

Flexible aliphatic poly(isocyanurate-oxazolidone) resins based on poly(ethylene glycol) diglycidyl ether and 4,4'-methylene dicyclohexyl diisocyanate

Ahmed Bakry,¹ Renato Aversano,² Lucio D'Ilario,² Valerio Di Lisio,² Iolanda Francolini,² Antonella Piozzi,² Andrea Martinelli²

¹Department of Chemistry, Helwan University, Ain, Cairo, 11795, Egypt, Helwan

²Department of Chemistry, University of Rome La Sapienza, P.Le a. Moro 5, Rome, 00185, Italy

Correspondence to: A. Martinelli (E-mail: andrea.martinelli@uniroma1.it)

ABSTRACT: New flexible aliphatic oxazolidone-isocyanurate networks (AISOX) are obtained by reacting a low molecular weight diisocyanate (4,4'-methylene dicyclohexyl diisocyanate, H₁₂MDI) and a macro-diepoxyde (poly(ethylene glycol) diglycidyl ether, $M_n = 526$, PEGDGE) in different molar ratio. The curing reaction, carried out from 25 °C to 200 °C, is studied by using DSC and FTIR. The effect of the molar ratio of the two monomers on thermal and mechanical properties of AISOX resins is investigated by DSC, thermogravimetric analysis, stress-strain measurements and optical microscopy. Independently from the feed composition, it is observed that the reaction steps are: (i) partial hydrolysis of isocyanate caused by water traces, (ii) incomplete trimerization of isocyanate to give isocyanurate, and (iii) formation of oxazolidone and complete conversion of isocyanate. At the highest concentration of the soft macrodiepoxyde (PEGDGE), the AISOX resin is in the rubbery state at room temperature and shows an elastomeric behavior. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43404.

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INTRODUCTION

Polyisocyanurate resins show applicative outstanding properties in terms of chemical, mechanical, electrical and thermal features. Generally, aromatic diisocyanates are used for preparation of these resins. Indeed, in proper conditions, aromatic diisocyanates trimerizes in isocyanurate rings leading to a densely cross-linked network, characterized by high stiffness, good electric resistance as well as chemical (hydrolytic), thermal, and dimensional stability.¹ However, the obtained materials suffer from high brittleness that limits their use in some applications. To decrease the crosslinking density by spacing apart the isocyanurate rings, a low molecular weight diepoxyde is usually added. An oxazolidone group is produced from the reaction between the epoxyde and the diisocyanate groups. Like isocyanurate, the oxazolidone ring is thermally and chemically stable. Therefore, the resulting poly(isocyanurate-oxazolidone) resins (also called ISOX) can exhibit thermal, mechanical and electrical properties better than the polyisocyanurate resins.² In addition, the mechanical properties of these poly(isocyanurate-oxazolidone) resins can be modulated by varying either the chemical struc-

ture of the reagents or the isocyanate:epoxyde molar ratio (r).³⁻⁷ Particularly, for $r = 1$, a linear high molecular weight polyoxazolidone can be obtained if the isocyanate trimerization is avoided. The reaction carried out with an isocyanate excess ($r > 1$) brings about a cross-linked resin, containing both isocyanurate and oxazolidone rings. In this latter case, the isocyanate concentration increases the cross-link density, the glass transition temperature (T_g) and the stiffness of the material.^{7,8}

ISOX resins are generally employed as matrices in high performance composites for heavy-duty applications, when high softening point, low flammability, hydrolytic resistance, chemical and solvent resistance as well dielectric rigidity are required. In addition, differently from other formulation for thermoset resins, liquid isocyanate and epoxy show lower viscosity. Moreover, in comparison to other isocyanate based resins, such as polyurethanes or polyureas, the isocyanurate or oxazolidone groups are formed at high temperature, well above room temperature. This permits to prepare casting resins with a long pot-life without blocking the isocyanate groups. However, since epoxyde can react with isocyanurate ring to give oxazolidone, blocked

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polyisocyanurate prepolymers could be anyway employed. This procedure makes the application process easier and increases the worker safety, allowing a higher control on resin pot-life, viscosity, and reagent vapor tension.⁹

In the literature, most of the studies report the preparation of poly(isocyanurate-oxazolidone) copolymers based on aromatic diepoxides and aromatic diisocyanates.^{3,10,11} Only few works concern the use of aliphatic and/or cycloaliphatic isocyanate compounds for the preparation of polyisocyanurates or polyoxazolidones.^{12–14} Poly(isocyanurate-oxazolidone)s based on aliphatic compounds show some advantages compared to those based on aromatic materials, such as UV stability and higher health safety.¹⁵

In this article we report the synthesis and the characterization of novel aliphatic isocyanurate-oxazolidone copolymers (AISOX resins) based on and 4,4'-methylene dicyclohexyl diisocyanate (H_{12} MDI) as aliphatic diisocyanate and poly(ethylene glycol) diglycidyl ether (PEGDGE) as the aliphatic diepoxide. The choice of the flexible macro-diepoxide was made to obtain new casting resins able to combine low softening point and mechanical flexibility with the typical ISOX features, such as simple processing procedure, hydrolytic and thermal stability. Moreover, the aliphatic character of monomers could increase the safety of the formulation. In fact, H_{12} MDI is currently employed as a building block in different polyurethane products, including polyurethane resins, aqueous dispersions, and elastomers for biomedical applications, showing the possible degradation products lower toxicity than those from hexamethylene diisocyanate or 4,4'-methylene diphenyl diisocyanate based materials.^{16–18} As far as the ISOX resins are concerned, H_{12} MDI was used only in mixtures with aromatic compounds, such as the diglycidyl ether of Bisphenol A, to obtain membranes for the separation of aromatic and aliphatic hydrocarbons.¹⁹

To the best of our knowledge, the monomer combination that we used was the first example in this area. The mechanism of the polymerization reaction as well as the influence of the diisocyanate:diepoxide molar ratio (r) on the thermal and mechanical properties of the AISOX resins were investigated. It was evidenced that the H_{12} MDI content in the reaction feed influenced the resin crosslink density, the glass transition temperature and the material stiffness. The sample with the minimum crosslink density showed an elastomeric behavior and a glass transition temperature of -13 °C.

EXPERIMENTAL PROCEDURE

AISOX Synthesis

Poly(isocyanurate-oxazolidone) copolymers were obtained by the bulk reaction between 4,4'-methylene dicyclohexyl diisocyanate (H_{12} MDI, Aldrich) and poly(ethylene glycol) diglycidyl ether (PEGDGE, $M_n = 526$, Aldrich) in different molar ratios ($r = H_{12}MDI:PEGDGE$). PEGDGE was dried under vacuum at 80 °C. All the other reactants were used as received. The absence of diisocyanate hydrolysis products was checked by FTIR analysis before its use. H_{12} MDI was rapidly mixed with PEGDGE at room temperature, giving a clear and a homogeneous mixture

Table I. Reaction Mixture Compositions and Codes of the Cured Resins

Reaction mixture code	$H_{12}MDI:PEGDGE$ molar ratio (r)	AISOX resin code
mixAISOX100	1.00	AISOX100
mixAISOX133	1.33	AISOX133
mixAISOX200	2.00	AISOX200
mixAISOX250	2.50	AISOX250

(mixAISOX). Triethylamine, used as the catalyst (Fluka), was then introduced (1 wt % with respect to $H_{12}MDI$ amount) before the curing process.^{8,20}

In Table I the feed composition and the codes of the reacting mixtures and resins after curing are reported.

Characterization of the Curing Process

The curing process was studied by differential scanning calorimetry (DSC) by using a Mettler DSC822e apparatus. The reaction mixtures (about 10 mg) were heated at 3 K min^{-1} from +25 °C to +200 °C under nitrogen atmosphere and kept at 200 °C to complete the curing.

The reagent conversion and the product formation in the curing process were analyzed by FTIR. Particularly, the reaction mixture was heated in DSC at 3 K min^{-1} from 25 °C to predetermined temperature up to 200 °C. Then, the samples into the DSC pans were rapidly cooled (-30 K min^{-1}) to room temperature, collected and analyzed by infrared spectroscopy (FTIR). The spectra were acquired in attenuated total reflection mode (ATR) by using a Thermo Nicolet 6700 instrument equipped with a Golden Gate diamond single reflection device (Specac). Measurements were accomplished at a resolution of 4 cm^{-1} and by co-adding 200 scans.

The progress of the curing reaction was followed by recording the integrated area variation of the reagent absorption bands at 2260 and 905 cm^{-1} for isocyanate and epoxy, respectively. The maximum absorbance of the isocyanate and epoxy groups was determined from the initial spectrum of the different mixtures without the catalyst.

Since different species were formed during the curing, in addition to the expected oxazolidone and isocyanurate groups, all absorbing in the C=O stretching region between 1600 cm^{-1} and 1825 cm^{-1} , the carbonyl band was deconvolved by Gaussian functions by Peakfit software (SeaSolve Software Inc.). The number and the position of Gaussian functions were determined by the second derivative of the smoothed spectra (Savitzky-Golay, 15 pt, 3rd order polynomial), base-line being corrected between 1825 cm^{-1} and 1600 cm^{-1} .

Characterization of the AISOX Resins

The thermal properties of the fully cured resins were characterized by DSC, heating about 5 mg of sample from -100 °C to +200 °C at 10 K min^{-1} under nitrogen atmosphere. The thermal stability of each AISOX resin was studied by thermal gravimetric analysis (TGA) by using a Mettler TG 50 thermobalance. About 5 mg of sample was heated from +25 to +500 °C in nitrogen atmosphere at 10 K min^{-1} .

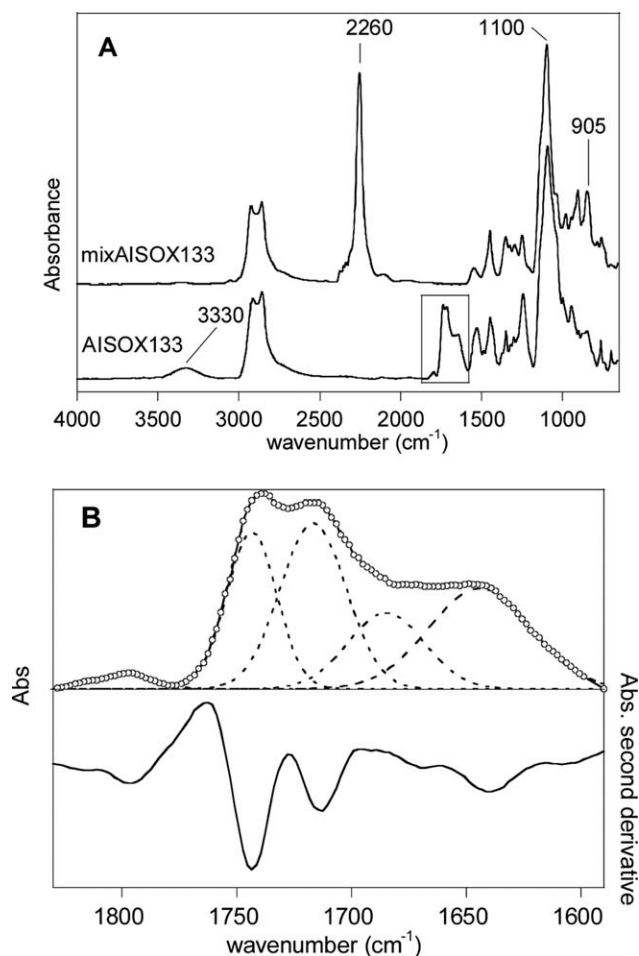


Figure 1. FTIR spectra of mixAISOX133 (without catalyst) and AISOX133 resin obtained after curing at 200°C for 2 h (A). Enlargement of the AISOX133 carbonyl stretching zone (1825–1600 cm⁻¹) and its second derivative (B). The dashed lines show the Gaussian functions used to decompose the band and the solid line is their sum.

The mechanical properties of the AISOX resins were investigated on samples prepared in rectangular Teflon molds, sealed in Pyrex vials under N₂ atmosphere. The curing process was carried out in an oil bath by heating the samples with the same temperature program used in the experiments performed in the DSC pans. Tensile stress-strain curves were recorded by an Instron 4502 mechanical tester with a 2 kN load cell at a cross head speed of 10 mm min⁻¹. Stress-strain curves were reported as the apparent stress $\sigma = F/A$ (Pa), where F is the tensile force and A is the initial cross-sectional area of each test specimen, versus the strain $\varepsilon = (L-L_0)/L_0$, where L_0 and L are the initial and the deformed sample length, respectively. The Young modulus E_y was calculated from the slope of the initial linear region of the stress-strain curves while the tensile strength was taken as the maximum stress. The tensile set, defined as $100x(L_b-L_0)/L_0$, was evaluated by measuring the sample length L_b 10 min after the break.

The morphology of the AISOX samples, stressed up to the break point, was investigated by transmission optical microscopy (OM) analysis performed by using an Optiphot2-Pol light

microscopy (Nikon). The images were acquired by a Motic Image Plus 2.0 ML camera.

RESULTS

In this study, flexible aliphatic poly(isocyanurate-oxazolidone) resins were prepared by curing in bulk different formulations of an aliphatic diisocyanate, H₁₂MDI, and an aliphatic macro-diepoxyde, PEGDGE, in the presence of triethylamine as a catalyst.

As described in Experimental section (Table I), different H₁₂MDI:PEGDGE molar ratios were employed to modulate thermal and mechanical properties of the resulting resins. The curing process of the different mixtures was carried out in DSC and analyzed by FTIR. In Figure 1(A), the spectrum of mixAISOX133 (without catalyst) before the curing process and the spectrum of the fully cured AISOX133 resin kept after the dynamic heating at 200 °C for 2 h are reported.

As it can be seen, in the adopted curing conditions the bands related to the isocyanate (2260 cm⁻¹) and epoxy (905 cm⁻¹) groups disappeared suggesting the completion of the curing process.

In Figure 1(B), an enlarged view of the carbonyl stretching zone (1825–1600 cm⁻¹) and its second derivative are reported. The complexity of this band indicates that in addition to the expected oxazolidone and isocyanurate groups other species were formed during the curing (Supporting Information Figure S1). The carbonyl band was deconvolved by Gaussian functions [dashed lines in Figure 1(B)] to have an estimation of the position and relative concentrations of the different formed species. FTIR band assignment of the mixAISOX133 and AISOX133 (C=O stretching region) used for the curing process analysis are reported in Table II.

These band assignments were accomplished according to literature data or from spectra of model molecules obtained by us and reported in Supporting Information.

Table II. FTIR Band Assignments of mixAISOX133 and AISOX133 (C=O Stretching Region) Used for the Curing Process Analysis

Wavenumber (cm ⁻¹) Assignment	
mixAISOX133	
2260	—N=C=O stretching
905	asymmetric in-plane epoxy ring deformation
AISOX133 (C=O stretching region)	
1800	Oxadiazine trione ^a
1740	Oxazolidone ^{b,d}
1715	Isocyanurate ^{c,d}
1670	free urea carbonyl groups ^e
1639	hydrogen-bonded urea carbonyl groups ^{b,e}

^a From Ref. 21.

^b Supporting Information.

^c From Ref. 22.

^d From Ref. 23.

^e From Ref. 24.

Particularly, urea and carbon dioxide were formed during the curing from the reaction of isocyanate with water (see Supporting Information Figure S1). This reaction occurred even when the curing was carried out under N_2 flux, probably due to PEGDGE hygroscopicity and the presence of triethylamine able to catalyze also the isocyanate-water reaction.^{25,26} The evolved carbon dioxide can further react with the isocyanate to give a cyclic anhydride, oxadiazine trione, characterized by the typical carbonyl stretching at high wavenumber (1800 cm^{-1}). Together with the trimer formation (isocyanurate), these side-reactions subtracted $-NCO$ groups from the reaction mixture. To confirm that, the FTIR spectrum of mixAISOX100 having a H_{12} MDI:PEGDGE molar ratio $r = 1$ after curing showed a complete conversion of H_{12} MDI but only a partial PEGDGE conversion (data not shown). The spectrum of the initial mixAISOX100 (without catalyst) and that of the final product (AISOX100) were normalized respect to the absorbance of the $C-H$ stretching ($3000 - 2500\text{ cm}^{-1}$), not involved in the reaction. By comparing the peak intensity at 905 cm^{-1} , epoxyde group residual of 25% was inferred. Hence, in order to convert all the PEGDGE epoxy groups in oxazolidone, a minimum $r = 1.33$ was necessary.

In Figure 2(A), the DSC thermogram of mixAISOX133 heated at 3 K min^{-1} from 25 to $200\text{ }^\circ\text{C}$ is reported.

As it can be seen, three main exothermic peaks can be observed between $25 - 70\text{ }^\circ\text{C}$, $70 - 100\text{ }^\circ\text{C}$, and $100 - 200\text{ }^\circ\text{C}$ and a shoulder at $120\text{ }^\circ\text{C}$. After this heating, a further isothermal treatment at $200\text{ }^\circ\text{C}$ was applied till the disappearance of the reagents IR absorption bands. In Figure 2(B), the conversion of the reactants (isocyanate and epoxy groups) and the formation of the products (urea, oxazolidone, isocyanurate, and oxadiazine trione) during reaction time are reported as percentage variation between the beginning and the end of the curing process. The vertical line at 60 min indicates the end of the dynamic heating at 3 K min^{-1} and the starting of the isothermal process.

Although the time resolution is lower than that of the DSC thermogram, a relationship between the exothermal DSC signals and the corresponding reactions can be inferred. The exothermic peak between 25 and $70\text{ }^\circ\text{C}$ can be assigned to the urea formation which showed in this temperature region the higher reaction rate. It must be noted that the urea was present already from the very early reaction stage soon after the catalyst addition. The reaction between isocyanate group and water continued up to $200\text{ }^\circ\text{C}$ to stop during the isothermal process. At about $70\text{ }^\circ\text{C}$, the isocyanate trimerization (isocyanurate formation) began and at the end of the dynamic heating, the isocyanurate group reached about 40% of its final concentration. The maximum amount of isocyanurate was obtained after 2 h of isothermal curing at $200\text{ }^\circ\text{C}$, when the isocyanate was completely consumed. The large and intense exothermic band centered at $160\text{ }^\circ\text{C}$ was attributed to the oxazolidone formation. The reaction between the isocyanate and the epoxy groups was rapid and nearly completed (90%) at $200\text{ }^\circ\text{C}$, before the isothermal treatment. The linear correlation between the epoxy conversion and oxazolidone formation, reported in Figure 2(C), excluded any side reactions involving the glycidyl ether, such as

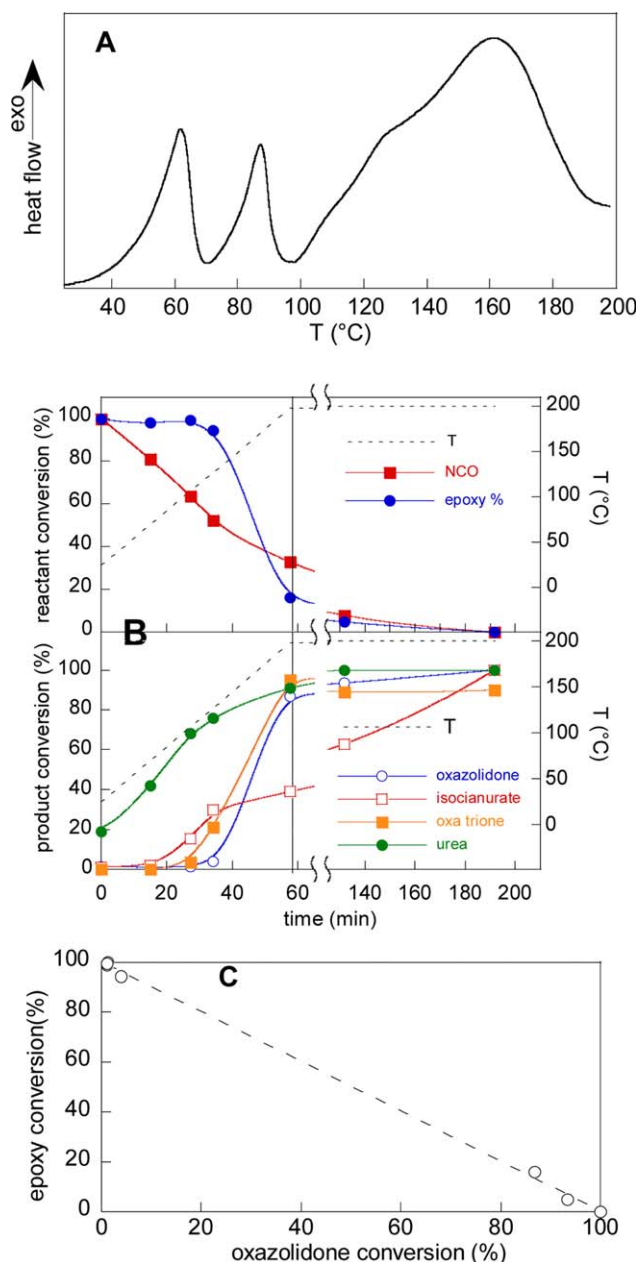


Figure 2. DSC thermogram of mixAISOX133 heated at 3 K min^{-1} from 25 to $200\text{ }^\circ\text{C}$ (A). Conversion of the reagents (isocyanate and epoxy groups) and formation of the products (urea, oxazolidone, isocyanurate and oxadiazine trione) during time as evaluated by IR analysis (B). Correlation plot of the epoxy conversion and oxazolidone formation (C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

epoxy homopolymerization. The shoulder at $120\text{ }^\circ\text{C}$ observed in the DSC thermogram could be presumably attributed to the formation of oxadiazine trione.

The sequence of the reactions found in this study is similar to that reported in literature for other isocyanurate-oxazolidone resin preparations, although some light difference in the temperatures at which the reactions take place exists, depending on type of reagents, catalyst, and reagent molar ratio.^{4,7,8,27}

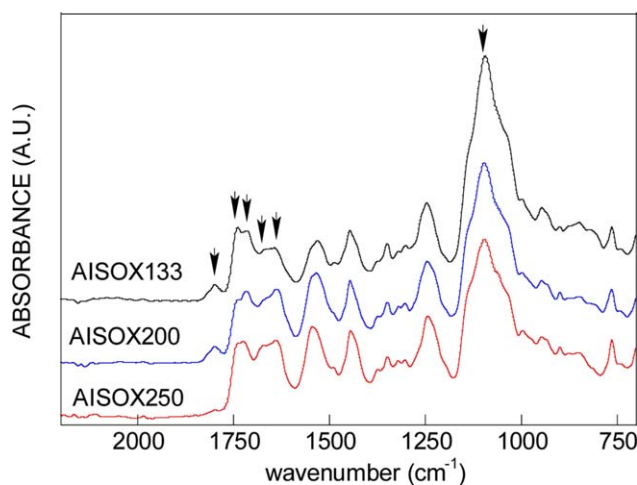


Figure 3. FTIR spectra of the three AISOX resins after complete curing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

By changing the feed formulation (Table I), the reaction progress and the temperature range of the exothermal peaks remained nearly unaltered. Only a slight modification in the relative intensities of the exothermal peaks as well as in the area of the normalized FTIR bands of involved groups occurred. Detailed description of mixAISOX200 and mixAISOX250 curing was reported in Supporting Information (Supporting Information Figures S3 and S4).

As for AISOX133, the epoxy conversion was nearly concluded during the dynamic heating of mixAISOX200 (conversion = 100%) and mixAISOX250 (conversion = 80%). On the other hand, in order to have the complete disappearance of the isocyanate group, AISOX200 and AISOX250 needed a further isothermal treatment at 200 °C for 3 and 4 h, respectively (Supporting Information Figures S3 and S4). All the fully cured

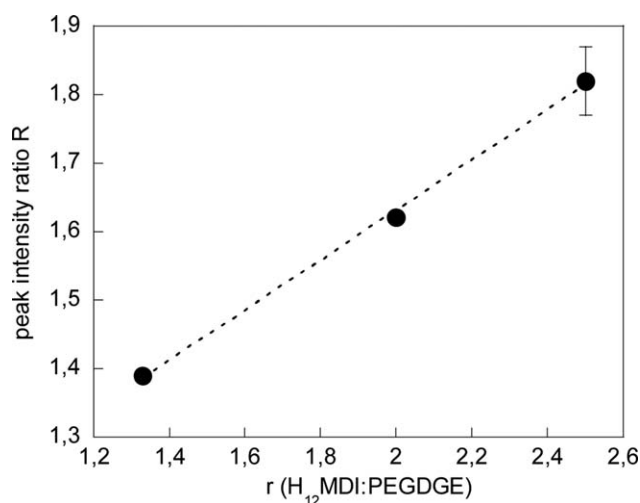


Figure 4. Ratio of the integrated peak area of the isocyanurate (1715 cm^{-1}) and oxazolidone (1740 cm^{-1}) groups as a function of the $\text{H}_{12}\text{MDI}:\text{PEGDGE}$ molar ratio (r). The results are reported as mean values of measurements carried out on three independent experiments \pm maximum deviation.

AISOXs were homogeneous, transparent, lightly yellow, and insoluble in water or organic solvents. In Figure 3, the IR spectra of the three fully cured resins are reported.

The different intensities of the band at about 1100 cm^{-1} , related to the C—O stretching of the poly(ethylene oxide) chain, is due to the decrease in PEGDGE concentration from AISOX133 to AISOX250 (Table I). Moreover, the urea concentration increased with the H_{12}MDI increase, as evidenced by the two absorptions at 1670 and 1639 cm^{-1} . The band at 1800 cm^{-1} was assigned to the oxadiazine trione. This absorption disappeared when samples were immersed in ethanol which caused the opening of the anhydride ring.

The carbonyl stretching region between 1840 and 1600 cm^{-1} was analyzed by deconvolving the overall absorbance, as previously described (Supporting Information Figure S5). The peak positions remained nearly unchanged in all the samples. In Figure 4, the area ratio (R) of the bands at 1715 and 1740 cm^{-1} , assigned to the isocyanurate and oxazolidone groups respectively, are reported as a function of the molar ratio of the reagents (r).

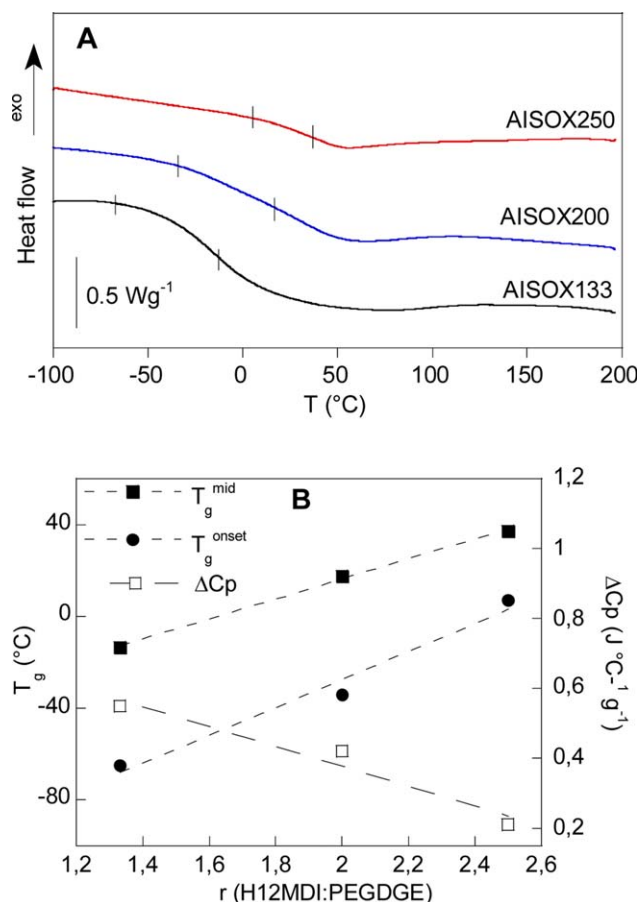


Figure 5. DSC thermograms of the AISOX resins. DSC thermograms recorded at 10 K min^{-1} . The vertical bars indicate the onset (T_g^{onset}) and the midpoint (T_g^{mid}) glass transition temperature (A). Glass transition temperature (T_g^{onset} and T_g^{mid}) and heat capacity change (ΔC_p) of AISOX resins as a function of the $\text{H}_{12}\text{MDI}:\text{PEGDGE}$ molar ratio (B). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

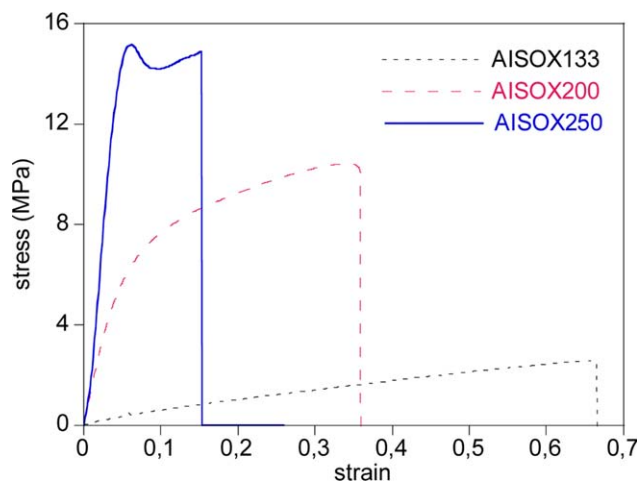


Figure 6. Representative stress-strain curves of the AISOX resins. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The parameter R is related to the isocyanurate ring concentration that is to the AISOX crosslinking density. Although isocyanate was partially consumed by the urea formation, R steadily increased by increasing the H_{12} MDI concentration. We expect this to influence the thermal and mechanical properties of the AISOX resins.

In Figure 5(A), the DSC thermograms of the AISOX resins are reported. Between -100 and $+200$ °C the polymers showed only the glass transition, occurring in a large temperature range. In Figure 5(B) the glass transition onset (T_g^{onset}) and midpoint (T_g^{mid}) and the specific heat change (ΔC_p) are reported as a function of the H_{12} MDI:PEGDGE molar ratio.

An increase in H_{12} MDI content into the reaction mixture brought about a reduction in the polymer chain mobility as evidenced by the increase of T_g and the decrease of ΔC_p involved in the transition. This is in agreement with the increase in the crosslinking density parameter (R) found in FTIR analysis (Figure 4).

The mechanical properties of the AISOX resins were determined by stress–strain experiments carried out at room temperature on samples prepared in Teflon molds. In Figure 6 the stress–strain curves are displayed. In Table III the Young modulus (E_y), the tensile strength, the elongation at break and the tensile set are reported.

The different mechanical behavior showed by the samples can be related to the crosslink density and to their glass transition

Table III. Young Modulus (E_y), Tensile Strength, Elongation at Break and Tensile Set of AISOXs Obtained from Stress–Strain Experiments

Sample	E_y (MPa)	Tensile strength (MPa)	Elongation to break (%)	Tensile set (%)
AISOX133	7.3 ± 0.3	2.4 ± 0.1	63 ± 2	0
AISOX200	15.1 ± 0.3	10 ± 1	33 ± 1	11 ± 1
AISOX250	36 ± 1	17 ± 1	12 ± 3	25 ± 5

The reported values are the mean values ($n = 3$) \pm maximum deviation.

temperature. Indeed, at room temperature AISOX133 is in the amorphous rubbery state and therefore showed an elastomeric behavior, characterized by a low Young modulus and tensile strength together with the highest elongation at break. Moreover, after break, this sample completely recovered its initial length (tensile set = 0), remained transparent and homogeneous and did not show any residual birefringent behavior when observed by polarized OM [Figure 7(A)].

On the other hand, the highly cross-linked AISOX250, having a T_g above RT ($T_g^{\text{mid}} = 38$ °C), showed a yield point and cold drawing. Polarized OM observations revealed that after break AISOX250 was no more homogeneous, presenting small birefringent zones and hackle-like cracks with the axis orthogonal

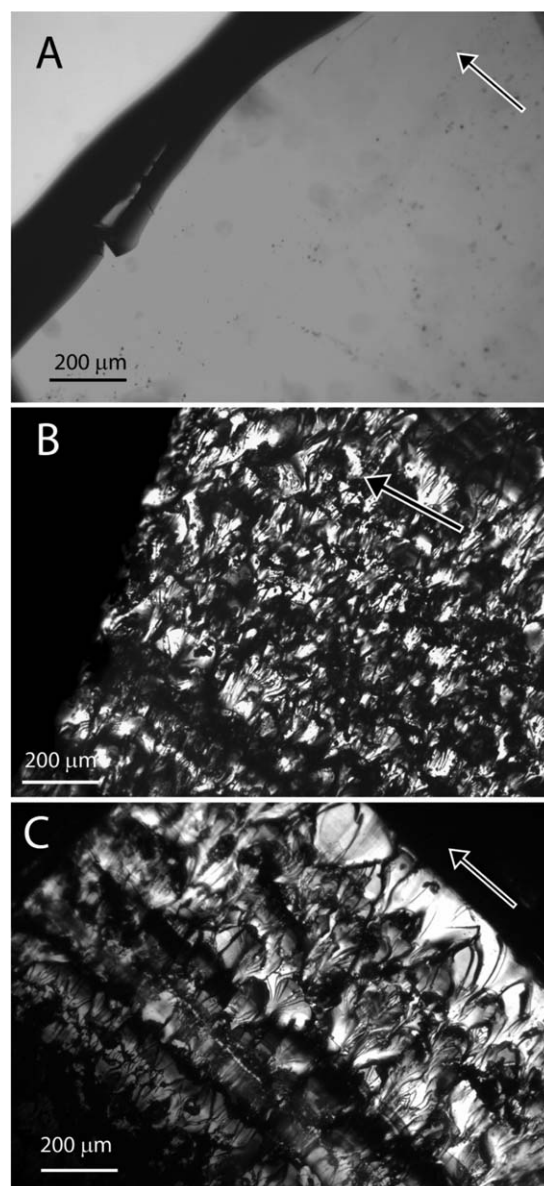


Figure 7. Images of AISOX133 (A), AISOX200 (B) and AISOX250 (C) resins acquired by transmission optical microscopy after the sample break. The arrow indicates the strain direction. In images B and C crossed polarizers condition were used.

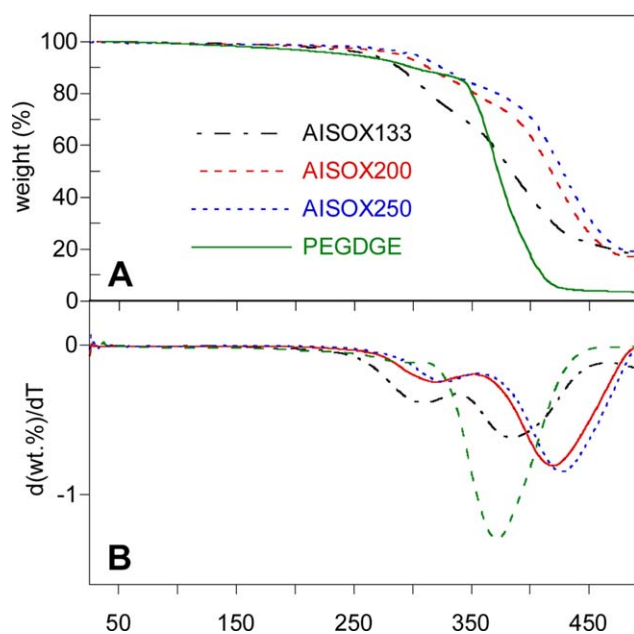


Figure 8. TGA (A) and DTGA (B) curves of the AISOX resins and PEGDGE. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to the strain direction [Figure 7(C)]. This behavior is typical of strained glassy materials. No permanent overall orientation along the elongation direction was observed after the relaxation of the broken AISOX250 sample.

The AISOX200 showed an intermediate mechanical behavior, with values of the Young modulus, tensile strength, elongation at break and tensile set between those of the other two resins. No stable necking appeared before the break point and polarized OM observations revealed the formation of hackles smaller than those found in the AISOX250 [Figure 7(B)]. As for the AISOX250, no permanent overall birefringence and, hence, no long range chain orientation can be observed after the sample break. As described in the Introduction section, the key feature of isocyanurate and oxazolidone groups is their thermal and chemical stability. Such a property is particularly valuable in the formulation of casting resins to be employed in extreme chemical and physical environments. The heat resistance of AISOX resins and of the macromonomer PEGDGE was studied by thermogravimetric analysis. Figure 8 shows the TGA curves obtained in nitrogen flux as well as their derivatives (DTGA). In Table IV, the temperature at 10% of weight loss (T_{d10}) and the temperatures of the two DTGA peaks (T_p^I and T_p^{II}) are reported.

All the resins showed good thermal stability, comparable with other aliphatic isocyanurate-oxazolidone polymers.²² The thermal degradation of the three AISOXs preceded in two steps. As far as the diepoxyde monomer thermal degradation, it took place by two weight loss processes characterized by DTGA peaks at 290 °C and 370 °C (Figure 8). Presumably, the decomposition of poly(ethylene oxide) chain contributed to the resin weight loss at higher temperature. In addition, an increase in T_{d10} , T_p^I , and T_p^{II} with the increase in the cross-link density was observed for all samples.

DISCUSSION

Di- or poly-isocyanate and diepoxyde are generally used for the preparation of poly(oxazolidone-isocyanurate) casting thermoset resins, with high stiffness and T_g . The rigid isocyanurate ring was also employed as crosslinker to increase the T_g of epoxy thermosets or the hardness of polyurethane coatings.^{28,29} Alternatively, the introduction of oxazolidone and isocyanurate groups is employed to improve the thermal stability of elastomers.⁶ The choice of the catalyst, the reaction feed and the curing temperature can affect the mechanical and thermal properties of the materials. Therefore, a proper balance between the two heterocyclic groups and, then, in the crosslink density can permit to modulate the material performance.³⁰ Thermally stable poly(urethane-oxazolidone) or poly(urethane-isocyanurate-oxazolidone) elastomers are usually prepared by multi-step reactions, consisting in the formation NCO terminated urethane or butadiene prepolymers, followed by the reaction with a low molecular weight diepoxyde, often diglycidyl ether of Bisphenol A.³¹ Alternatively, to increase the chemical stability of the prepolymer, the isocyanate group can be converted into an epoxyde by its reaction, for instance, with glycidol.³² In any case, the soft segment, which provides elastomeric properties to the resin, is originally a diisocyanate capped prepolymer that is either directly cured with an epoxyde compound or converted first into an epoxyde and, then, cured with a di- or -polyisocyanate. In the present research, a new strategy was investigated to produce flexible poly(oxazolidone-isocyanurate) resins. Particularly, a macro-diepoxyde (PEGDGE) was used as soft segment, and the polymer extension and cross-linking reactions were carried out by using a low molecular weight diisocyanate (H_{12} MDI). We found that this method offers the advantages of the one step synthesis and the possibility to tune easily the crosslink density of the fully cured materials. Moreover we observed that the reaction mixture is stable before the addition of the catalyst and that the reagents can be mixed and stored at room temperature in dry conditions for almost one month, observing only a slight decrease of about 10% in the concentration of the isocyanate or epoxyde groups (data not reported).

We also observed that the reaction mixtures remained viscous up to about 150–160 °C, when the oxazolidone formation brings about the molecular weight increase. The gelation, one of the most important drawbacks of thermoset systems, is delayed because the isocyanate trimerization takes place slowly during all the curing process (after a first incomplete and relatively fast reaction at about 70–100 °C).

Table IV. Thermogravimetric Analysis Results

Sample	T_{d10} (°C)	T_p^I (°C)	T_p^{II} (°C)
AISOX133	285	310	385
AISOX200	310	317	420
AISOX250	325	330	430
PEGDGE	302	290	370

The temperature at 10% of weight loss (T_{d10}) and temperature of the two DTGA peaks (T_p^I and T_p^{II})

In addition to isocyanurate and oxazolidone, formation of urea from the reaction of the isocyanate groups with water, even under nitrogen, was observed. We have inferred that this is due to the hydroscopicity of PEGDGE that brings water into the reaction mixture. This side reaction could be reduced by using a more hydrophobic diepoxyde, such as poly(propylene oxide) diglycidyl ether, or a steadily blocked polyisocyanate having high chemical stability at room temperature.

As far as the thermal and mechanical properties are concerned, it was evidenced that the introduction of the flexible poly(ethylene oxide) into the resin has a great influence on the chain mobility. In fact, all the AISOX resins showed low values of T_g and Young modulus, well below those of conventional poly(oxazolidone-isocyanurate) resins.

The obtained resins showed to be able to strongly adhere on metals and glass substrates. Currently, we are evaluating the possibility to use our AISOX resins as sealants, coatings, or glues.

CONCLUSIONS

Resins containing aliphatic oxazolidone and isocyanurate were successfully obtained by using a soft macro-diepoxyde segment, which imparts flexibility, and a low molecular weight diisocyanate, which ensures cross-links. The molar ratio of the two monomers controls the cross-links density and the material thermal and mechanical behavior. The analysis of the curing process carried out by heating the reaction mixture, evidenced that the reaction sequence is: (i) partial hydrolysis of isocyanate caused by water, (ii) incomplete trimerization of isocyanate to give isocyanurate, and (iii) formation of oxazolidone and isocyanate consumption. The characterization of the fully cured samples showed that the isocyanate concentration in the feed influences the cross-link density, the T_g and material stiffness. The AISOX resin with the lowest cross-link content is in the rubbery state at RT and shows elastomeric behavior.

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