (DMF) was obtained from Fluka.

Polymer synthesis

The polymers were prepared in a two-step polymerization process under nitrogen atmosphere. Typically, synthesis of PUs was done by the following procedure and the moles of the added reagents for the various PU are shown in Table 1. The OH_{diol}/OH_{triol} molar ratio used was of 1/1 in each of the synthesized polyurethane samples. The sample obtained without the use of catalysts were noted with PU1, PU2, PU3 and those for which catalysts were used with PU1c, PU2c, PU3c.

The synthesis of PUs was performed in a 1-L glass reactor at normal pressure, under a nitrogen blanket and vigorous agitation. The NCO/OH ratio of all formulations was 1.03–1.05. In the case of the prepolymer procedure, polyether diol was reacted with a diisocyanate at 80 °C for 2 h to yield a prepolymer that was mixed in the second step with chain extenders at 80 °C for 10 min. The fluorescein, chain extender, was used in a DMF solution. The course of the reaction was followed by infrared absorption of the isocyanate stretching band at 2200–2300 cm^{-1} and the reaction was considered to be complete when this band disappeared. The polymer film was prepared by the casting of the polymer solution in DMF (70%) onto glass plates and that was allowed to dry at 80 °C for 20 h, post-curing of the PU proceeding at laboratory temperature for 7 days. The polyurethane films thus prepared were used for the determination of mechanical and physical properties and for the thermal resistance study.

Instrumentation

Infrared spectroscopy (FT-IR) was done using a VERTEX 7 Instruments equipped with a Golden Gate single-reflection ATR accessory, spectrum ranging from 600 to 4000 cm^{-1}.

The thermal stability of PUs was performed on a DERIVATOGRAF Q-1500 D apparatus (Hungary). The rate of heating was of 10 °C/min in air atmosphere. The initial weight of the samples was about 50 mg and the temperature range was 30–700 °C.

The thermal transition behavior was studied using differential scanning calorimetry (DSC) measurements involving a temperature range of −100 to 80 °C on a Perkin Elmer 7 Series DSC, purging with N_2 and chilling with liquid N_2. Runs were conducted on samples of about 10 mg at a heating rate of 10 °C/min to observe the glass transition temperature (T_g).

Stress–strain measurements were performed on dumbbell-shaped samples cut from the obtained polyurethane sheets. The tests were performed at room temperature using a Shymadzu EZTest (Japan), equipped with a 5 kN load cell. The cross-head speed that was used was of 50 mm/min. At least five identical dumbbell-shaped specimens for each PU type were tested, and their average mechanical properties are reported.

Fluorescence spectra were measured by using UV spectroscopy on JEOL-60 MHz, SPECORD M-80, and SPECORD UV–VIS spectrophotometers. The fluorescence spectra were obtained at room temperature with equipment containing a double monochromator with a diffraction network of the GDM-1000 type, a compensatory printer of the K-201 type and a selective amplifier.

Results and discussion

The PU multiblock copolymers based on polyether polyol with fluorescein and cross-linkers were prepared by a two-step method.

In these reactions a Terathane-1400 soft segment was reacted with 2.1 mol of aliphatic diisocyanates in the presence of catalysts or without catalysts, respectively. The prepolymer was mixed in the second step with fluorescein in a solution with DMF and cross-linkers. This method provided copolymers that have polyurethane blocks that are connected with fluorescein linkages.

Table 1 Formulations and hardness of the fluorescein-based polyurethanes obtained

Nr.	Designation samples	Rate polyol/HDI/ chain extenders	Chain extenders	Hardness Shore A
1.	PU1	1:2:1	Fluorescein	86
2.	PU1c	1:2:1	Fluorescein + dibutyltin dilaurate	91
3.	PU2	1:2:1	Fluorescein + glycerin	63
4.	PU2c	1:2:1	Fluorescein + glycerin dibutyltin dilaurate	68
5.	PU3	1:2:1	Fluorescein + castor oil	67
6.	PU3c	1:2:1	Fluorescein + castor oil dibutyltin dilaurate	76

The compositions used and their hardness are shown in Table 1. In this way, the average soft-segment length was maintained constant, while the hard segment structure was systematically varied.

Fluorescein and cross-linkers lead to polyurethanes with hardness of about 60–70 Shore A that may be ranked as soft grade PUs. By using only fluorescein in hard segments it was possible to prepare a PU with hardness as high as 80–90 Shore A.

The role of the chain extenders structure and the type of OH groups can also be seen from the Table 1. All these elastomers have similar properties; however, the use of catalyst resulted in an increase of Shore hardness and a change in mechanical and glass transition temperature.

IR spectroscopy

FT-IR spectra of the polymers indicated the absence of any residual isocyanate (no absorption at 2270 cm^{-1}) and showed strong absorptions at 1700 and 3300 cm^{-1} indicating the formation of the urethane linkage (Figs. 1, 2, and 3).

The FT-IR spectra of PU exhibited characteristic absorption bands of the amide group around 3300 cm^{-1} (N–H stretching) and 1700 cm^{-1} (C=O stretching), as well as peaks at 1736 cm^{-1} (non-H-bonded C=O stretching, urethane) and 1700 cm^{-1} (H-bonded C=O stretching, urethane). Characteristic absorption peaks were present at 1600 cm^{-1} C–N versus NH (amide II), 1200 cm^{-1} C–O–C ether of Terathane.

The IR spectrum of PU1 showed a peak at 3290 cm^{-1} for the N–H stretching and strong peaks at 1630, 1685, and 1700 cm^{-1} for carbonyl groups.

The appearance of a sharp peak for the N–H stretch and for NHCOO (urethane) at 1700 cm^{-1} verifies the formation of polyurethane. The C–O–C stretching at (1400 cm^{-1}) is characteristic for ester with the inclusion of fluorescein in the polymer chain. If catalysts are used during the preparation of polyurethane, modifications can be observed, such as a widening of the band at 3300 cm^{-1}, as well as modifications of the 1700 cm^{-1} peak.

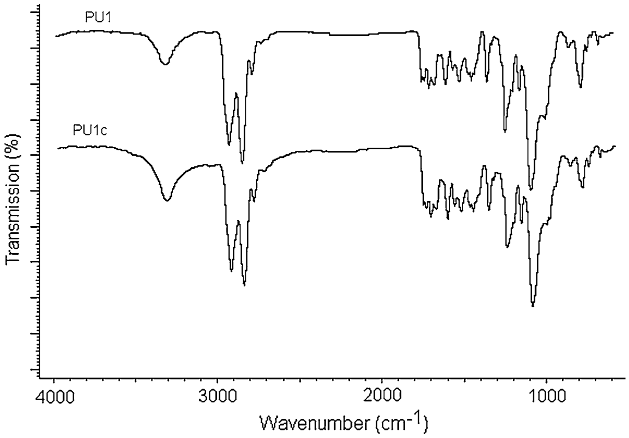


Fig. 1 IR spectra of PU1-polyurethane samples synthesized with (PU1c) and without catalyst (PU1)

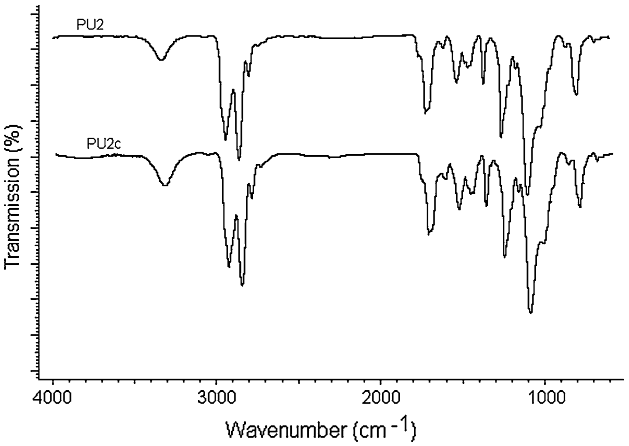


Fig. 2 IR spectra of PU2-polyurethane samples synthesized with (PU2c) and without catalyst (PU2)

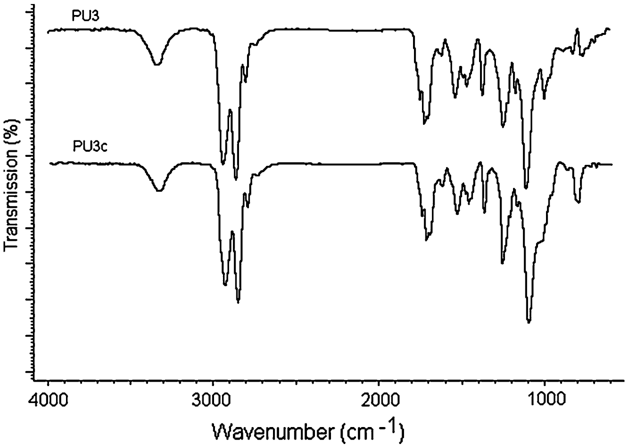


Fig. 3 IR spectra of PU3-polyurethane samples synthesized with (PU3c) and without catalyst (PU3)

Thermal properties

The thermal properties of the polymers (PU1–PU3) were measured by DSC and TGA/DTG. The same testing conditions were used for all the copolymer samples. The open-air TG was used to study a number of urethane elastomers because some components in the structure of these polymers play an important role in increasing the thermal stability. The TGA data of these novel polyurethanes (Table 2) provide information regarding their thermal stability and thermal degradation behavior.

An examination of the data reveals that all of the above polymers are thermally stable up to 200 °C. The polymers

Table 2 Thermal characteristics of the fluorescein-based polyurethanes obtained

Sample code	Weight losses global (%)	T_i (°C)	T 5% losses (°C)	T_{max} (°C)	T_f (°C)
PU1	94	210	310	410	590
PU1c	92	225	320	420	600
PU2	96	250	330	400	580
PU2c	94	265	335	405	590
PU3	96	275	335	405	570
PU3c	93	275	345	410	595

(PU1, PU2, PU3 without catalyst) show a 5% weight loss at 310, 330, and 335 °C, respectively. The residual weights for these polymers at 550 °C are 6%, 4%, and 4%, respectively.

The physical cross-links are important for providing dimensional stability and for stopping cold flow in the uncured materials. The effect of restricting segmental motion in a three-dimensional network by chemical cross-link sites is similar to that of microdomain physical cross-linking, except that the latter is irreversible [19].

The temperature domain in which weight losses were maximum was that at 280–570 °C The uses of catalyst lead to relative stability because there is an increase in polymerization reactions and a higher tendency for chain ordering. In the DTG curve of the polyurethanes a maximum inflexion is present at about 400–420 °C

DSC thermograms of fluorescein-PUs are shown in Figs. 4 and 5. The DSC scan of the fluorescein-based PU1 exhibits a T_g from −51 to −55 °C depending on catalyst use. The value of T_g is higher than the T_g of pure soft segment oligomer, indicating that there is some mixing of hard segments in the soft segment phase [20, 21]. The DSC scan of fluorescein-based PU cross-linked with glycerin exhibits a T_g from −63 to −64.35 °C.

The transitions at higher temperature correspond probably, according to Cooper et al., to the disruption of ordered segments [22]. Between the completely amorphous and perfectly crystalline states there is a continuum of ordered segment morphologies. This has been called an order–disorder transition [23].

The DSC curve of the polymer PU1 also showed two endotherm peaks with the maximum at 7–9 °C and 53–56 °C which correspond to the hard glass transition temperature The endotherm peaks appearing at 53–56 °C in the DSC thermogram should not be associated with the polymer (PU1) melting temperature.

The DSC curve of the PU2 polymer showed an endothermic shift around 8–10 °C which corresponds to the hard glass transition temperature. When using catalysts to create these polymers, the glass transition temperature presents an increase of 2–3 °C, compared to the case of polymers created without the aid of catalysts.

For fluorescein-based polyurethanes, glass transition values indicate the influence of the hard segment composition on the polyurethanes' soft micro-domains composition.

In this case, the difference might also be due to the differences in the various chain extenders employed.

Mechanical properties

The mechanical behavior of polyurethane elastomers is dependent on the intermolecular interactions between their hard segments.

Stress–strain, modulus and elongation are important for polymer characterization and depend on the variation of the

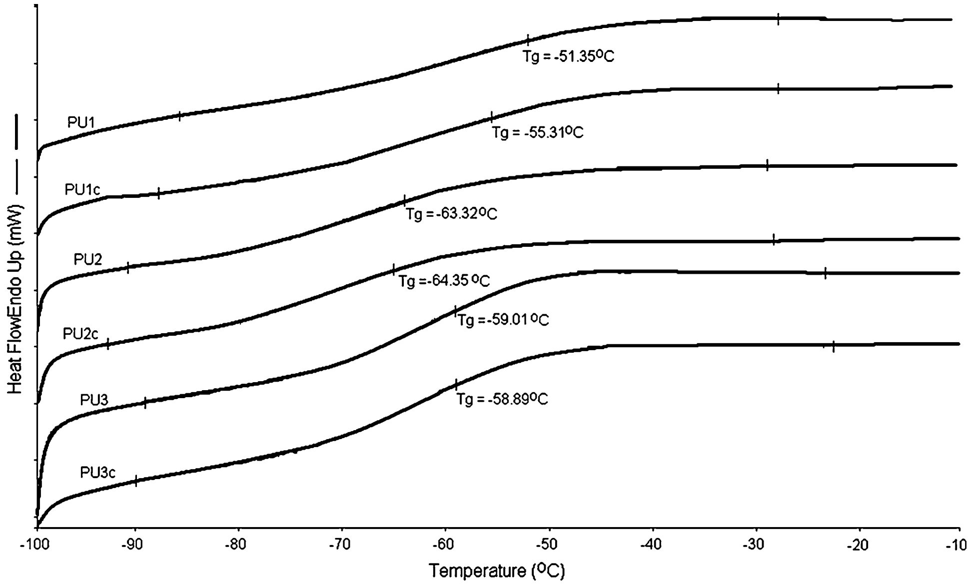
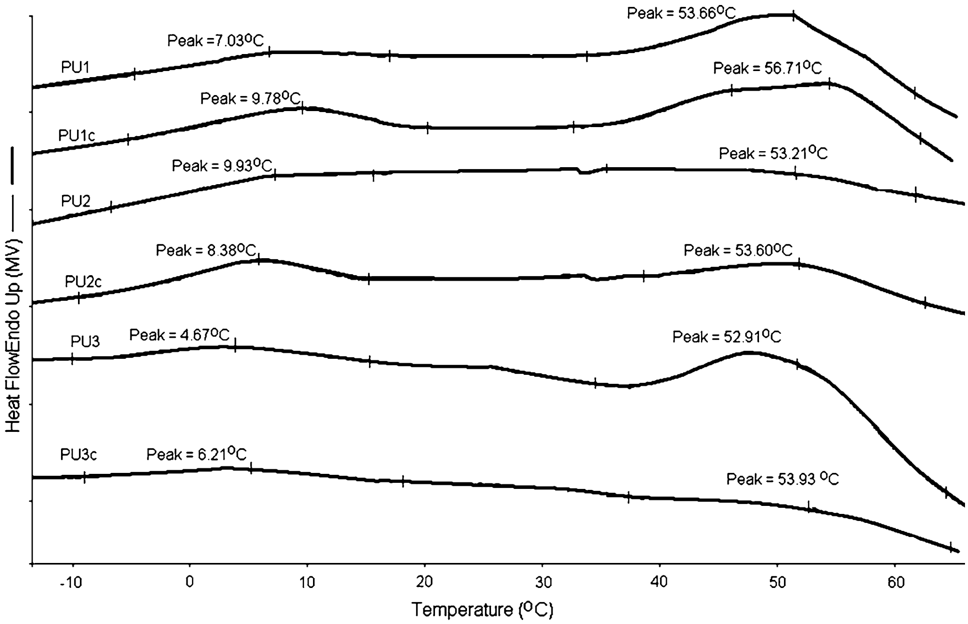


Fig. 4 DSC thermograms of the fluorescein-polyurethane elastomers obtained (−100 to −10 °C)

Fig. 5 DSC thermograms of the fluorescein-polyurethane elastomers obtained (−10 to 80 °C)



structure of chain extenders, which leads to modifications of these properties [24].

The stress–strain curves representing the various chain extenders, but with a common soft segment, are grouped in Figs. 6, 7, and 8.

In the case of PU1 sheets with only fluorescein, the tensile strength at break is of 2–3 MPa and maximum elongation is 210–260%. The PU sheet with fluorescein and glycerin had a tensile strength at break of 4–5 MPa and maximum elongation of 540–580%. PU sheets with fluorescein and castor oil display strength of 3.2–8 MPa and elongation of 900–950%.

The properties could be enhanced by modification of the diol chain extenders or/and the types of isocyanate.

Fluorescence spectra

The fluorescence emission spectra of the fluorescein-PUs films are in Figs. 9, 10, and 11.

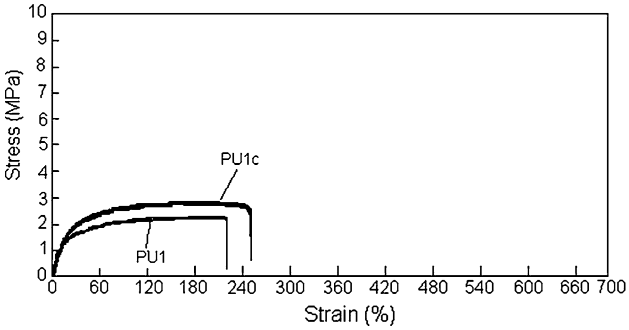


Fig. 6 Stress–strain curves of polyurethanes prepared with fluorescein (PU1—without catalyst and PU1c—with catalyst)

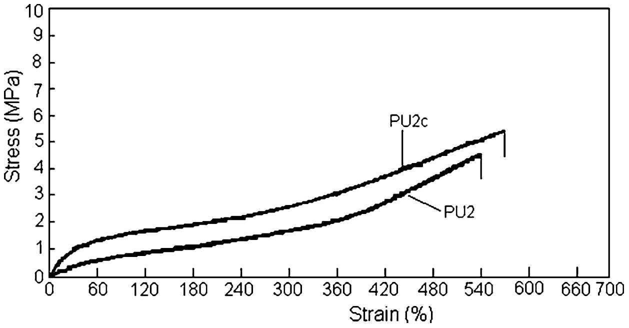


Fig. 7 Stress–strain curves of fluorescein-polyurethanes prepared with fluorescein and glycerin (PU2—without catalyst and PU2c—with catalyst)

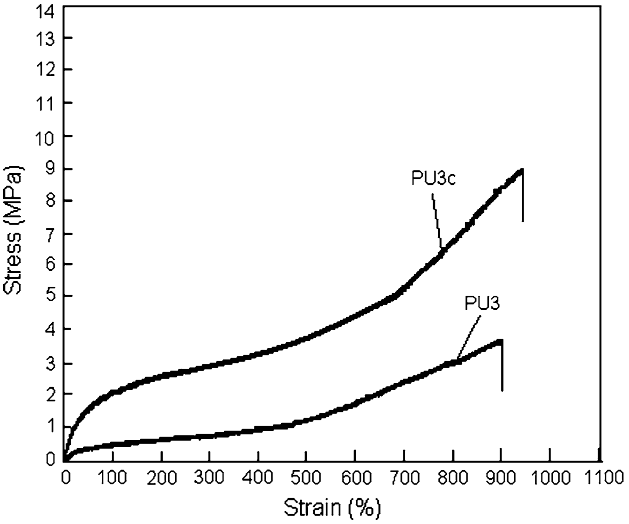


Fig. 8 Stress–strain curves of fluorescein-polyurethanes prepared with fluorescein and castor oil (PU3—without catalyst and PU3c—with catalyst)

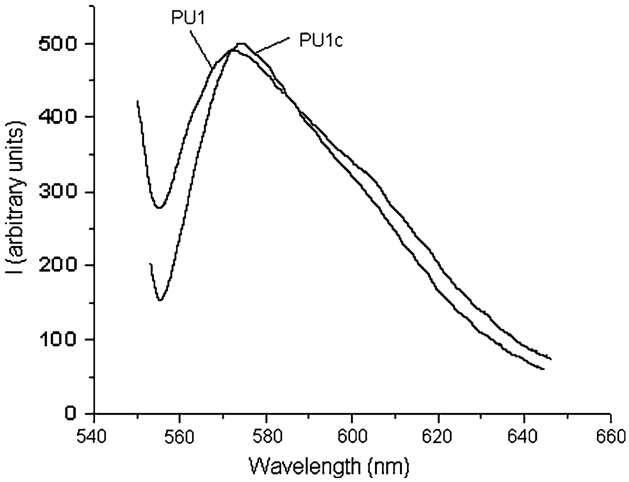


Fig. 9 Emission spectra of the PU1 (without catalyst) and PU1c (with catalyst)

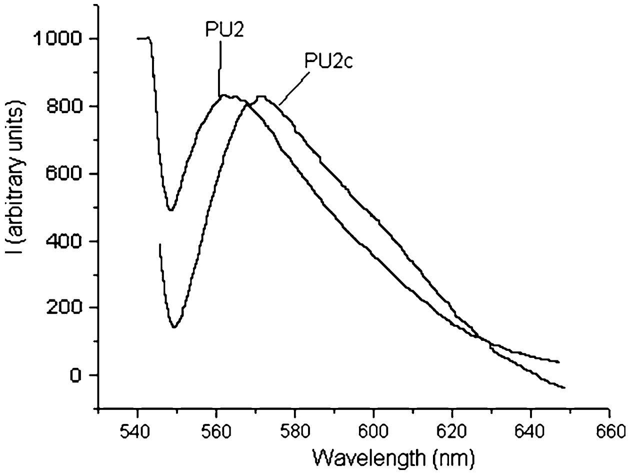


Fig. 10 Emission spectra of the PU2 (without catalyst) and PU2c (with catalyst)

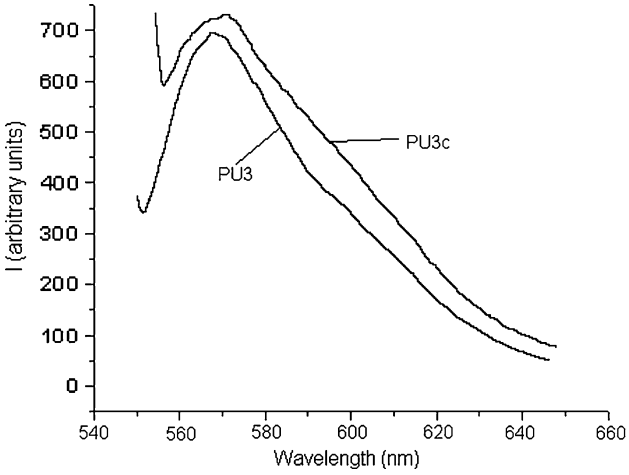


Fig. 11 Emission spectra of the PU3 (without catalyst) and PU3c (with catalyst)

For PU1 there is a fluorescence peak at a wavelength of 572 nm presented by the fluorescein-polyurethane obtained without catalyst and a peak at 574 nm for the polyurethane created with catalyst. In the case of polyurethanes cross-linked with glycerin, a peak appeared at a wavelength of 563 nm for the sample obtained without catalyst and at 570 nm for polyurethane film with catalyst as shown in Fig. 10.

The fluorescence intensity increased in the case of polyurethane elastomers (PU3) cross-linked with castor oil, as shown in Fig. 11.

Conclusions

Fluorescein, glycerin, and castor oil were found to be suitable chain extenders for polyurethanes based on cross-linking, both when catalysts were employed and when they were not.

Depending on the nature of the formulation, the resulting PUs exhibited hardness of about 60–90 Shore A, making them prospective materials falling into the category of the soft grade PUs.

The thermal stability depends on the components present in the formulation. The presence of cross-linking and catalyst increased the fuorescein-polyurethanes' thermal stability.

The chemical cross-links produce higher elongations at break. The cross-linking process increases the urethane domain rigidity and decreases the soft segment crystallinity. These factors enhance the tensile strength of the materials.

The effects of various cross-linkers and the presence of the catalyst on the fluorescence were also observed in different formulations, which indicated differences in localization and orientation of the fluorescein in the polymer.

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