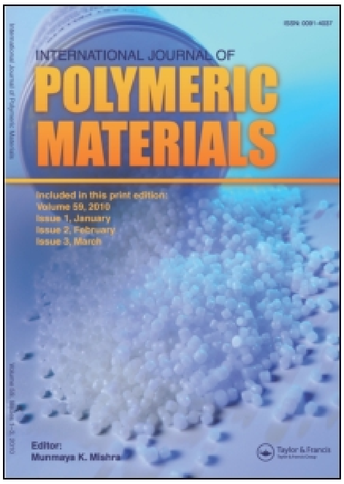

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PHOTOCHEMICAL DEGRADATION OF POLYMERS CONTAINING URETHANE GROUPS IN THE SOLID PHASE: INFLUENCE OF <i>S</i> BLOCK CATIONS ON THE DEGRADATION

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PHOTOCHEMICAL DEGRADATION OF POLYMERS CONTAINING URETHANE GROUPS IN THE SOLID PHASE: INFLUENCE OF *S* BLOCK CATIONS ON THE DEGRADATION

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Modification of the physico-mechanical properties of films made of biologically compatible polymers, with urethane groups, complexed with metallic ions from the s-block (Soft Block), have been investigated according to cation nature and photochemical irradiation time. Strain at the break, remnant elongation, elasticity modulus and resistance at the break were the main physico-mechanical properties measured. Experiments were carried out by irradiation with ultraviolet light, on solid film, under condition of accentuated degradation. Ions of both alkaline metals and alkaline-earth metals in the first step of irradiation improve the physico-mechanical properties. But in the middle of the investigated range they strongly decrease, concomitantly with the appearance of some deep photochemical induced structural modifications in the structure of the investigated polyesterurethane.

Keywords: cation, elasticity modulus, elongation at the break, ligand, photochemical degradation, polyurethanes

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INTRODUCTION

Macromolecular compounds with urethane groups have multiple uses. During the last years, a series of papers concerning this field were published [1–6].

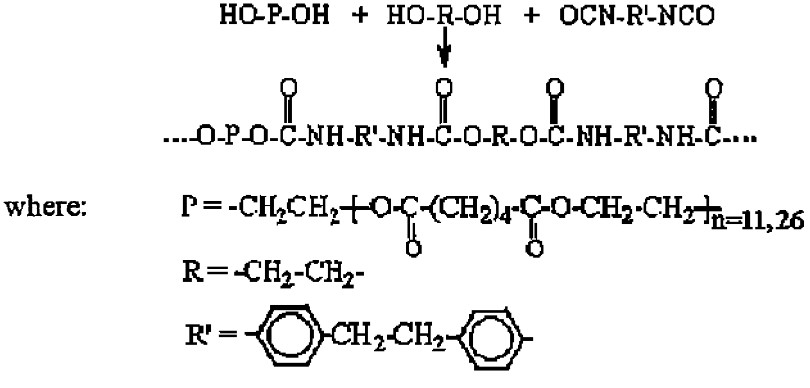
In several previous studies the authors were concerned with the study of thermal and photochemical degradation of polymers containing urethane groups in both solution [7–10] and solid phase [11,12]. Modification of the physico-mechanical properties of the polyesterurethane films has been investigated versus isocyanate structure [13], polyester structure [14], antioxidants structure and UV absorbents [15] as well as irradiation time.

This paper deals with an investigation of the influence of the cations of the *s*-block elements with their electronically structure ns^{1-2} having $n = 2 \div 6$ over modification of physico-mechanical properties of polyesterurethane films versus the irradiation time.

EXPERIMENTAL

The inorganic salts $LiNO_3$, $NaNO_3$, KNO_3, $RbNO_3$, $CsNO_3$, $Be(NO_3)_2$, $Mg(NO_3)_2$, $Ca(NO_3)_2$, $Sr(NO_3)_2$, $Ba(NO_3)_2$, delivered by Aldrich, were applied to these investigations.

The model ligand utilized in these studies is a polyesterurethane (PEU) with a content of 2.33×10^{-3} mol urethane/g obtained from the poly(ethylene adipate) *4* diol (PEA) with molecular weight of 2000, oxydryl index of 50 mg KOH/g, acidity index of 0.8 mg KOH/g, diphenyl ethane 4,4′-diisocyanate and ethylene glycol, according to the scheme [16].



Polyurethane microporous films with a specific surface of 5 square meters/g were obtained at 45°C by precipitation in water, from dimethylformamide as solvent, and were 0.5 mm in mean thickness. The treatment with metallic ions was carried out by immersion in aqueous solution with concentration of 10^{-3} mol ion gram 1^{-1} for 12 h, after which samples were dried under vacuum at 40°C for 48 h. The concentration of metalic ions attained through the microporous films by this treatment was determined by flamephotometry, emission and respectively absorption atomic spectroscopy and the values are in the range 10^{-5} to 10^{-4} moles ion-gram per g of urethane.

The samples were exposed to UV irradiations in a device of hexagonal shape. The distance between samples and lamp was 100 mm. A mercury lamp of medium pressure of LVF 100 type, placed in the center of the device, has been employed. The lamp was provided with thermostating mantle. The operating temperature was kept at 25 ± 0.5°C. The quantum flux, determined according to the literature cited [17] was 11.69×10^{16} quanta s^{-1}. The physico-mechanical properties were determined in an apparatus TIRA-TEST 2161 type, equipped with computer. The movement speed of its head was of 20 mm min^{-1}.

Both exposure to radiations and measurement of physico-mechanical properties were carried out in the atmosphere under normal humidity conditions.

The polyurethane films modified with cations from *s*-block were irradiated with UV light for 3, 5, 7.5, 12.5, 25, 35, and 50 h. These seven times of irradiation were chosen because up to 30 h irradiation time the reference sample has deep chemical transformation, and the physico-mechanical properties exhibit the biggest modifications [11,12]. After these irradiation times, in almost all cases, degradation is so strong that its practical interest becomes un-important. The polyesterurethane untreated with metallic ions was used as reference sample (R).

The polyesterurethane treated with metallic ions was noted as PEU-M, where M = Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba.

RESULTS AND DISCUSSION

The modifications in the physico-mechanical properties of the urethane groups containing polymers with metallic ions, at respective irradiation times, in comparison with the reference sample, are represented in Figures 1–4.

If the samples with urethanic groups, which have retained metallic ions, are not irradiated photochemically or heated, their physical and

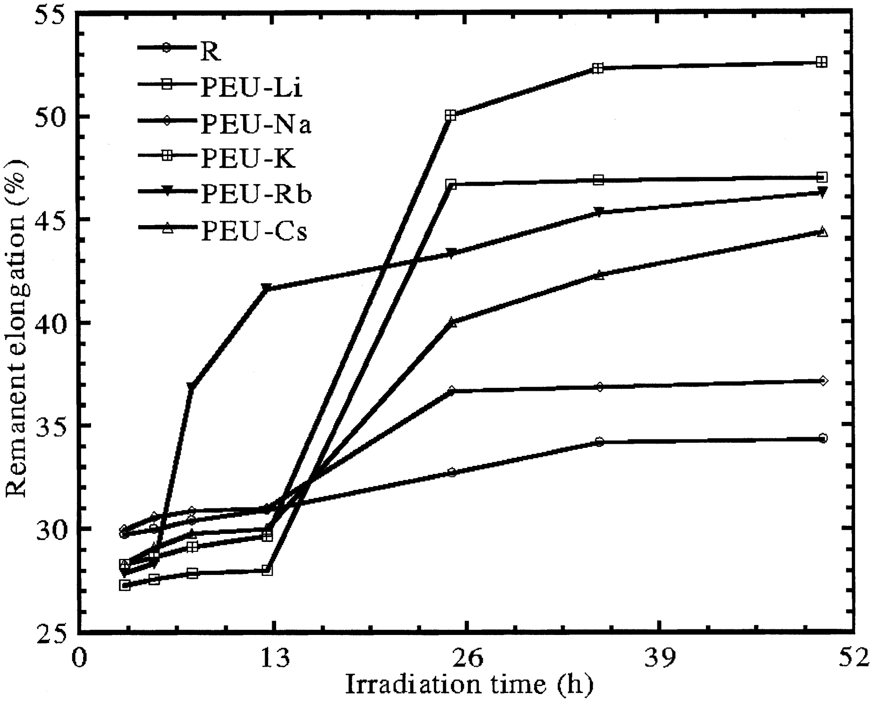


FIGURE 1 Modification of the remnant elongation versus reference for ligand with urethane groups that contain ions of alkaline metals.

mechanical properties do not modify. In films containing metallic ions and irradiated photochemically, these properties are modified substantially.

The remnant elongation is lower than the reference value up to 5 h of irradiation, PEU-Na being an exception. After 12.5 h of irradiation all samples have a remanent elongation larger than the reference due to the deep structural modifications created by elimination of certain compounds with small molecules from the macromolecular chain structure. An interesting behavior can be seen for the sample with rubidium whose remnant elongation increases suddenly in the range of 3 ÷ 12.5 h or irradiation (Figure 1).

Elongation at break decreases below reference value for all ions of alkaline metals (Figure 2).

For elongations of 50%, the elasticity modulus increases, the curve attaining a maximum at 12.5 h of irradiation in the case of PEU-Na, followed by a new decrease for all samples below the reference value (Figure 3).

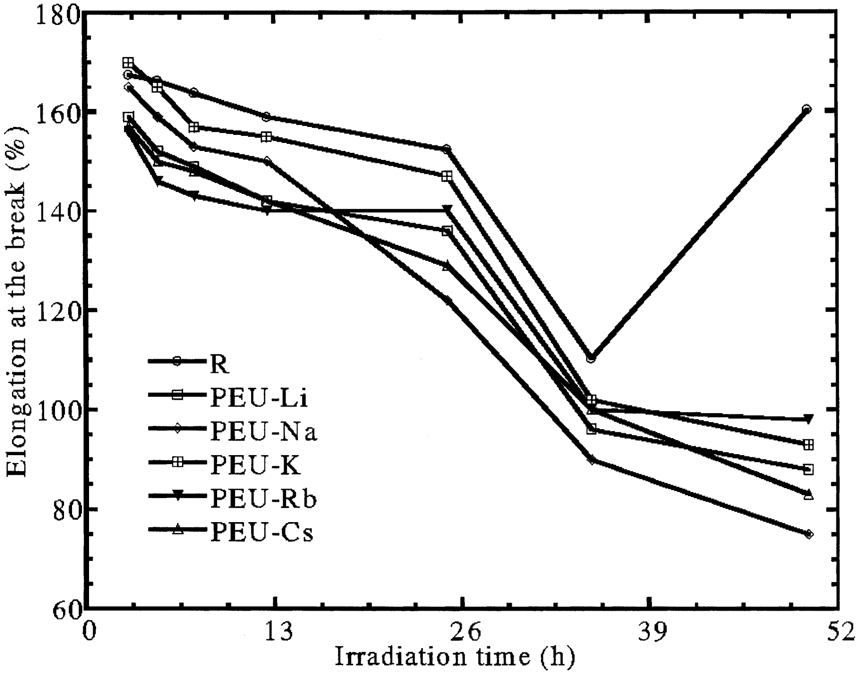


FIGURE 2 Modification of the elongation at break versus reference for ligand with urethane groups that contain ions of alkaline metals.

For elongation of 100% for the Cs^+, Rb^+ and Li^+ ions, the elasticity modules decrease below that of reference sample, having a maximum value for PEU-Na and intermediate value for PEU-K. After 25 h irradiation times, all samples have elasticity modulus lower than the value of the reference, the series being identical for the other irradiation times, indicating deep structural transformations and the possibility of hydrogen bonds being established between the macromolecular chains, transforming the polymer from an elastomer to a rigid and friable material (Figure 3).

The resistance to break varies according to a similar curve, presenting a minimum for the Li^+ and Cs^+ ions for Rb^+ it attains the value of the reference and for Na^+ and K^+ it goes beyond the value of the reference (Figure 4).

Finally, between 3 and 12.5 h of irradiation time, except for the elongation at break, all physico-mechanical properties are improved.

The curves of physico-mechanical properties are of very similar shape. All curves exhibit a minimum in the case of Na^+. The K^+ and Rb^+ have an intermediate behavior.

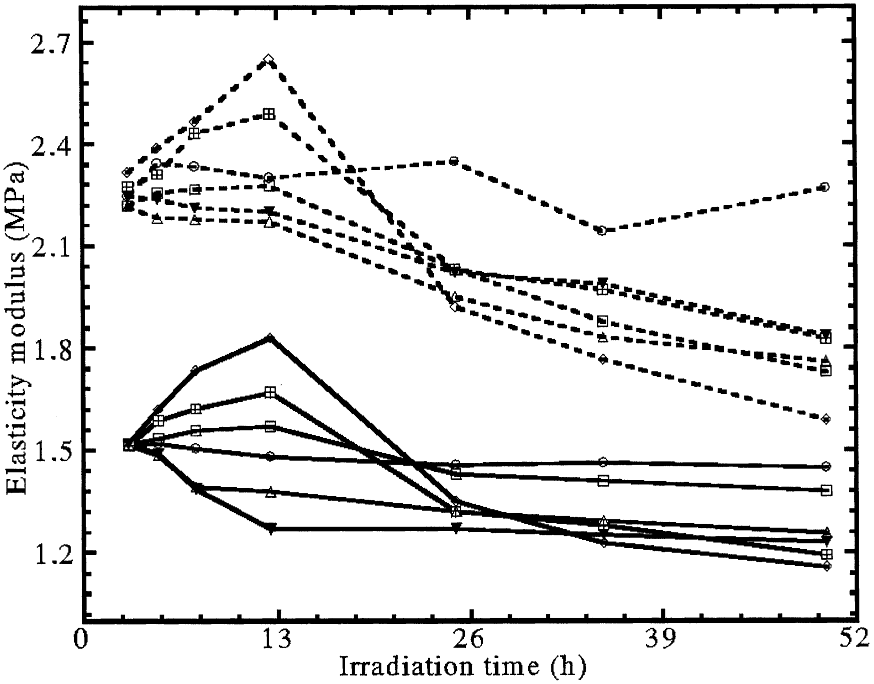


FIGURE 3 Modification of the elasticity modulus at elongation of 50% (—) and 100%(---) versus reference for ligand with urethane groups that contain ions of alkaline metals. ○: R, □: PEU-Li, ◇: PEU-Na, ⊞: PEU-K, ▼: PEU-Rb, △: PEU-Cs.

The alkaline-earth ions differently influence the photochemical degradation of polyesterurethane, in the two irradiations ranges mentioned above.

Remnant elongation: Figure 5 shows that at 12.5 h of irradiation, the reference polyesterurethane has the biggest permanent elongation, but after 25 h of irradiation, the phenomenon is inverted. The reference has in this case the least remnant elongation, due to the fact that deep chemical modifications took place in the chemical structure of polyesterurethane.

Elongation at break: A decrease below the value of the reference for all irradiation ranges is observed. As is apparent from Figure 6, in the case of the reference sample there is a strong decrease of the elongation at break at 35 h irradiation time. Conversely, the samples with metallic ions exhibit a linear decrease for all ions, except the sample complexed with Mg^{2+}.

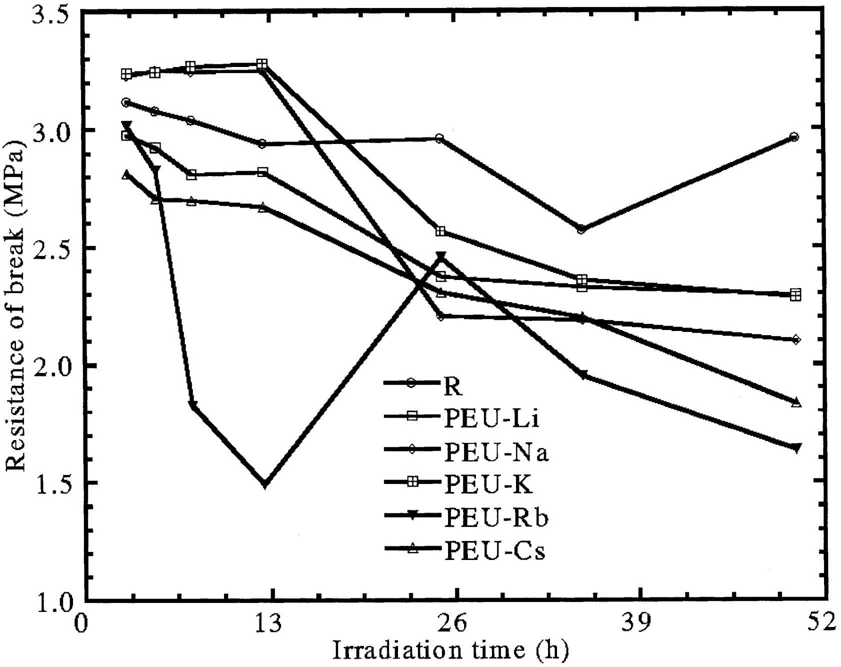


FIGURE 4 Modification of the resistance to break versus reference for ligand with urethane groups that contain ions of alkaline metals.

Elasticity modulus at elongation of 50% and 100%: For both irradiation ranges, it can be seen that the elasticity modulus for elongation as high as 50% increases. This fact can be explained by the increase of the reticulation between macromolecular chains of the polyurethane.

If the fact is not excluded, at an increase of elasticity modulus to participate also the water molecules of the hydrated ions of the $[M(H_2O)_n]^{2+}$ type crystallization. The phenomenon is also repeated for elongations of 100%. All samples have an elasticity modulus larger than the reference (Figure 7).

Resistance to break: In the case of the breaking strain it can be seen that the reference has, after the first 12.5 h of irradiation, the best breaking strain, with all modifications that take place in this time range in the structure of PEU. After 25 h of irradiation, the structural modifications get enhanced in the presence of ions of alkaline and alkaline-earth metals, the reference being in the middle of the series (Figure 8).

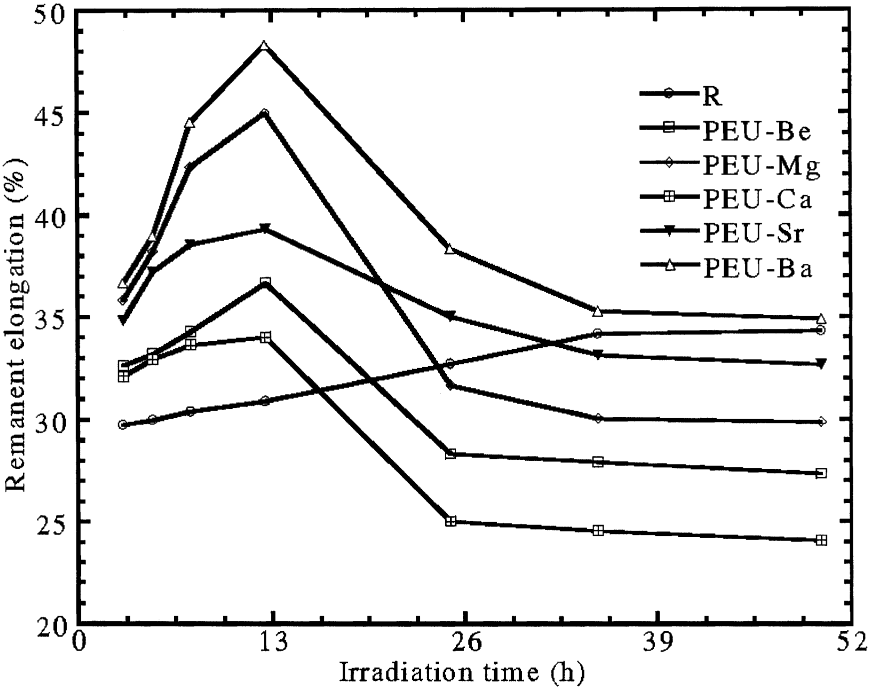


FIGURE 5 Modification of the remnant elongation versus reference for ligand with urethane groups that contain ions of alkaline-earth metals.

In Figures 9 and 10, modification of the physico-mechanical properties relative to the reference value is represented as function of the ionic radii of the respective cations. Pedersen and Busch obtained similar curves as a function of ionic radius for variation of the stability constants of alkaline cryptands [18,19]. Taking into account this similarity, it can be supposed that in our case coordination compounds with different ionocovalance degree between the functional urethane and ester groups and the ions of alkaline metal can be formed. Taking into consideration also the polymer conformation, the curves presented in Figures 9 and 10 indirectly reflect the stability of these coordination structures.

Action of the alkaline metals ions M^+ under these conditions can be appreciated by the term "ionic potential." Let us consider the ionic potential as being proportional to the ratio of electric charge (z) to ion radius under discussion (z/r). This is an energetic characteristic, which can be considered in the first approximation as a measure of the electrostatic field created by the cation. The quantity calculated in

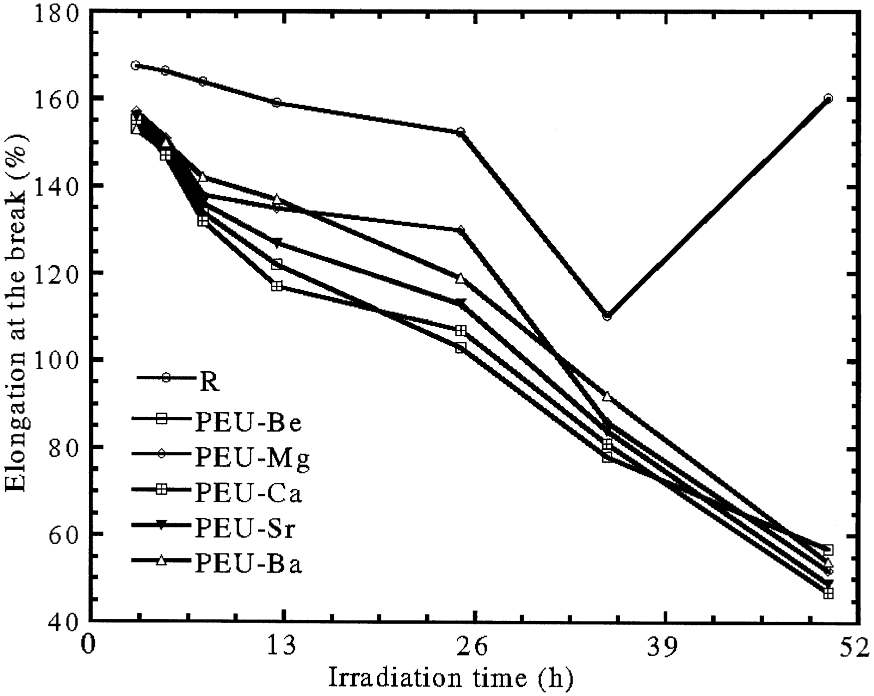


FIGURE 6 Modification of the elongation at break versus reference for ligand with urethane groups that contain ions of alkaline-earth metals.

such a manner is dependent on dielectric constant of the medium. Iatzimirski using a similar quantity (z^2/r) has estimated the ion-covalent degree of chemical bonds established in coordination compounds formed between cations and functional groups in the studied polymers [20]. Taking into account the value of ionic potential and the graphic representations in Figures 9 and 10, the following comments may be done. The Li^+ ion with an ionic potential of 1.66 creates a stronger electrostatic field interacting much strongly with the polar groups in the chemical structure of polyurethane. For this reason, besides hydrogen bonds and other bonds already existing, other weak interactions appear between macromolecules of PEU-Li [21]. These bonds lead to additional reticulation, which finally modify unfavourably, in comparison with other ions in series, the physico-mechanical properties [22].

Diminution of the physico-mechanical properties in the case of polyurethane, which contains ions of Rb^+ (PEU-Rb) has, probably, another explanation. The Rb^+ was a weak ionic potential, i.e. 0.602, therefore it creates a weak electric field, but has a big ionic

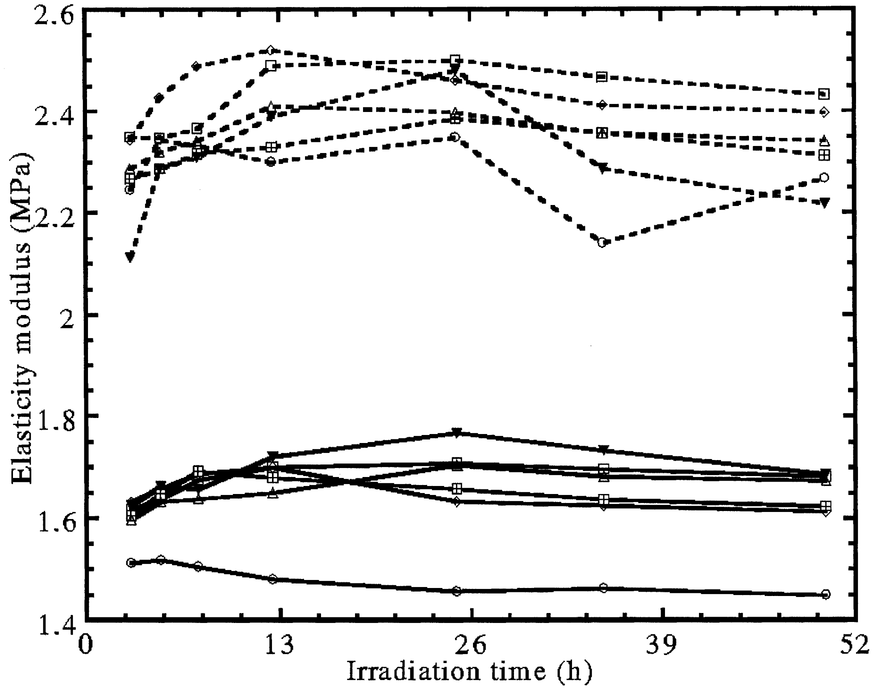


FIGURE 7 Modification of the elasticity modulus at elongation of 50% (—) and 100% (---) versus reference for ligand with urethane groups that contains ions of alkaline-earth metals. ○: R, □: PEU-Be, ◇: PEU-Mg, ⊞: PEU-Ca, ▼: PEU-ST, △:PEU-Ba.

volume, being an element in the sixth period of periodic system. Penetrating between the polyurethane macromolecules and moving them away, it prevents the steric approach of certain sequences of the polar groups that participate in formation of hydrogen bonds such as the –NH–CO–O– and –CO–O– groups, so that it contributes to the diminution of the physico-mechanical properties of polyurethane.

It is well known that polyurethanes of the type studied in this investigation are elastomers whose weak elastic properties are due mostly to the hydrogen bonds established between polar groups in their structure [21–23].

The Na^+ and K^+ have an intermediate behavior. In the case of Na^+ ion, ionic potential and volume have optimum values to establish some bonds between the PEU-Na macromolecules, which can be detached and reformed during strain according to a mechanism similar to detaching and remaking of the hydrogen bonds between

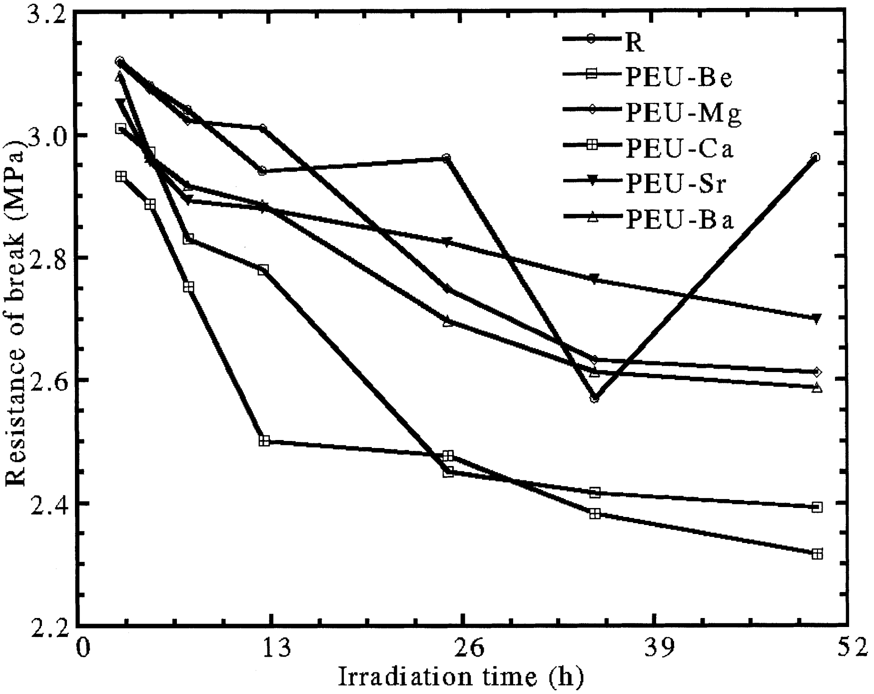


FIGURE 8 Modification of the resistance to break versus reference for ligand with urethane groups that contain ions of alkaline-earth metals.

macromolecules of PEU as a reference under mechanical strain. We may not exclude the fact that due to the created electric field, the ions of alkaline metals, depending on their ionic potential, may retain around them molecules of water [24]. After 12.5 h of irradiation the physico-mechanical properties of polymers containing ions of the alkaline metals improve, except for breaking tension which decreases. After 25 h of irradiation, the polymer containing alkaline metal ions undergoes severe degradation. Looking over the experimental, it can be observed that all physico-mechanical properties decrease relative to the reference sample. A singe, 5% improvement is seen for the elasticity modulus at elongation of 50%, in the case of polyesterurethane containing ions of Li^+ (PEU-Li) relative to the reference. The elasticity modulus at an elongation of 100% is close to reference. Under this irradiation range, variation of the physico-mechanical properties is unsimilar to those from 12.5 h of irradiation.

The least modification of the physico-mechanical properties has the polyesterurethane containing the K^+ ions (PEU-K). Explanation can

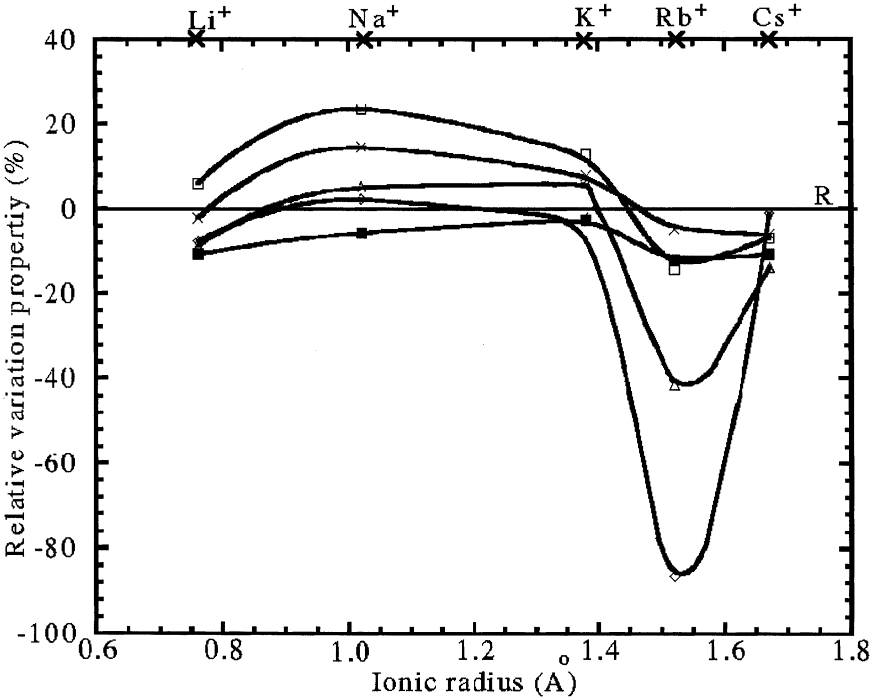


FIGURE 9 Relative variation of the physico-mechanical properties of polymers with urethane groups containing ions of the alkaline metals versus ionic radius after 12.5 h of irradiation. □: modulus at elongation of 50%, x: modulus at elongation of 100%, ◇: remanent elongation, ■: elongation at break, △: resistance to break.

be given by the fact that K^+ ions, with a radius of 1.33 Å are not hydrated. The Na^+ ion, which up to 12.5 h of irradiation with ultraviolet light retained around it molecules of water, by further irradiation loses the water, contributing to a deeper degradation of polyurethane by photohydrolytic degradation especially the ester structure.

As in the case of ions of the alkaline metals, in Figures 11 and 12 are plotted modifications of physico-mechanical properties against both reference sample and ionic radius of cations of the alkaline-earth metals. Taking into account the values of ionic potentials and based on these plots, for 12.5 h of irradiation, the following conclusions can be drawn.

In the case of remnant elongation, the Be^{2+} ion with an ionic potential of 5.00 creates more intense electrostatic field interacting

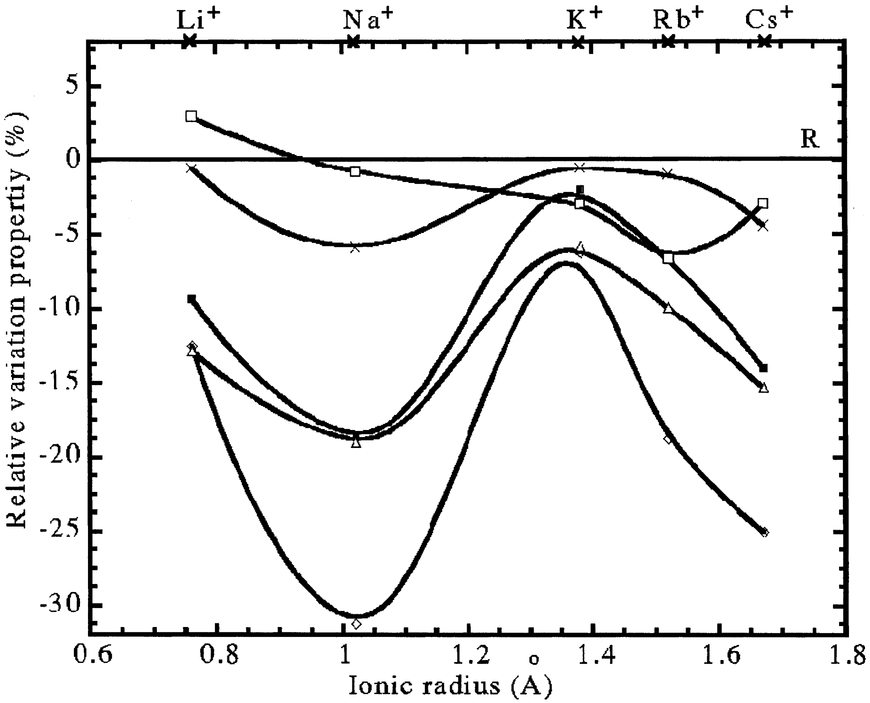


FIGURE 10 Relative variation of the physico-mechanical properties of polymers with urethane groups containing ions of the alkaline metals versus ionic radius after 25 h of irradiation.

strongly with the functional groups in PEU, creating additional bonds, having a similar behavior as the Li^+ ions.

The Mg^{2+} having an ionic potential of 2.33 coordinates with both urethane and ester group, and the concentration in the hydrogen bonds decreases, leading to the higher remnant elongation [25].

The Ca^{2+} ion with a electrostatic interaction of 1.75 order has, in their case, an interesting behavior in the case of permanent elongation, the PEU-Ca having the smallest value of this property. The PEU-Ba has a similar behavior as PEU-Cs.

In the case of the elasticity modulus at elongations of 50% and 100%, breaking strain and breaking tension a poorer dependence can be seen of the physico-mechanical properties values on ionic radius of cation, the minimum values being recorded in the case of PEU-Ca, the values of breaking strain and breaking tension being below the reference value except breaking tension for PEU-Mg.

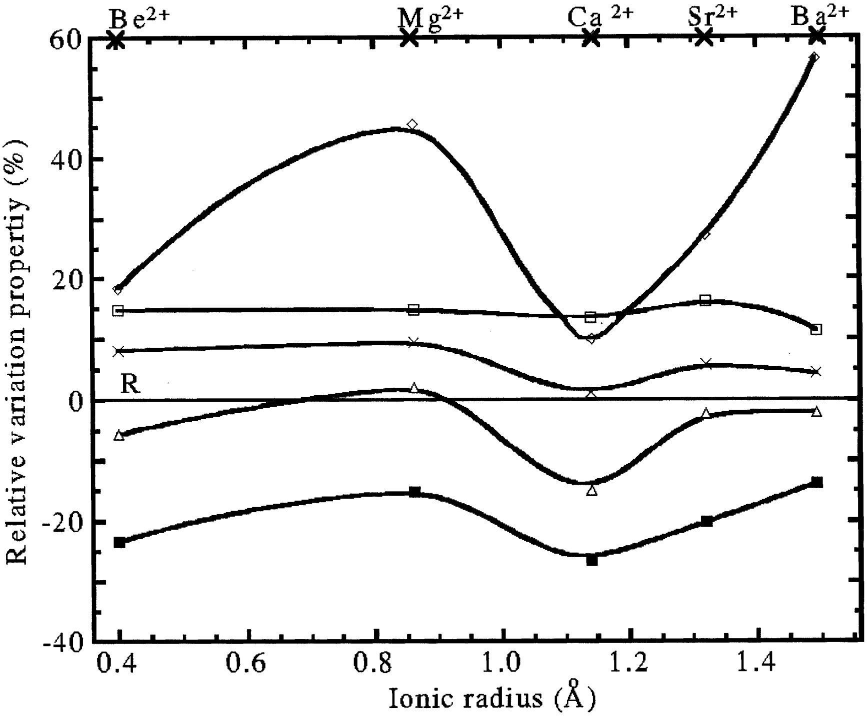


FIGURE 11 Relative variation of the physico-mechanical properties of polymers with urethane groups containing ions of the alkaline-earth metals versus ionic radius after 12.5 h of irradiation. □: modulus at elongation of 50%, x: modulus at elongation of 100%, ◇: remnant elongation, ■: elongation at break, △: strain at break.

After 25 h of irradiation time, the values of elasticity modulus at elongations of 50% and 100% are higher than reference or very close to it, while the values for remnant elongation, breaking strain and breaking tension are lower than the reference value, except PEU-Mg, which is closer to reference value.

Water molecules may play a role in the degradation of the poly(ester urethanes) under U.V. irradiation, but we have failed to find any quantitative correlations of their effects on degradation.

CONCLUSIONS

Referring to the influence of metal ions in the *s*-block on photochemical degradation of polyesterurethane based on diphenyl ethane 4,4′-diisocynate, the following conclusions can be drawn:

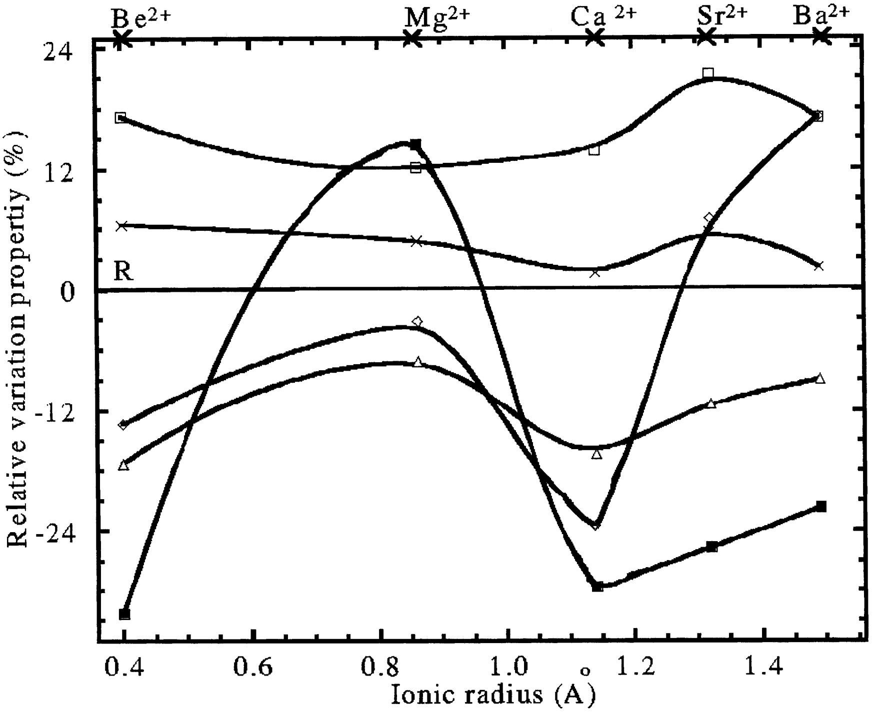


FIGURE 12 Relative variation of the physico-mechanical properties of polymers with urethane groups containing ions of the alkaline-earth metals versus ionic radius after 25 h of irradiation. □: modulus at elongation of 50%, x: modulus at elongation of 100%, ◇: remnant elongation, ■: elongation at break, △: strain at break.

i) During the first irradiation hours the ions of alkaline metals improve the elasticity modulus at elongations of 50% and breaking strain, and as a consequence of this phenomenon the breaking tension decreases. On the other hand, decrease of the breaking tension is a result of reticulation that leads to an increase of both elasticity modulus and stain at break. After 25 h of irradiation under UV light, all physico-mechanical properties decrease, but transformations in the polymer structure in the presence of these ions are much stronger than in the reference sample irradiation under the same conditions.
ii) In all cases, in the first step of photochemical irradiation, an increase of the elasticity modulus can be seen, a fact that points to the appearance of branches and photochemical induced reticulations, which may be exploited from a practical point of view.

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