

Synthesis and Characterization of Polyurethane Elastomers Based on 4,5-Dibromofluorescein and Various Crosslinkers

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Two series of new self-coloured segmented polyurethane elastomers were successfully synthesized via the reaction of poly (tetramethylene ether) glycol (Terathane 1400) and hexamethylene diisocyanate / 4,5-dibromofluorescein with glycerine or castor oil as hard segments in a N,N-dimethylformamide solution. Polyurethane structure formation has been proven by infrared (IR) spectroscopy. Photosensitive-dibromofluorescein polyurethane elastomers exhibited high thermal stability and the addition of 4,5-dibromofluorescein in the preparation of the fluorescent polyurethane elastomers enhanced the tensile strength. This may be attributed to an increased cross-linking due to strong intermolecular interaction between the fluorescein polyurethane molecules. The fluorescence performance for the fluorescent polyurethane elastomers films appears at 560-580 nm, and increased concentration of 4,5-dibromofluorescein enhances the fluorescence performance of these polyurethane elastomers.

Keywords: polyurethanes, fluorescence, chain extender, mechanical properties, thermal behavior

Polyurethane (PU) is one of the most versatile polymer and can be easily prepared by a simple polyaddition reaction of a polyol, on isocyanate and a chain extender. PUs have excellent properties and can be used as flexible elastomer, coatings, adhesives, leather, thermoplastic elastomers and composites [1-8].

The improvement of the thermal stability of PU was made through structural chemical modification by introducing thermally-stable heterocyclic polymers [9, 10].

Polymers with fluorescent properties have been investigated and they are already used as fluorescent labels and photo-harvesters [11, 12]. Linear polyurethanes were prepared using fluorescein as a chain extender. These materials are soluble in most organic solvents and provide films with excellent transparency [13, 14].

The bi-functional colorants can be utilized as monomers for functional polymers via polyaddition and polycondensation reactions [15]. Such polymers present good light- fastness which is combined with the special properties of polymers [16, 17].

Bio-renewable feedstocks (i.e. castor oil, triglycerides of a hydroxy acid, ricinoleic acid) for PU manufacturing have become an increasing interest for both economic and environmental reasons [18, 19].

In this article we wish to report the synthesis of new polyurethane elastomers with dibromofluorescein groups, as well as polyurethane elastomers with a cross-linked polyurethane molecule, obtained through the direct reaction between 4,5-dibromofluorescein as chain extender and glycerine or castor oil as crosslinker, diisocyanate and Terathane 1400 polyether polyol.

This study was based on the investigation of the effect of various reaction formulations, such as amount of 4,5-dibromofluorescein, nature of the crosslinker (glycerine or castor oil), on the polymer chain-growth as well as the properties of such polymers. The effects of the introduction of 4,5-dibromofluorescein on different properties of the resulting photosensitive polyurethane elastomers such as thermal, spectroscopic properties were also studied.

Experimental part

Materials

All chemicals employed in this study were used as received from the suppliers. Polyether and crosslinkers were dried under vacuum until the content of water was below 0.03%. 1,6-hexamethylene diisocyanate (HDI) was obtained from Fluka. The polyetherdiol was poly

Table 1

FORMULATIONS OF 4,5-BROMOFLUORESCEIN-BASED POLYURETHANE ELASTOMERS

Nr.	Designation samples	Molar ratio polyol / HDI / Chain extenders	Chain extenders
1.	PBF1	1:2:1	4,5-dibromofluorescein (0.1 mole) Glycerine (0.9 mole)
2.	PBF2	1:2:1	4,5-dibromofluorescein (0.05 mole) Glycerine (0.95 mole)
3.	PBF3	1:2:1	4,5-dibromofluorescein (0.02 mole) Glycerin (0.98 mole)
4.	PBF4	1:2:1	4,5-dibromofluorescein (0.1 mole) Castor oil (0.9 mole)
5.	PBF5	1:2:1	4,5-dibromofluorescein (0.05 mole) Castor oil (0.95 mole)
6.	PBF6	1:2:1	4,5-dibromofluorescein (0.02 mole) Castor oil (0.98 mole)

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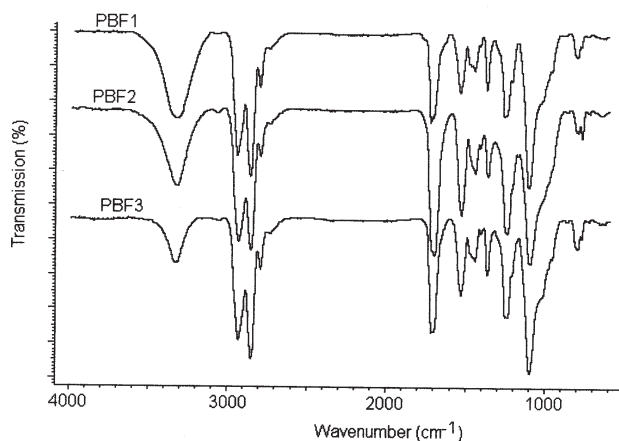


Fig. 1. IR spectra of 4,5-dibromofluorescein-polyurethane samples synthesized with glycerine as crosslinker

(tetramethylene ether) glycol (Terathane 1400) and it was obtained from Fluka. The polyetherdiol average molecular weight is 1400 g/mol. 4,5-dibromofluorescein, glycerin (Gly) and castor oil (CO) were obtained from Aldrich. Dimethylformamide (DMF) was obtained from Fluka.

Polymer synthesis

The elastomers were prepared as it was described in a previous work [20], in a two-step polymerization process. Synthesis of PUs elastomers was done by the following procedure and the moles of the added reagents for the various PU are shown in table 1. The $\text{OH}_{\text{diol}}/\text{OH}_{\text{triol}}$ molar ratio used was of 1/1 in each of the synthesized polyurethane samples.

The synthesis of PUs was performed in a 500 mL glass reactor at normal pressure, under 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 4,5-dibromofluorescein, as chain extender, was used in a DMF solution. The end 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 casting the polymer in DMF (60%) solution onto glass plates and then was allowed to dry at 80 °C for 20 h. The polyurethane films thus prepared were used for the determination of mechanical and physical properties and for the thermal stability study.

Measurements

Infrared spectroscopy (FT-IR) was done using a VERTEX 7 Instruments equipped with a Golden Gate single-reflection ATR accessory, its spectrum ranging from 600 to 4.000 cm^{-1} .

The thermal stability of PUs was tested 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.

Stress-strain measurements were performed on dumbbell-shaped samples that were cut from the obtained polyurethane sheets. The tests were performed at room temperature using a Shimadzu EZTest (Japan), equipped with a 5kN load cell. The cross-head speed employed was of 50 mm/min. At least five identical dumbbell-shaped

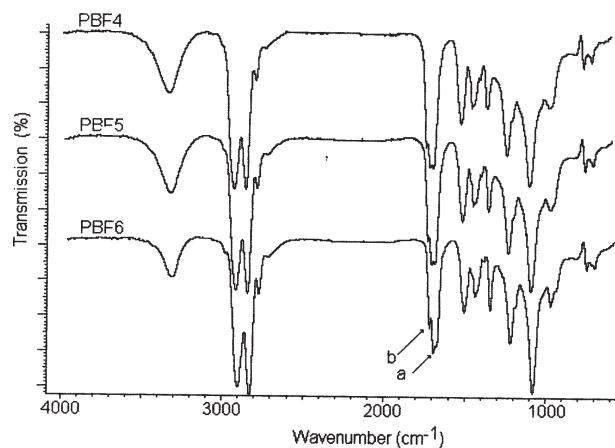


Fig. 2. IR spectra of 4,5-dibromofluorescein-polyurethane samples synthesized with castor oil as crosslinker

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 an 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.

Contact Angle Measurements (CA) were performed using deionized water and ethylene glycol droplets of 5 μL applied over the different neat polyurethane surfaces using a Dataphysics Contact Angle System KSV Instruments LTD, Finland. The contact angle was measured within 45–60 s of the addition of the liquid drop with an accuracy of $\pm 1^\circ$. Measurements were repeated six to ten times with different test pieces of the same PU sheet to check the accuracy.

Results and discussion

The PU multiblock copolymers with 4,5-dibromofluorescein in the main chain were successfully prepared by a two-step method. The compositions used are shown in Table 1 where, the average soft-segment length was maintained constant, while the hard segment structure was systematically varied.

IR Spectroscopy

The FT-IR spectra of the prepared photosensitive-dibromofluorescein polyurethane material are given in figures 1, 2. They show that the band at 3300 cm^{-1} as broad and decreasing in intensity with the decrease in amount of 4,5 dibromofluorescein. This peak corresponds to the stretching vibration of free and hydrogen-bonded NH- group. The absence of an absorption band at 2270 cm^{-1} (corresponding to the characteristic absorption of isocyanate group) indicated that all the monomers were consumed.

The FT-IR spectra of PU exhibited characteristic absorption bands for the amide group around 3300 cm^{-1} (N-H stretching) and 1700 cm^{-1} (C=O stretching), as well as characteristic absorption peaks were present at 1500 cm^{-1} for the C-N vs NH (amide II), and at 1200 cm^{-1} for the C-O-C ether of Terathane.

The IR spectrum of polyurethane elastomers crosslinked with castor oil presents characteristic peaks at 1736 cm^{-1} (non-H-bonded C=O stretching, urethane, fig. 2, b) and 1690 cm^{-1} (H-bonded C=O stretching, urethane fig. 2 a).

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 that includes 4,5-dibromofluorescein in the polymer chain.

Thermogravimetric analysis

The thermal stability of a polymeric material is very important for the use of polyurethane at high temperature, due to the possible release of decomposition products. The TGA thermograms of 4,5-dibromofluorescein polyurethanes are shown in figures 3,4.

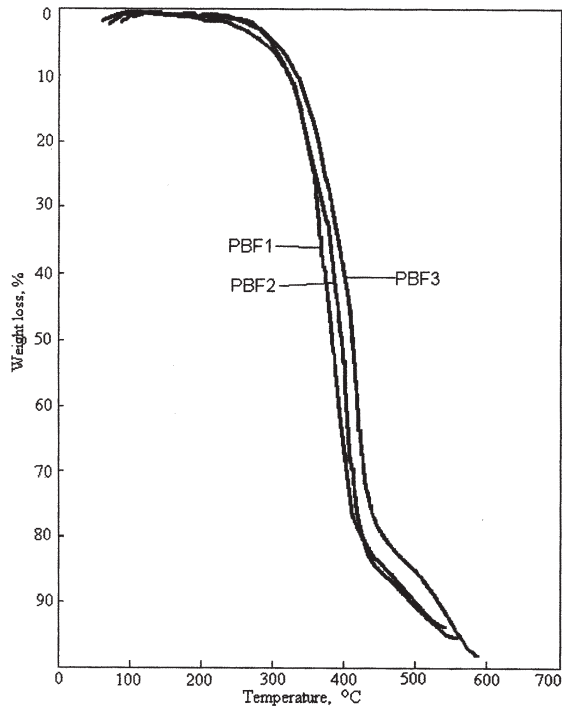


Fig. 3. TG curves of polyurethane elastomers crosslinked with glycerine

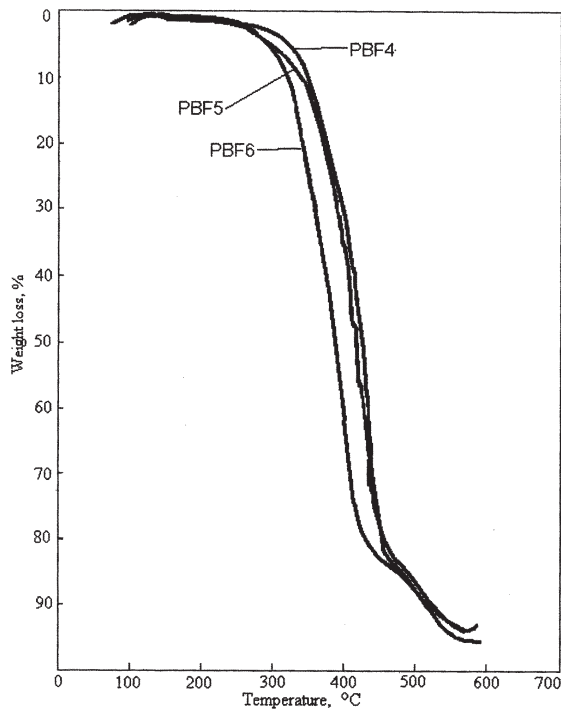


Fig. 4. TG curves of polyurethane elastomers crosslinked with castor oil

An examination of the data reveals that all of the above polymers are thermally stable up to 280-300 °C. As can be seen, polyurethane elastomers with a higher content of 4,5-dibromofluorescein initially have higher decomposition

temperatures and higher residues. The increase of initial decomposition temperatures may be attributed to the presence of bromine in these formulations.

Also, 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 [21].

Mechanical properties

Mechanical properties such as elongation (%), tensile strength, and hardness are important for polymer characterization and depend on the variation of the chain extenders' structure, which causes modifications of these properties [22].

Tensile strength is largely influenced by the presence of aromatic groups, length of chain extender, branching and cross-linking and degree of secondary bonding.

The stress-strain curves representing the various chain extenders (that have a common soft segment) are grouped in figures 5, 6.

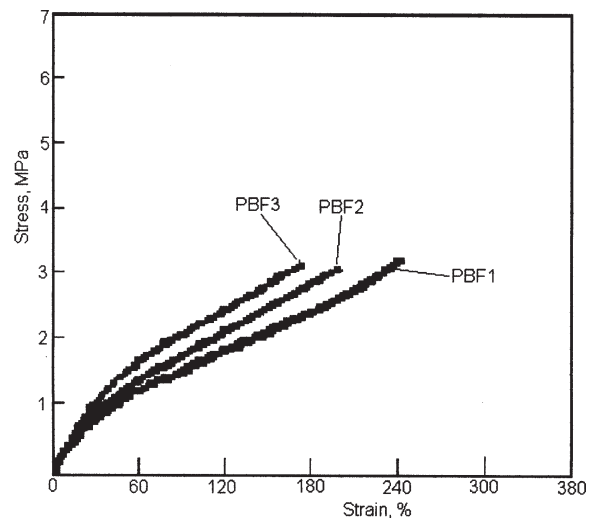


Fig. 5. Stress-strain curves of polyurethanes prepared with 4,5-dibromofluorescein and glycerine as crosslinker

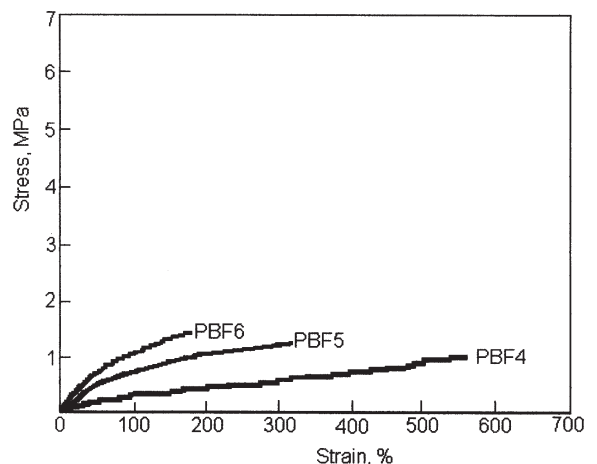


Fig. 6. Stress-strain curves of polyurethanes prepared with 4,5-dibromofluorescein and castor oil as crosslinker

In the case of polyurethane sheets with glycerine as a crosslinker, the tensile strength at break is of 3-3.5 MPa and maximum elongation is 180-250 %. Polyurethane sheets with castor oil as cross-linker display a strength of 1-1.5 MPa and elongation of 200-550 %. In this case, the dangling chain from the castor oil acts as a plasticiser thus increasing elongation.

The addition of 4,5-dibromofluorescein introduces some degree of flexibility for the polyurethane elastomers. The lower tensile strength in polyurethanes films is due to the low molecular-weight between the crosslinks and higher density of cross-links. It has been reported that hardness is primarily governed by the hard segment concentration [23]. Increase in elongation in polyurethane elastomer is due to the flexibility of the chain caused by the introduction of a chain extender.

Fluorescence spectra

The fluorescence emission phenomenon often occurs in cyclic, rigid molecules that contain p electrons, and is enhanced by the presence of electron-donating groups. The fluorescence emission spectra of the 4,5-dibromofluorescein polyurethanes films are presented in figures 7, 8.

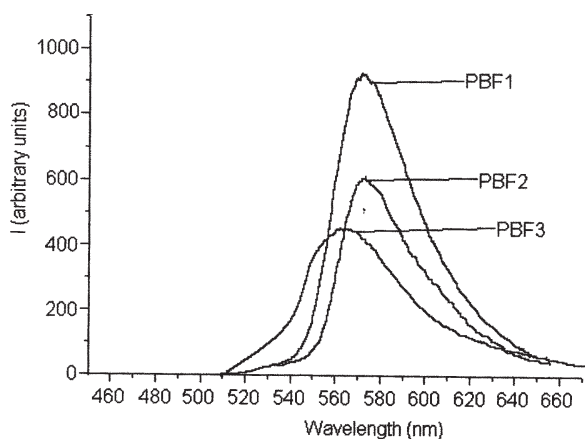


Fig. 7. Emission spectra of the polyurethanes prepared with 4,5-dibromofluorescein and glycerine as crosslinker

Amongst polyurethanes that were crosslinked with glycerine, the ones that had the largest quantity of 4,5-dibromofluorescein exhibited a fluorescence emission peak at 570 nm and an intensity of 900, while the polyurethanes created with the smallest amount of 4,5-dibromofluorescein presented a peak at 560 nm with intensity of 400. In the case of polyurethanes cross-linked with castor oil, a peak appeared at a wavelength of 590 nm (intensity of 750) for the sample obtained with the largest quantity of 4,5-dibromofluorescein and at 570 nm (intensity of 550) for polyurethane film with the smallest amount of 4,5-dibromofluorescein, as shown in figure 8.

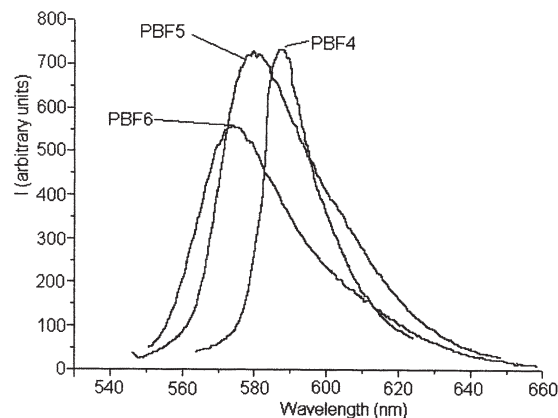


Fig. 8. Emission spectra of the polyurethanes prepared with 4,5-dibromofluorescein and castor oil as crosslinker

Comparing the data it can be seen that the polyurethanes obtained with glycerine showed stronger fluorescence intensity than the polyurethanes obtained with castor oil. This can be due to the presence of the rigid structure for polyurethane cross-linked with glycerine in comparison with polyurethane cross-linked with castor oil that have flexible moieties coming from the dangling chain of the castor oil.

Surface wettability

The contact angle (CA) is the angle at the junction of three phases – a drop of liquid on a solid surface, in an air environment. The contact angle reflects the tendency of a liquid to wet a surface. Surface wettability and reduced friction are considered to play a major role in the wearing comfort of implants. The wettability of polyurethane elastomers was examined by CA measurements using two probe liquids, water and ethylene glycol. Table 2 presents the contact angles and the work of adhesion obtained for the polyurethane elastomers depending on the hard segment composition used.

The sample with higher contents of 4,5-dibromofluorescein showed the lowest value of contact angle (PBF1) in the case of polyurethane crosslinked with glycerine. This means that the hydrophilicity of the final polyurethane film increases by incorporating the 4,5-dibromofluorescein into the PU formulations. These variations in contact angles can be ascribed to the modification of the surface chemistry of the PU samples.

In the case of polyurethanes cross-linked with castor oil we can see from the results that the hydrophilic character

Table 2
CONTACT ANGLE (θ) AND WORK OF ADHESION (W_a) VALUES OF
POLYURETHANE FILM SURFACES

Sample	Water		ethylene glycol	
	θ ($^\circ$)	W_a (mN/m)	θ ($^\circ$)	W_a (mN/m)
PBF1	82.5	82.3	75.4	60.1
PBF2	87.8	75.5	84.2	52.8
PBF3	111	46.6	82.3	54.4
PBF4	111.3	46.3	93.6	45
PBF5	104.3	54.8	85.5	51.8
PBF6	104.7	54.2	85.8	51.5

Sample	λ_{sv}^p (mN/m)	λ_{sv}^d (mN/m)	γ_{sl} (mN/m)	
			Water	ethylene glycol
PBF1	20.2	3.8	14.4	11.8
PBF2	19.6	1.7	18.6	16.5
PBF3	0.01	26.2	52.4	19.8
PBF4	1.2	10.8	38.5	15
PBF5	2.2	13	33.2	11.4
PBF6	2	13.1	33.7	11.7

p-polar, d-disperse

Table 3
INTERFACIAL TENSION FOR OBTAINED
SOLID-LIQUID SYSTEM (γ_{sl})
POLYURETHANE ELASTOMERS

of the final PU film decreases by increasing the contents of 4,5-dibromofluorescein into the final PU formulations. Polyurethane elastomers cross-linked with castor oil exhibit a hydrophobic behaviour with a high contact angle of about 105-110 deg.

This indicates that the surface energy of the oil component is lower than that of the glycerine-composed polyurethane, which can lead to the formation of a surface layer, in which the polyurethane hard component would be dominant.

The work of adhesion, W_a , was calculated using the following equation:

$$W_a = \gamma_{lv}(1 + \cos \theta)$$

where γ_{lv} is the surface tension of the liquid used for the contact angle measurement.

The work of the water adhesion to glycerine cross-linked PU surfaces decreases with the decrease of 4,5-dibromofluorescein contents.

The interfacial tension for a solid-liquid system (γ_{sl}) was calculated from the contact angle measurements using the following equation [24-26].

$$\gamma_{sl} = \left(\sqrt{\gamma_{lv}^p} - \sqrt{\gamma_{sv}^p} \right)^2 + \left(\sqrt{\gamma_{lv}^d} - \sqrt{\gamma_{sv}^d} \right)^2$$

The resulting interfacial tensions are listed in table 3.

The changes in the polar and dispersive components are attributed to the formation of different dispersive groups on PU film caused by the incorporation of 4,5-dibromofluorescein and various cross-linkers, which increase surface hydrophobicity and decrease the share of polar interactions between polymer and water. This phenomenon is due to the fact that the increase in contact angle values leads to a decrease in surface energy.

Conclusions

Two series of new self-colored cross-linked polyurethane elastomers containing 4,5-dibromofluorescein in the main-chain with excellent thermal stability and good mechanical properties were synthesized.

The thermal stability depends on the components present in the formulation. Polyurethane elastomers with a higher content of 4,5-dibromofluorescein have higher initial decomposition temperatures and higher residues.

The cross-linking process increases the urethane domain's rigidity and decreases the soft segment crystallinity. The addition of 4,5-dibromofluorescein introduces some degree of flexibility in the polyurethane elastomers.

The effects of various cross-linkers and the presence of the 4,5-dibromofluorescein on fluorescence were also

observed in different formulations, which indicated differences in localization and intensity of the emission spectra.

The present study revealed that the nature of the segment components in cross-linked elastomers could exert a significant influence on the surface properties.

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