

# PROOF COVER SHEET

---

Author(s): Gabriel Estan-Cerezo, Diego A. Alonso, and José Miguel Martín-Martínez

Article title: Structural and adhesion properties of poly(ethyl 2-cyanoacrylate) post-cured at different temperatures and times

Article no: TAST\_A\_1509502

Enclosures: 1) Query sheet  
2) Article proofs

---

Dear Author,

**1. Please check these proofs carefully.** It is the responsibility of the corresponding author to check these and approve or amend them. A second proof is not normally provided. Taylor & Francis cannot be held responsible for uncorrected errors, even if introduced during the production process. Once your corrections have been added to the article, it will be considered ready for publication.

Please limit changes at this stage to the correction of errors. You should not make trivial changes, improve prose style, add new material, or delete existing material at this stage. You may be charged if your corrections are excessive (we would not expect corrections to exceed 30 changes).

For detailed guidance on how to check your proofs, please paste this address into a new browser window:

<http://journalauthors.tandf.co.uk/production/checkingproofs.asp>

---

Your PDF proof file has been enabled so that you can comment on the proof directly using Adobe Acrobat. If you wish to do this, please save the file to your hard disk first. For further information on marking corrections using Acrobat, please paste this address into a new browser window: <http://journalauthors.tandf.co.uk/production/acrobat.asp>

**2. Please review the table of contributors below and confirm that the first and last names are structured correctly and that the authors are listed in the correct order of contribution.** This check is to ensure that your name will appear correctly online and when the article is indexed.

Sequence	Prefix	Given name(s)	Surname	Suffix
1		Gabriel	Estan-Cerezo	
2		Diego A.	Alonso	
3		José Miguel	Martín-Martínez	

Queries are marked in the margins of the proofs, and you can also click the hyperlinks below.

### General points:

1. **Permissions:** You have warranted that you have secured the necessary written permission from the appropriate copyright owner for the reproduction of any text, illustration, or other material in your article. Please see <http://journalauthors.tandf.co.uk/permissions/usingThirdPartyMaterial.asp>.
2. **Third-party content:** If there is third-party content in your article, please check that the rightsholder details for re-use are shown correctly.
3. **Affiliation:** The corresponding author is responsible for ensuring that address and email details are correct for all the co-authors. Affiliations given in the article should be the affiliation at the time the research was conducted. Please see <http://journalauthors.tandf.co.uk/preparation/writing.asp>.
4. **Funding:** Was your research for this article funded by a funding agency? If so, please insert 'This work was supported by <insert the name of the funding agency in full>', followed by the grant number in square brackets '[grant number xxxx]'.
5. **Supplemental data and underlying research materials:** Do you wish to include the location of the underlying research materials (e.g. data, samples or models) for your article? If so, please insert this sentence before the reference section: 'The underlying research materials for this article can be accessed at <full link>/ description of location [author to complete]'. If your article includes supplemental data, the link will also be provided in this paragraph. See <http://journalauthors.tandf.co.uk/preparation/multi-media.asp> for further explanation of supplemental data and underlying research materials.
6. The **PubMed** (<http://www.ncbi.nlm.nih.gov/pubmed>) and **CrossRef databases** ([www.crossref.org/](http://www.crossref.org/)) have been used to validate the references. Changes resulting from mismatches are tracked in red font.

## AUTHOR QUERIES

- Q1: Please provide “Abbreviations” list for this article.
- Q2: A disclosure statement reporting no conflict of interest has been inserted. Please correct if this is inaccurate.
- Q3: Please provide the caption for Schemes 1 and 2.
- Q4: The ORCID details of the authors have been validated against ORCID registry. please check the ORCID ID details of the authors.

- Q5: The funding information provided has been checked against the Open Funder Registry and we failed to find a match. Please check and resupply the funding details if necessary.
- Q6: Please check and resupply corresponding author email address if the given is inaccurate.

### **How to make corrections to your proofs using Adobe Acrobat/Reader**

Taylor & Francis offers you a choice of options to help you make corrections to your proofs. Your PDF proof file has been enabled so that you can mark up the proof directly using Adobe Acrobat/Reader. This is the simplest and best way for you to ensure that your corrections will be incorporated. If you wish to do this, please follow these instructions:

1. Save the file to your hard disk.
2. Check which version of Adobe Acrobat/Reader you have on your computer. You can do this by clicking on the Help” tab, and then About”.

If Adobe Reader is not installed, you can get the latest version free from <http://get.adobe.com/reader/>.

3. If you have Adobe Acrobat/Reader 10 or a later version, click on the Comment” link at the right-hand side to view the Comments pane.
4. You can then select any text and mark it up for deletion or replacement, or insert new text as needed. Please note that these will clearly be displayed in the Comments pane and secondary annotation is not needed to draw attention to your corrections. If you need to include new sections of text, it is also possible to add a comment to the proofs. To do this, use the Sticky Note tool in the task bar. Please also see our FAQs here: <http://journalauthors.tandf.co.uk/production/index.asp>.

5. Make sure that you save the file when you close the document before uploading it to CATS using the Upload File” button on the online correction form. If you have more than one file, please zip them together and then upload the zip file. If you prefer, you can make your corrections using the CATS online correction form.

### **Troubleshooting**

**Acrobat help:** <http://helpx.adobe.com/acrobat.html>

**Reader help:** <http://helpx.adobe.com/reader.html>

Please note that full user guides for earlier versions of these programs are available from the Adobe Help pages by clicking on the link Previous versions” under the Help and tutorials” heading from the relevant link above. Commenting functionality is available from Adobe Reader 8.0 onwards and from Adobe Acrobat 7.0 onwards.

**Firefox users:** Firefox's inbuilt PDF Viewer is set to the default; please see the following for instructions on how to use this and download the PDF to your hard drive: [http://support.mozilla.org/en-US/kb/view-pdf-files-firefox-without-downloading-them#w\\_using-a-pdf-reader-plugin](http://support.mozilla.org/en-US/kb/view-pdf-files-firefox-without-downloading-them#w_using-a-pdf-reader-plugin)



# Structural and adhesion properties of poly(ethyl 2-cyanoacrylate) post-cured at different temperatures and times

Q4 Gabriel Estan-Cerezo<sup>a,b</sup> , Diego A. Alonso<sup>b</sup>  and José Miguel Martín-Martínez<sup>a</sup>

<sup>a</sup>Adhesion and Adhesives Laboratory, University of Alicante, Alicante, Spain; <sup>b</sup>Organic Chemistry Department and Institute of Organic Synthesis, University of Alicante, Alicante, Spain

## ABSTRACT

The structure and properties of poly(ethyl 2-cyanoacrylate)s (pECNs) cured at 25 °C during 24 hours, and post-cured at different temperatures (45–90 °C) and times (2–6 hours) were studied. Irrespective of the post-cure conditions, pECN was not fully polymerized and two different structures of different molecular weights and topographies were obtained. The post-cure decreased the shear strength values in joints made with aluminum and ethyl cyanoacrylate due to the decrease in the percentage of higher molecular weight polymeric chains and the formation of new short polymeric chains by unzipping de-polymerization mechanism, both contributed to decrease the mechanical properties. On the other hand, the post-cure changed the morphology of pECN because of nano-spheres were produced by curing at 25 °C which were not present after post-cure at 90 °C.

## ARTICLE HISTORY

Received 7 April 2018  
Revised 15 July 2018  
Accepted 6 August 2018

## KEYWORDS

Poly(ethylcyanoacrylate); thermal post-cure; adhesion; unzipping mechanism; DSC; TGA

Q1

## 1. Introduction

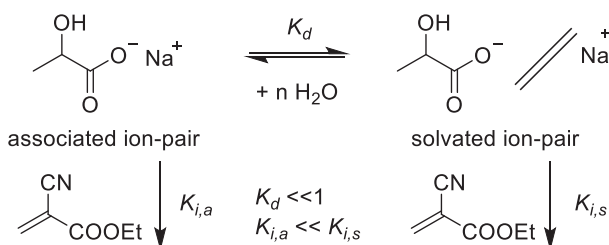
The polymerization conditions of cyanoacrylates such as the initiator [1], the temperature [2–4], and the pH [5], among other, determine their structure and properties. For instance, Dossi et al. [5] have shown that during cyanoacrylate polymerization and depending on the pH, two main structures with different molecular weights can be formed. Thus, high molecular weight fractions were not observed under acidic polymerization conditions carried out at 0 or 65 °C. However, the polymerization of cyanoacrylates at 25 °C produced the formation of two main structures with different molecular weights, and the polymerization under neutral pH led to high molecular weight polymers only. On the other hand, Puglisi et al. [1] established differences in the size, the topography and the properties of the nano-capsules formed during the polymerization of ethyl cyanoacrylate by using different solvents as initiators. Thus, the use of aprotic and water-miscible solvents, such as acetone and acetonitrile, caused the formation of suspensions of polymer nano-capsules, while water-miscible solvents,

Q6 CONTACT José Miguel  Martín-Martínez [jm.martin@ua.es](mailto:jm.martin@ua.es)  Adhesion and Adhesives Laboratory, University of Alicante, Alicante, Spain

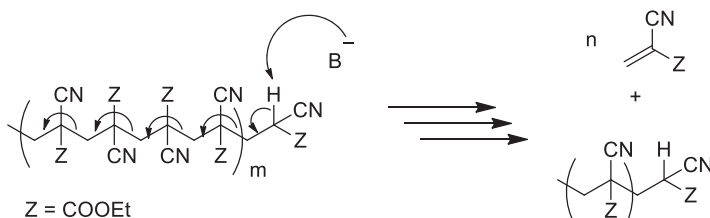
46 such as alcohols, led to colloidal suspensions consisting of nano-spheres and nano-  
47 capsules. Furthermore, the solvent used as polymerization initiator determined the  
48 nanoparticle size and the polydispersity of poly(ethyl cyanoacrylate)s. These results  
49 have been explained by the co-existence of two different polymerization mechanisms,  
50 i.e., interfacial precipitation of pre-formed polymer and interfacial polymerization.

51 The influence of the temperature on the polymerization of ethyl cyanoacrylate has  
52 been studied elsewhere [2–4,6–8], but different conclusions have been obtained  
53 depending on the polymerization conditions. For example, the particle size of  
54 poly(ethyl 2-cyanoacrylate)s (pECNs) has been related to the polymerization  
55 temperature by Reddy et al. [2] whose have demonstrated that the higher was the  
56 polymerization temperature, the larger was the polymer particle size because of some  
57 agglomeration of particles was produced. Under vapour phase conditions, the  
58 influence of the polymerization temperature on the morphology of pECN has been  
59 also studied, and it has been shown the formation of nanofibers at 100 °C but spheres  
60 at 180 °C [3]. On the contrary, Algaier et al. [4] have considered the use of ethyl  
61 cyanoacrylate in revealing fingerprints in thermostatic chamber (20–80 °C) and they  
62 have found that higher polymerization degree of ethyl cyanoacrylate at lower tem-  
63 perature by using sodium lactate as polymerization initiator was obtained. Algaier  
64 et al. [4] have related the ionic pair of the sodium lactate with the polymerization  
65 rate of the ethyl cyanoacrylate, concluding that they were more reactive than the  
66 associated ionic pairs, especially at low temperature (Scheme 1). Interestingly, these  
67 authors did not observe a significant variation of the molecular weight of the  
68 poly-cyanoacrylate by changing the polymerization temperature, likely due to high  
69 polymerization rate caused by the solvated ion pairs in the sodium lactate initiator.

70 On the other hand, Senchenya et al. [6] have studied the influence of the polymer-  
71 ization temperature on the adhesion properties of different cyanoacrylates. They have  
72 demonstrated that the polymerization at high temperature decreased the adhesion  
73 because of the thermal degradation of the cyanoacrylate was favoured. Thus, the com-  
74 plete degradation and the loss of adhesion were produced by curing joints made with  
75 composites and ethyl cyanoacrylate at 150 °C during 8 hours. In the same direction,  
76 Guthrie et al. [7] have studied the effect of the thermal treatment at 90 °C during dif-  
77 ferent times on the adhesion of steel-ethyl cyanoacrylate joints, and they have  
78 observed an important decrease in adhesion and a slight reduction in the molecular  
79 weight of the polymer by increasing the time of the thermal treatment. The negative  
80 effects of the increase of the temperature on the poly-cyanoacrylate properties have  
81 also been studied by Chorbadjiev et al. [8], ascribing them to the formation of free  
82 monomer during the thermal decomposition of the polymer. In addition, Robello  
83 et al. [9] have established that the presence of residual amounts of organic or  
84 inorganic base (usually the initiator) at the end of the polymerization may favour the  
85 degradation of the poly-cyanoacrylates. This base-induced depolymerization process,  
86 also known as “unzipping” mechanism (Scheme 2), has been proposed for explaining  
87 the low stability and the decreased adhesion of poly-cyanoacrylates after long storage  
88 periods under aqueous conditions [7]. Ryan et al. [10] have also studied the  
89 influence of the temperature on the polymerization-depolymerization reactions of  
90 poly-cyanoacrylates, and they have proposed that the unzipping depolymerization



Q3 Scheme 1.



Q3 Scheme 2.

process in polycyanocrylates was initiated by the abstraction of one terminal proton in the “parent” polymer chain producing monomeric units by a retro-Michael cascade reaction. The liberated free monomer was then able to initiate a new base-catalyzed polymerization generating new low molecular weight “daughter” polymer chains.

On the other hand, depending on the initiator nature, the polymerization of cyanoacrylates can take place through three different mechanisms: radical, anionic, and zwitterionic. Pepper [11] has proposed a SINT (slow-initiated, non-terminated) process for zwitterionic polymerizations using tertiary amines as initiators. Furthermore, based on kinetic studies, Johnston and Pepper [12] supported the absence of intrinsic termination process in the polymerization of cyanoacrylates.

Because of the contradictory evidences found in the literature dealing with the influence of the polymerization temperature on the properties of ethyl cyanoacrylate, the effect of the temperature and the time on the structure and properties of the pECNs are considered in this study. To the best of our knowledge, no systematic studies have been performed so far on the influence of the post-cure temperature and time on the structure and properties of the pECNs. Thus, in this study, ethyl cyanoacrylate was polymerized at 25 °C and later post-cured at different temperatures during different times and the changes in the structure, the topography and the adhesion properties of the pECNs were determined.

## 2. Experimental

### 2.1. Materials

Ethyl cyanoacrylate (ECN) was supplied by Adhbio S.L. (Elche, Spain). ECN contains hydroquinone and *p*-toluenesulphonic acid stabilizers, and its water content obtained by Karl-Fisher titration is  $566 \pm 40$  ppm.

136 A 1.0% (v/v) aqueous (ultrapure water) solution of triethylamine (Sigma-Aldrich,  
137 Steinheim, Germany) was used as polymerization initiator.

## 138 **2.2. Polymerization of ethyl cyanoacrylate (ECN)**

139 ECN was polymerized in an aluminum container by drop-wise addition of 1.0% (v/v)  
140 aqueous solution of triethylamine over 1 ml of ECN under continuous stirring. The  
141 mixture was allowed to react under open air at 25 °C during one hour, and a white  
142 polymer was obtained. For removing the non-reacted initiator, the polymer was  
143 washed several times with ultrapure water until neutral pH in the washing liquid was  
144 obtained. The solid pECN was completely dried under open air at 25 °C during  
145 24 hours. Then, the cured pECN was post-cured at 45-90 °C during 2-6 hours in  
146 Selecta 2000208 oven (Barcelona, Spain).

## 147 **2.3. Experimental techniques**

### 148 **2.3.1. Attenuated total reflection infrared spectroscopy (ATR-IR)**

149 ATR-IR spectra of the pECNs were obtained in a Tensor 27 FT-IR spectrometer  
150 (Bruker Optik GmbH, Erlanger, Germany) by using Germanium prism ATR acces-  
151 sory. In absorbance mode, 64 scans were recorded with resolution of 4 cm<sup>-1</sup> in the  
152 wavenumber range of 4000 to 400 cm<sup>-1</sup>.

### 153 **2.3.2. Nuclear Magnetic Resonance (NMR)**

154 <sup>1</sup>H NMR spectra of the pECNs were obtained in a Bruker AC-400 spectrometer  
155 (Bruker, Rheinstetten, Germany), proved with 400 MHz magnet. 30-40 mg simple dis-  
156 solved in deuterated chloroform (CDCl<sub>3</sub>) was placed in NMR flasks and the spectra  
157 were processed with Mestrec 5.0 program (Mestrelab Research S.L., Santiago de  
158 Compostela, Spain).

159 <sup>1</sup>H DOSY experiment was performed in a Bruker Advance DRX500, QNP300MHz  
160 S1 with Z-gradient equipment (Bruker, Rheinstetten, Germany). Stimulated echo  
161 sequence using bipolar gradient pulses for diffusion and 1 spoil gradient, with a spec-  
162 tral width of 6172.84 Hz, were used. Stebbpgp1s avance-version pulse program for  
163 acquisition data was used. D1 value of relaxation delay was 1 second, the delay for  
164 gradient recovery was 0.2 ms and the diffusion time (big DELTA) was 80.0 ms  
165 (16 gradient, Gradient Calib Contant 5.19 G/mm). The gas flow used at 25 °C was  
166 535 l/h. Data were processed after the Fourier transformation of each FID with  
167 TopSpin3.2 to obtain the chemical shift as the x-axis along with logD as thee y-axis.  
168 Diffusion coefficient values (D) were corrected based on the D value of CDCl<sub>3</sub> as an  
169 internal standard.

### 170 **2.3.3. Differential Scanning Calorimetry (DSC)**

171 The structural changes and the existence of post-polymerization of the pECNs were  
172 analyzed in DSC Q100 instrument (TA Instruments, New Castle, DE, USA). 5–10 mg  
173 of sample were placed in a hermetic aluminum pan and heated between -50 and  
174 150 °C under nitrogen atmosphere (flow rate: 50 ml/min) by using a heating rate of  
175



181 10 °C/min. Then, the sample was cooled down from 150 to -50 °C by using a cooling  
182 rate of 10 °C/min. The existence of post-polymerization in the cured and post-cured  
183 pECN was evidenced from the first DSC heating run. Afterwards, a second heating  
184 run from -50 to 300 °C was also performed by using a heating rate of 10 °C/min, the  
185 glass transition temperature ( $T_g$ ) and the decomposition temperature ( $T_{dec}$ ) of the  
186 pECNs were determined from the DSC thermograms.

#### 187 **2.3.4. Thermal gravimetric analysis (TGA)**

188 The thermal stability of the pECNs was analyzed in TGA Q500 instrument  
189 (TA Instruments, New Castle, DE, USA). 5-10 mg of sample were placed in a  
190 platinum crucible under nitrogen atmosphere (flow rate: 100 ml/min) and they were  
191 heated from room temperature to 350 °C by using a heating rate of 10 °C/min.

#### 192 **2.3.5. Molecular weight measurement**

193 The molecular weights of the pECNs were determined in Waters gel permeation  
194 chromatograph (Waters, Milford, MA, USA) equipped with refractive index detector.  
195 Tetrahydrofuran (THF) was used as solvent, and the measurements were carried out  
196 at 35 °C and by using a flow rate of 1 ml/min that was controlled by 1515 HPLC  
197 pump (Waters, Milford, MA, USA). Polystyrene standards and Stryabel columns  
198 (300 x 7.9 mm, 5  $\mu$ m) (Waters, Milford, MA, USA) were employed.

#### 199 **2.3.6. Transmission Electronic Microscopy (TEM)**

200 The topography of the pECN surfaces was analyzed by transmission electron  
201 microscopy in Jeol JEM-1400 Plus equipment (Jeol, Tokyo, Japan) provided with  
202 LaB<sub>6</sub> filament. A voltage of 120 V was used and TEM micrographs were recorded  
203 with Orius camera (Gatan, Pleasanton, USA).

#### 204 **2.3.7. Scanning Electron Microscopy (SEM)**

205 The topography of the pECN surfaces was also analyzed by scanning electron  
206 microscopy in Jeol JSM 840 equipment (Jeol, Tokyo, Japan) equipped with a  
207 scintillator-photomultiplier of 4 nm resolution. A voltage of 10 keV was employed  
208 and the samples were gold coated before analysis.

#### 209 **2.3.8. Single lap-shear test**

210 The adhesion properties of ethyl cyanoacrylate (ECN) were obtained from single lap-  
211 shear tests of aluminum/ECN/aluminum joints. Aluminum 5754 test samples of  
212 dimensions 150 x 30 x 1.5 mm were used, and, before joint formation, they were  
213 mildly scored with green Scotch Brite<sup>®</sup> scourer followed by washing with isopropyl  
214 alcohol (Javer, Móstoles, Spain) and drying at room temperature during 15 minutes.  
215 The joined area of the aluminium test samples was 30 x 30 mm, and an amount of  
216 15  $\mu$ l of ethyl cyanoacrylate was placed over one of the aluminium test sample; then,  
217 the other aluminium test sample was immediately placed over and a pressure of  
218 0.11 MPa was applied during 10 minutes. The joints were allowed to cure at 25 °C  
219 during 24 hours. Afterwards, some of the adhesive joints were post-cured in oven at  
220 45 or 90 °C during 2 hours, and then kept at room temperature during 72 hours.

Single lap-shear tests were carried out in universal testing machine Instron 8516 (Instron, Buckinghamshire, UK), a cross-head speed of 10 mm/min was used. Five replicates were carried out and averaged. The loci of failure of the joints were assessed by visual inspection.

### 3. Results and discussion

#### 3.1. Influence of the post-cure temperature on the properties of pECN

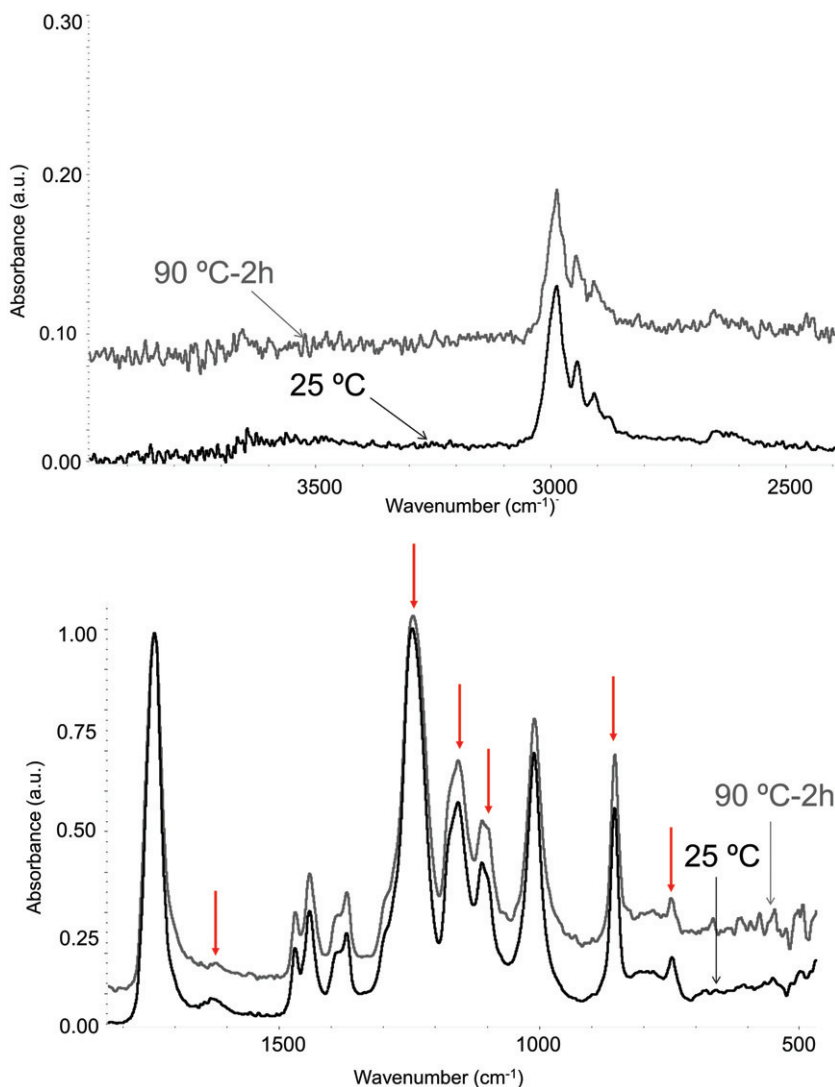
Figure 1 shows, as typical example, the ATR-IR spectra of pECN cured at 25 °C for 24 hours and post-cured at 90 °C for 2 hours. Typical bands of cyanoacrylates can be distinguished in the ATR-IR spectra of Figure 1: C=C stretching at 3128 and 1625 cm<sup>-1</sup>, methylene bands at 2987-2860, 1447, 720 y 856 cm<sup>-1</sup>, C=O stretching at 1731 cm<sup>-1</sup>, and C-O-C bands at 1090, 1150 and 1243 cm<sup>-1</sup>. The post-cure does not cause the formation of new absorption bands pointing to the de-polymerization of pECN chains by unzipping mechanism. However, the intensities of the C=C bands at 3128 and 1625 cm<sup>-1</sup> are reduced after post-cure, indicating higher degree of polymerization. Furthermore, after post-cure the intensities of the C-O-C bands at 1090, 1150 and 1243 cm<sup>-1</sup> increase and the ones of the methylene bands at 2987-2860, 720 y 856 cm<sup>-1</sup> decrease, likely due to the existence of polymer with lower molecular weight caused by de-polymerization of pECN by unzipping mechanism. Therefore, the post-cure of pECN cured at 25 °C for 24 hours seems to create two different structures of different molecular weights, one with higher degree of polymerization and the other with lower degree of polymerization; this hypothesis has also been proposed elsewhere [5].

<sup>1</sup>H NMR spectra of pECN cured at 25 °C for 24 hours and post-cured at 90 °C for 2 hours are given in Figure 2(a,b) respectively. The <sup>1</sup>H NMR spectra of pECN cured at 25 °C during 24 hours (Figure 2(a)) show the broads signals of the protons of the ethyl group at 1.32 and 4.32 ppm, and the signals of the protons of the double C=C bond appear at 6.67 and 7.09 ppm. The post-cure of pECN at 90 °C for 2 hours reduced notably the intensities of the signals of the protons of the double C=C bond (Figure 2(b)), confirming the higher degree of polymerization evidenced by ATR-IR spectroscopy.

Differential scanning calorimetry (DSC) was used for assessing the structural changes in the cured and post-cured pECNs. Figure 3(a) shows the DSC thermograms corresponding to the first heating run of the cured pECN at 25 °C for 24 hours and post-cured at 45 and 90 °C for two hours. All pECNs show an endothermic post-polymerization peak indicating that, under the experimental conditions used in this study, the polymerization of ECN is not complete at 25 °C not even after being post-cured at 90 °C for 6 hours. The post-polymerization peak of the cured pECN appears at 106 °C and the one for the post-cured pECN is produced at higher temperature (115 to 128 °C), the higher is the post-cure temperature, the higher is the temperature of the post-polymerization peak (Table 1). On the other hand, the post-polymerization enthalpy of pECN cured at 25 °C for 24 hours is 26 J/g and it is reduced noticeably (11 to 3 J/g) after post-cure (Table 1). Therefore, the post-cure of pECN at 45 °C and, more markedly, at 90 °C decreases the extent of post-polymerization of pECN, since the

271  
272  
273  
274  
275  
276  
277  
278  
279  
280  
281  
282  
283  
284  
285  
286  
287  
288  
289  
290  
291  
292  
293  
294  
295  
296  
297  
298  
299  
300  
301  
302  
303  
304  
305  
306  
307  
308  
309  
310  
311  
312  
313  
314  
315

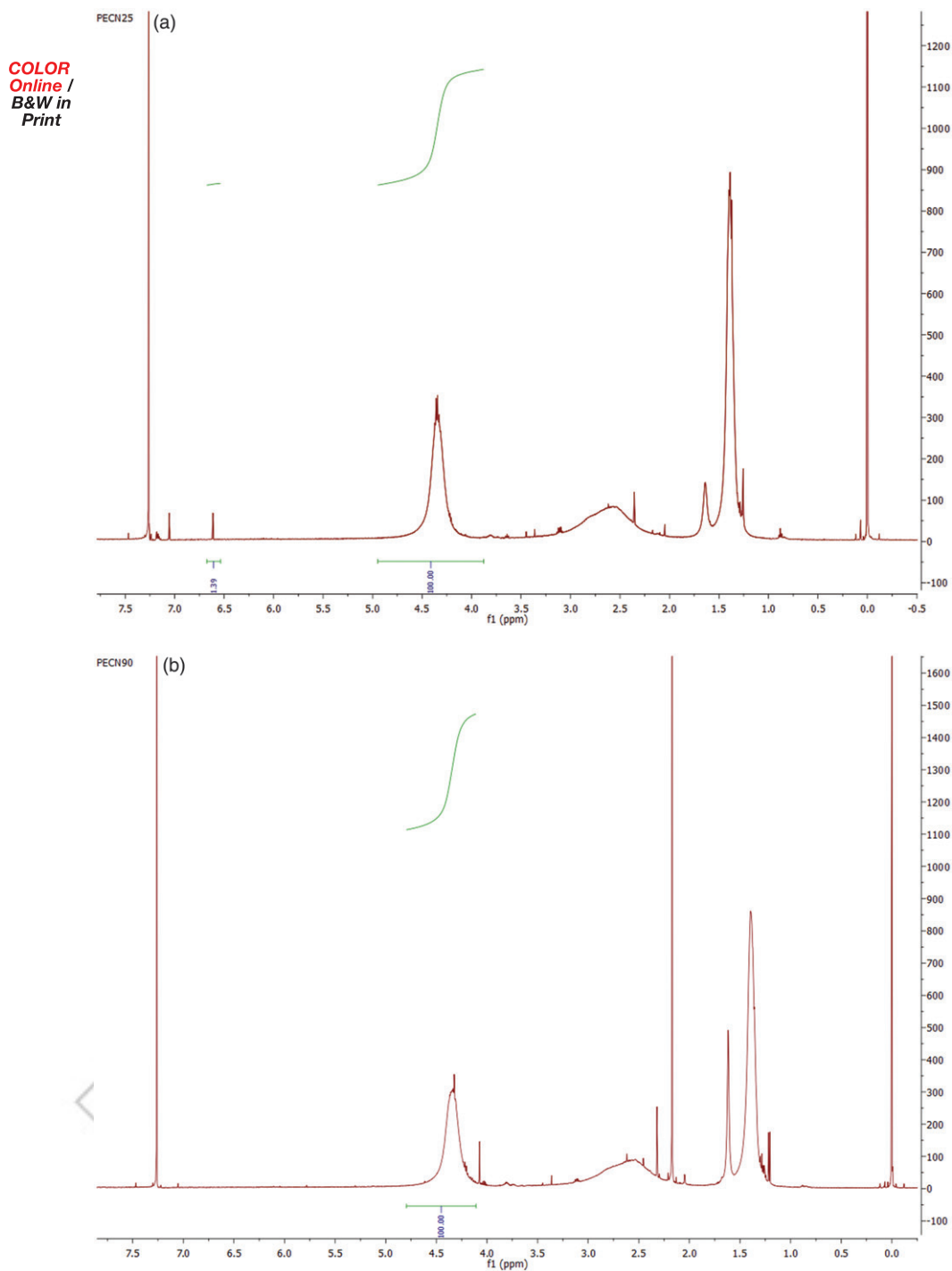
COLOR  
Online /  
B&W in  
Print



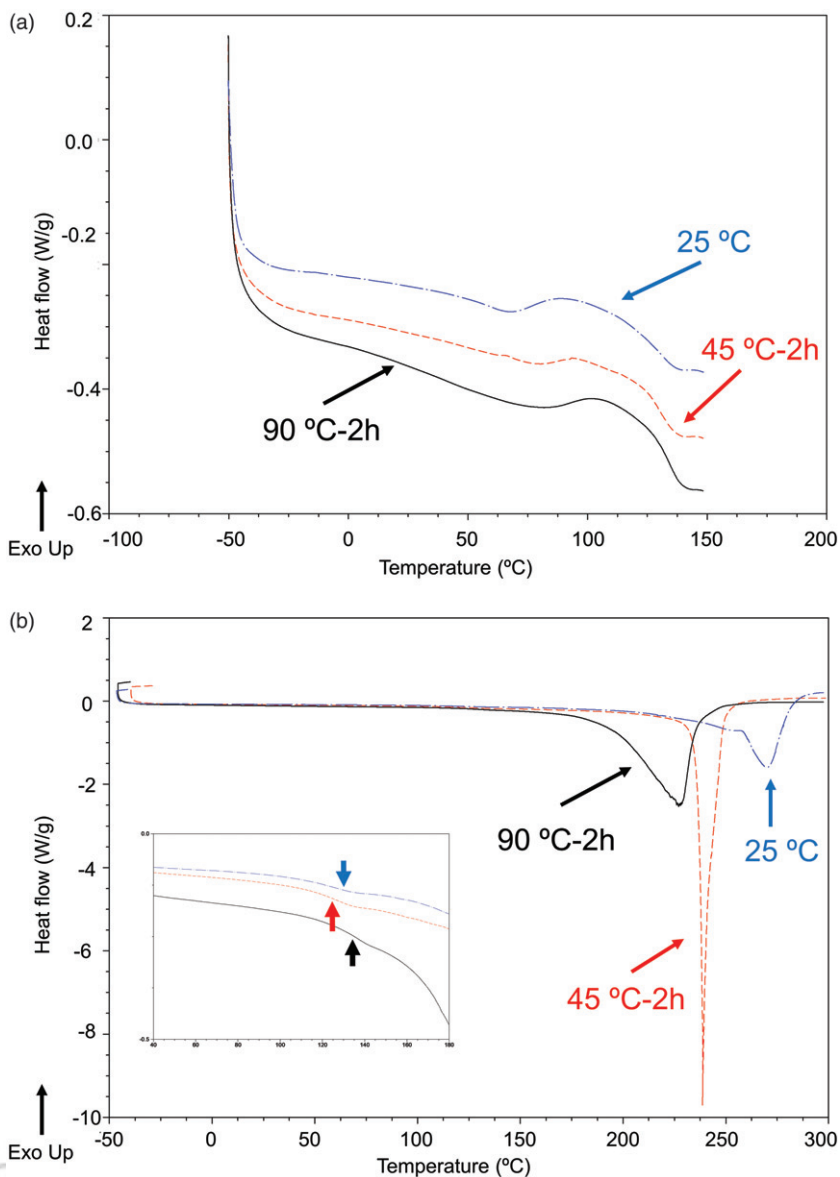
**Figure 1.** ATR-IR spectra of pECN cured at 25 °C for 24 hours and post-cured at 90 °C for 2 hours.

thermal treatments usually favored the termination step by a SINT (slow-initiated, non-terminated) mechanism in zwitterionic polymerizations initiated by tertiary amines [11].

During the second DSC heating run, none of the DSC thermograms show an exothermic peak (Figure 3(b)), indicating the complete polymerization of pECN during the DSC experiment. Therefore, vitrification is produced during post-cure of pECN as the post-cure temperatures are below the glass transition temperature ( $T_g$ ) of the polymer (above 130 °C). During the first DSC heating run carried out above 130 °C, the vitrification does not persist and polymerization of ECN is completed. The second DSC heating run of pECN shows the glass transition temperature as an endothermic inflexion in the thermogram and the decomposition of pECN at higher temperature as well. Table 1 shows that the  $T_g$  value of pECN is somewhat similar regardless the polymer is post-cured or not (130 °C for cured pECN at 25 °C and 134-136 °C for



**Figure 2.** (a)  $^1\text{H}$  NMR spectrum of pECN cured at  $25^\circ\text{C}$  for 24 hours and post-cured at  $90^\circ\text{C}$  for 2 hours. (b)  $^1\text{H}$  NMR spectrum of pECN post-cured at  $90^\circ\text{C}$  for 2 hours.

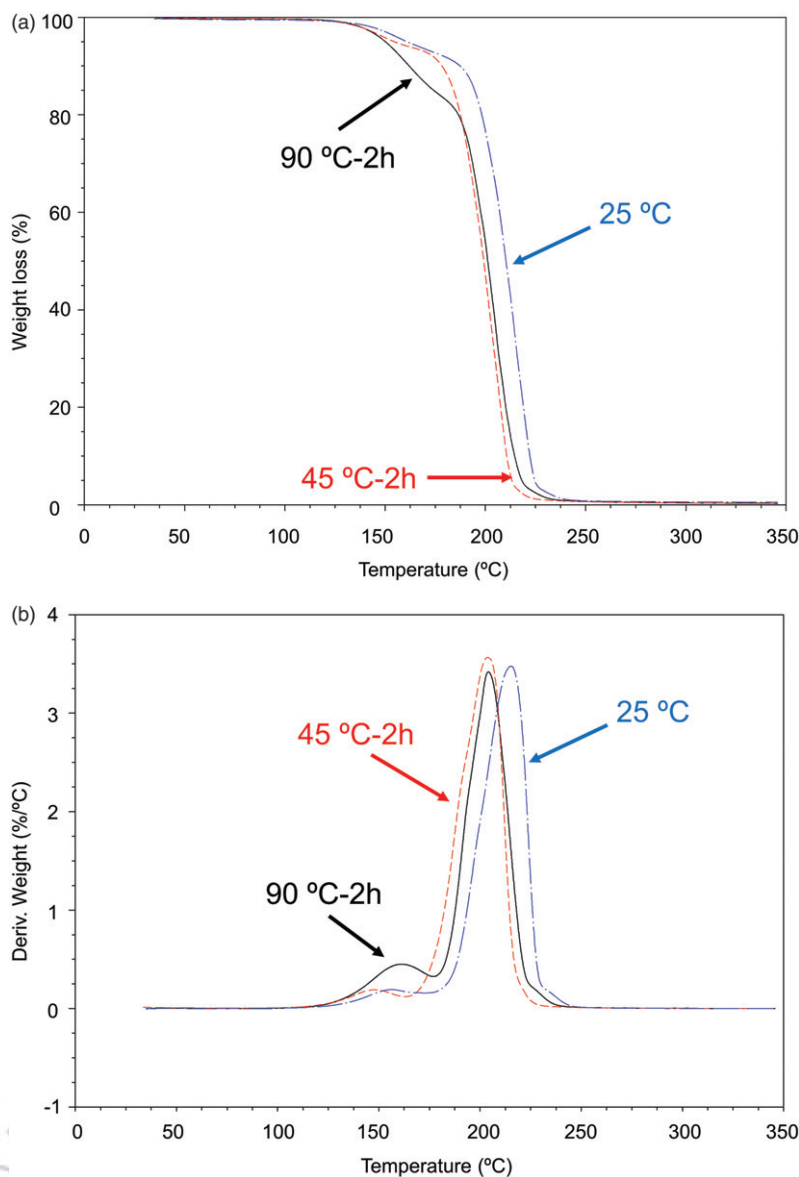
COLOR  
 Online /  
 B&W in  
 Print


**Figure 3.** (a) DSC thermograms of pECN cured at 25 °C for 24 hours and post-cured at 45 and 90 °C for 2 hours. First heating run. (b) DSC thermograms of pECN cured at 25 °C for 24 hours and post-cured at 45 and 90 °C for 2 hours. Second heating run.

**Table 1.** Temperature ( $T_{\text{post}}$ ) and enthalpy ( $\Delta H_{\text{post}}$ ) of post-polymerization, glass transition temperature ( $T_g$ ), and decomposition temperature ( $T_{\text{dec}}$ ) and enthalpy ( $\Delta H_{\text{dec}}$ ) of pECNs cured at 25 °C for 24 hours and post-cured at 45 and 90 °C for different times.

Post-cure condition	1 <sup>st</sup> heating run		2 <sup>nd</sup> heating run		
	$T_{\text{post}}$ (°C)	$\Delta H_{\text{post}}$ (J/g)	$T_g$ (°C)	$T_m$ (°C)	$\Delta H_m$ (J/g)
25 °C	106	26	130	226	775
45 °C-2h	115	11	124	239	571
90 °C-2h	124	6	134	264	504
90 °C-6h	128	3	136	268	500

COLOR  
Online /  
B&W in  
Print



**Figure 4.** (a) Variation of the weight as a function of the temperature for pECN cured at 25 °C for 24 hours and after being post-cured at 45 and 90 °C for 2 hours. TGA experiments. (b) Variation of the derivative of the weight as a function of the temperature for pECN cured at 25 °C for 24 hours and after being post-cured at 45 and 90 °C for 2 hours. TGA experiments.

post-cured pECN at 90 °C); the  $T_g$  values obtained in this study agree well with the ones previously reported for pECN [13]. On the other hand, the decomposition temperature increases and the decomposition enthalpy decreases for the post-cured pECNs, in greater extent by increasing the post-cure temperature, confirming higher extent of polymerization of pECN caused by a SINT mechanism [11].

TGA was used to assess the thermal stability and the structural changes in the cured and post-cured pECN. Figure 4(a) shows, as typical example, the TGA curves of pECN

**Table 2.** Temperatures at which 5 ( $T_{5\%}$ ) and 50 ( $T_{50\%}$ ) wt% losses are produced, and their corresponding weight losses for the two thermal decompositions of pECN cured at 25 °C for 24 hours and post-cured at 45 and 90 °C for 2 and 6 hours.

Post-cure condition	$T_1$ (°C)	Weight loss <sub>1</sub> (%)	$T_2$ (°C)	Weight loss <sub>2</sub> (%)	$T_{5\%}$ (°C)	$T_{50\%}$ (°C)
25 °C	156	10	215	85	160	210
45 °C-2h	148	6	204	90	153	199
90 °C-2h	161	18	205	77	150	201
90 °C-6h	163	21	208	72	149	204

**Table 3.** Diffusion coefficients (D) of pECN cured at 25 °C for 24 hours and pECN post-cured at 90 °C for 2 hours.

Post-cure condition	D ( $10^{-10}$ ms <sup>-1</sup> )		$D^{\text{pECN}}/D^{\text{TMS}}$
	TMS	pECN	
25 °C	30.2	8.39	0.28
90 °C-2h	30.1	8.98	0.30

cured at 25 °C for 24 hours and after being post-cured at 90 °C for 2 hours. The post-cure diminishes the thermal stability of pECN, more markedly by increasing the post-cure temperature, as it starts to degrade at a lower temperature and the temperatures at which 5 and 50% mass of pECN decreased (Table 2). The main thermal decomposition is obtained at 215 °C for pECN cured at 25 °C for 24 hours and at 204–208 °C after post-curing at 45 or 90 °C for two hours. Furthermore, the post-cure of pECN increases the amount of mass loss at 148–163 °C, particularly for the post-cure at 90 °C, due to the formation of new short polymer chains (18 wt% in pECN post-cured at 90 °C and 10 wt% in pECN cured at 25 °C for 24 hours). These evidences point out again to the de-polymerization of pECN by unzipping mechanism produced during post-cure, and is also confirmed by the decrease of the temperatures at which 5 and 50 wt% are lost after post-cure of pECN (Table 2). On the other hand, the pECN shows two main thermal decompositions that are better evidenced in the derivative TGA curves (Figure 4(b)). The two thermal decompositions appear at 156 °C and 215 °C (for the pECN cured at 25 °C for 24 hours) and at 148–163 °C and 204–208 °C (for the pECN post-cured at 45 and 90 °C for two hours). These results clearly indicate the existence of two different main polymeric structures of different molecular weights in both polymers, in accordance with previously reported data [5]. The thermal decomposition of pECN at higher temperature points to the dominance of polymeric chains with high molecular weights whereas the one at lower temperature can be ascribed to shorter polymeric chains.

Diffusion-ordered NMR spectroscopy (DOSY) studies were also performed in pECN cured at 25 °C for 24 hours and after being post-cured at 90 °C. According to Table 3, the diffusion coefficient of the pECN post-cured at 90 °C is higher than the one of the pECN cured at 25 °C for 24 hours, this confirm the existence of shorter polymeric chains in the polymer post-cured at 90 °C, in agreement with the evidences shown by TGA experiments.

The molecular weights of the pECN cured at 25 °C for 24 hours and after being post-cured at 90 °C for 2 hours were determined by GPC (Table 4). The molecular weight distribution of the pECNs is relatively narrow (polydispersity: 2.2 for pECN cured at 25 °C and 1.6 for pECN post-cured at 90 °C). After the post-cure of pECN at 90 °C, a decrease in Mw and Mz values of the polymer is observed indicating a

**Table 4.** Molecular weights of pECN cured at 25 °C for 24 hours and post-cured at 90 °C for 2 hours.

Post-cure condition	Mn (Da)	Mw (Da)	Mz (Da)	Mw/Mn
25 °C	10670	23270	39760	2.2
90 °C-2h	12700	20240	30700	1.6

reduction of the medium and larger polymeric chains. Furthermore, a slight increase in the Mn value is also noticed in pECN post-cured at 90 °C because of the formation of new shorter polymeric chains of pECN through an unzipping de-polymerization mechanism. These results confirm the evidences shown above by ATR-IR spectroscopy, DOSY and TGA studies. On the other hand, Guthrie et al. [7] have also found a slight reduction in the molecular weight of the polycyanoacrylate by increasing the time of the thermal treatment at 90 °C, although the reported values of the molecular weights of the pECNs are lower than the ones in this study likely due to the different initiators of the polymerization used in both studies.

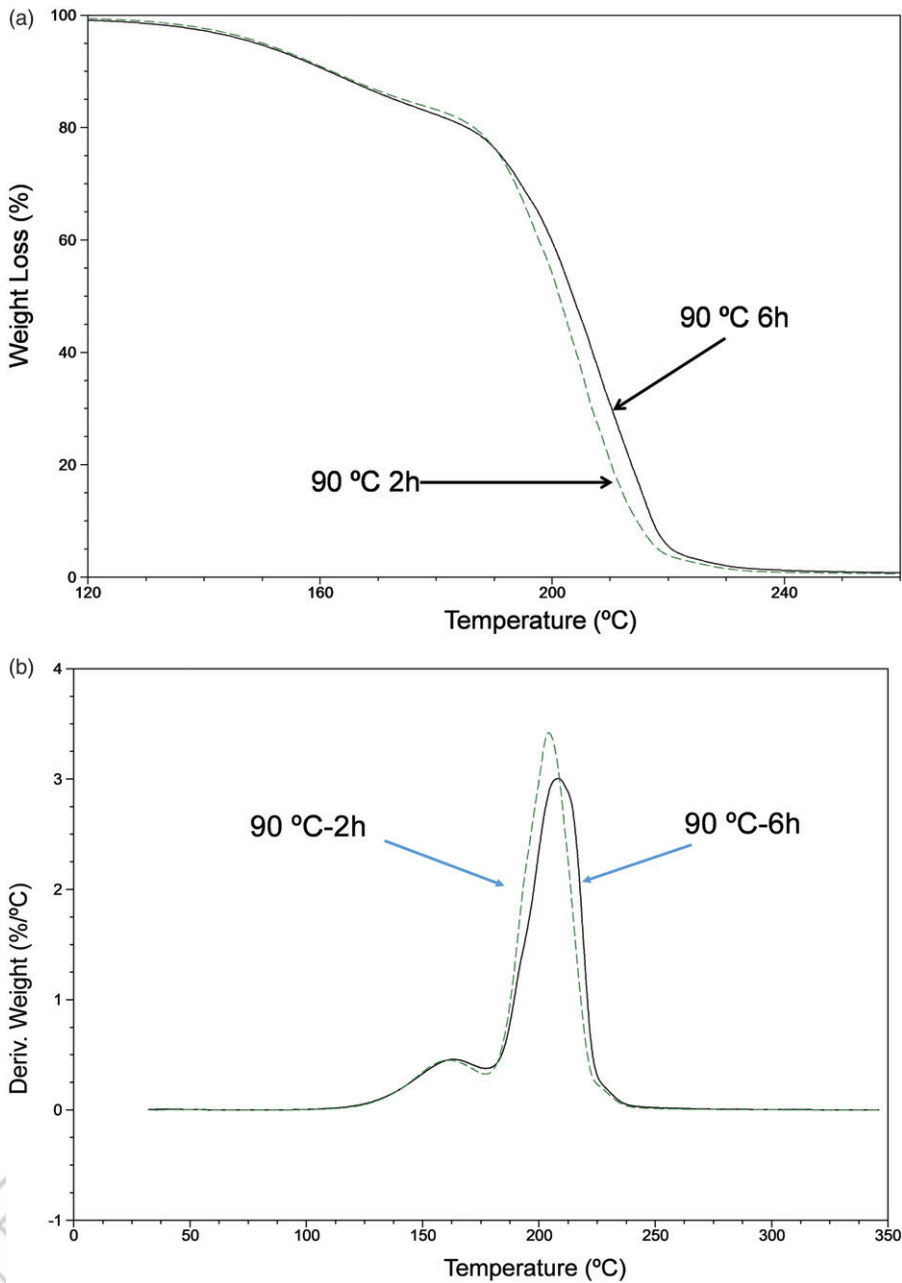
### 3.2. Influence of the duration of the post-cure on the structure and morphology of pECNs

The duration of the post-cure may also affect the structure of the pECN. The structural characterization of the pECNs post-cured at 90 °C for 2 and 6 hours was carried out. Table 1 shows some parameters obtained from the DSC thermograms of the pECNs post-cured at 90 °C for 2 and 6 hours. The post-polymerization temperature is higher and the enthalpy of post-polymerization of pECN is slightly lower when the duration of the post-cure treatment at 90 °C increases. On the other hand, the  $T_g$  value of pECN slightly increases by extending the duration of the post-cure at 90 °C. Therefore, the longer is the post-cure at 90 °C, the more complete is the polymerization, although a complete polymerization is not observed.

Figure 5(a) shows the TGA curves of pECN post-cured at 90 °C for 2 and 6 hours. The thermal stability up to 170 °C of pECN post-cured at 90 °C for 2 and 6 hours is similar but above this temperature, the thermal stability of the post-cured pECN during 6 hours is higher. In fact, according to Table 2, the temperature at which 50 wt% is lost is higher when the post-cure treatment lasted up to 6 hours. On the other hand, the post-cured pECN showed two main thermal decompositions clearly seen in the derivative TGA curves (Figure 5(b)). These decompositions appear at 161 °C and 205 °C in the post-cured pECN at 90 °C for 2 hours whereas they appear at 163 °C and 208 °C in the post-cured pECN at 90 °C for 6 hours. These results confirm again the existence of two different main polymeric structures of different molecular weights in the post-cured pECN. On the other hand, the increase of the time of the post-cure at 90 °C increases the weight loss and the maximum temperature of thermal decomposition of the post-cured pECN in the TGA curve. Thus, the longer duration of the post-cure at 90 °C, the higher is the percentage of the polymeric chains with higher molecular weight. This result contradicts the so far accepted unzipping mechanism in thermally treated poly-cyanoacrylates [7]. In our study, a longer post-cure at 90 °C might favour the termination step in the post-polymerization of pECN with



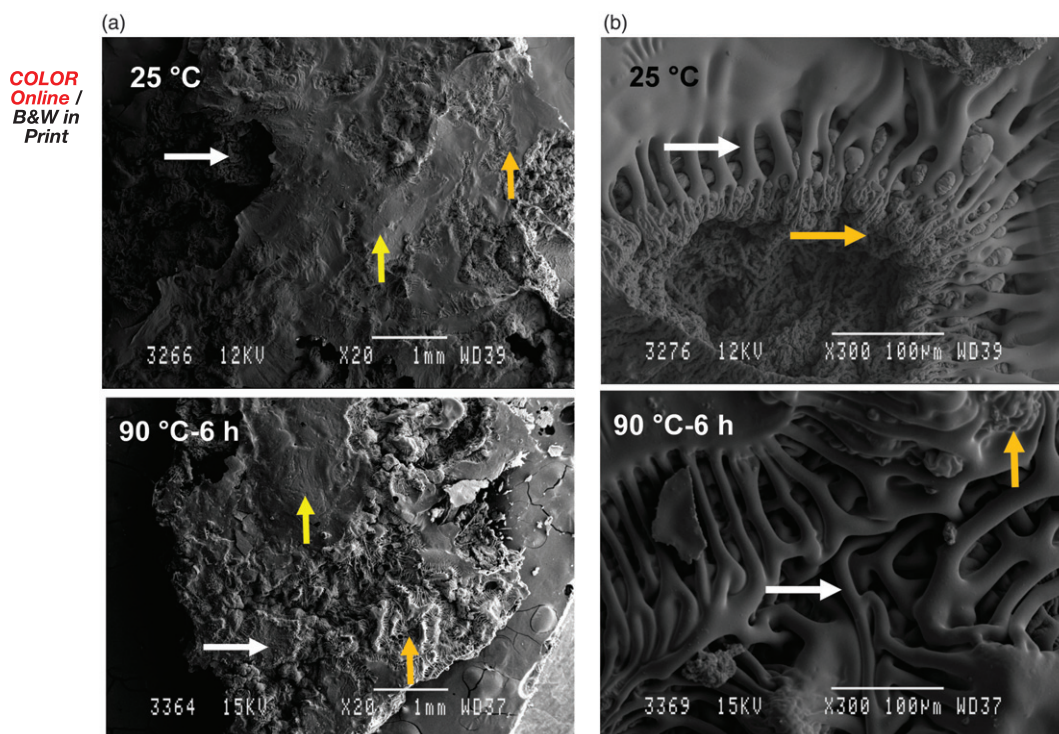
COLOR  
Online /  
B&W in  
Print



**Figure 5.** (a) Variation of the weight as a function of the temperature of pECN post-cured at 90 °C for 2 and 6 hours. TGA experiments. (b) Variation of the derivate weight as a function of the temperature of pECN post-cured at 90 °C for 2 and 6 hours. TGA experiments.

respect to the unzipping mechanism, being this result consistent with the small decrease in the post-polymerization enthalpy obtained in the first DSC heating run.

The post-cure treatment also affected the morphology of the pECN. Figure 6(a,b) shows the SEM micrographs at different magnifications of the pECN cured at 25 °C for 24 hours and post-cured at 90 °C for 6 hours. The non-post-cured pECN shows a



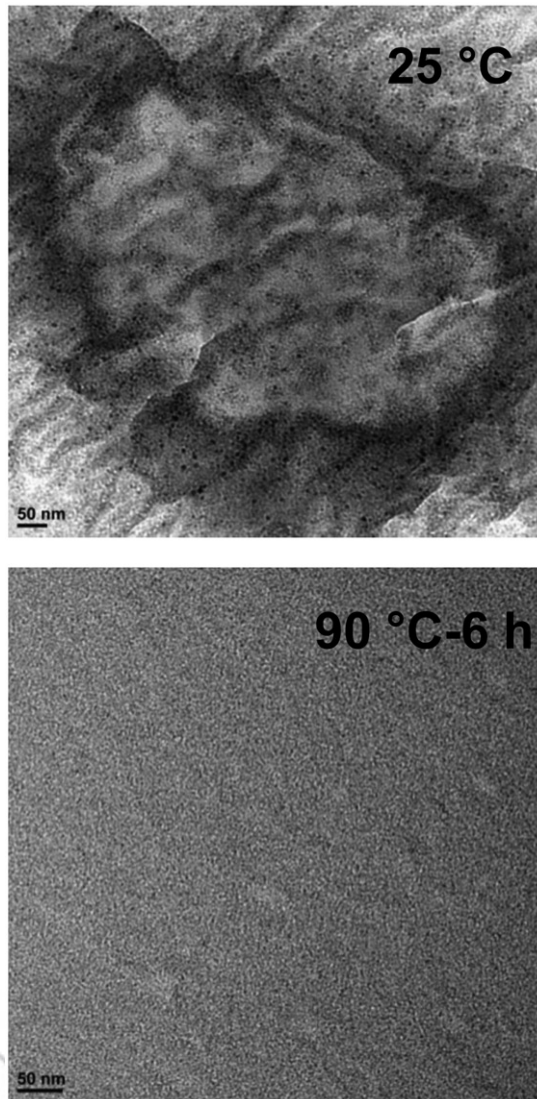
**Figure 6.** (a) SEM micrographs of pECN cured at 25 °C for 24 hours (up) and post-cured at 90 °C for 6 hours (down). White arrows: porosity. Orange arrows: wrinkle structures. Yellow arrows: compact crust. X 20. (b) SEM micrographs of pECN cured at 25 °C for 24 hours (up) and post-cured at 90 °C for 6 hours (down). White arrows: smooth areas. Orange arrows: rough areas. X 300.

heterogeneous structure, some porosity and wrinkle structures can be distinguished over a compact crust. The pECN post-cured at 90 °C shows a change of the topography with respect to that of pECN cured at 25 °C as the presence of compact crust is less important and the number of wrinkled structures increases (Figure 6(a)). On the other hand, Figure 6(b) shows the existence of two different structure domains in the pECN, one relatively smooth and another quite rough that may correspond to the two polymeric structures with different molecular weights evidenced by the TGA experiments. Figure 6(b) shows that the relatively smooth structure domains are dominant over the rough ones.

Figure 7 shows the TEM micrographs of the pECN cured at 25 °C for 24 hours and post-cured at 90 °C for 6 hours. The non-post-cured pECN shows abundant wrinkled structures and about 5 nm size nano-spheres (shown as black dots) which are disseminated into the continuous polymeric matrix. The existence of the nano-spheres in pECNs has been previously shown [2]. On the contrary, in the post-cured pECN at 90 °C for 6 hours, the nano-spheres and the wrinkles disappear and a homogeneous and relatively smooth surface is observed.

### 3.3. Influence of the post-cure temperature of pECN on the adhesion properties

ECN was cured at 25 °C for 24 hours and later was post-cured at 45 and 90 °C for 2 hours. Table 5 shows that the shear strength value of the joint made with ECN



**Figure 7.** TEM micrographs of pECN cured at 25 °C for 24 hours (up) and post-cured at 90 °C for 6 hours (down).

cured at 25 °C is high and a mixed locus of failure (50% adhesion and 50% cohesive failure of the adhesive) is obtained, indicating that the cure of pECN was not complete. The post-cure of the adhesive joints decreases the shear strength more markedly by increasing the post-cure temperature, and always mixed loci of failure of adhesion and cohesive failure of the adhesive are observed; however, the increase of the post-cure temperature causes an increase of the percentage of cohesive failure in the adhesive which may explain the decrease in shear strength of the adhesive joints.

The decrease in the shear strength values of the post-cured joints made with ECN is in agreement with previously reported studies made with composite-ethyl cyanoacrylate [6] and steel-ethyl cyanoacrylate [7] joints. The decrease in the shear strength values of the joints made with ECN after being post-cured can be related to

**Table 5.** Single lap-shear strength values and loci of failure of aluminium 5754/ECN/aluminium 5754 joints.

Post-cure condition	Shear strength (MPa)	Locus of failure*
25 °C	3.21 ± 0.31	50% A+ 50% C
45 °C-2h	1.94 ± 0.07	40% A+ 60% C
90 °C-2h	1.40 ± 0.05	25% A + 75% C

\*A: Adhesion failure; C: Cohesive failure of p-ECN.

changes in the physical and chemical structure of the cured pECN. The decrease in the shear strength value of the post-cured pECN can be ascribed to the degradation through an “unzipping” mechanism according to Scheme 2, i.e., the unzipping de-polymerization process initiated by the abstraction of one terminal proton in the “parent” polymer chain producing monomeric units by a retro-Michael cascade reaction [10]. The post-cure creates new low molecular weight polymeric chains that decrease the mechanical properties of pECN. As a consequence, the post-cure produces an increase in the  $T_g$  value, a decrease of the enthalpy and an increase in the temperature of post-polymerization. Furthermore, the post-cure changed the structure of the pECN and the molecular weight distribution of the two distinct polymeric domains.

#### 4. Conclusions

The post-cure at 90 °C reduced the single lap-shear strength values of aluminum/ECN/aluminum joints because of the termination step by SINT (slow-initiated, non-terminated) mechanism in zwitterionic polymerizations initiated by tertiary amines was favored. The increase in the post-cure temperature produced the de-polymerization of high molecular weight polymeric chains of pECN by an unzipping mechanism creating new low molecular weight polymeric chains that decreased the mechanical properties of pECN. The post-cure produced a slight increase in the  $T_g$  value, a decrease of the enthalpy and an increase in the temperature of post-polymerization. Furthermore, the post-cure changed the structure of the pECN and the molecular weight distribution of the two distinct polymeric domains. On the other hand, the topography of the pECN surface was affected by the post-cure favoring the creation of smooth structures and removing the wrinkles and the nano-spheres produced in pECN cured at 25 °C for 24 hours. Finally, the influence of the temperature of the post-cure determined in greater extent the structure, thermal and topographical properties of pECN than the time of post-cure did.

#### Acknowledgments

The Authors thank Dr. E. Lorenzo from the Research Technical Services of Alicante University for carrying out the  $^1\text{H}$  NMR experiments.

#### Disclosure statement

Q2 No potential conflict of interest was reported by the authors.

## Funding

This work was supported by the University of Alicante [VIGROB-001, VIGROB-173] and the Spanish Ministerio de Economía y Competitividad [CTQ2015-66624-P].

## ORCID

Gabriel Estan-Cerezo  <http://orcid.org/0000-0002-6247-1831>

Diego A. Alonso  <http://orcid.org/0000-0002-9069-1188>

## References

- [1] Puglisi G, Fresta M, Giammona G, et al. Influence of the preparation conditions on poly(ethylcyanoacrylate) nanocapsule formation. *Int J Pharm.* 1995;125:283–287.
- [2] Harivardhan-Reddy L, Murthy RSR. Study of influence of polymerization factors on formation of poly(butylcyanoacrylate) nanoparticles and in vitro drug release kinetics, *ARS Pharmaceutica.* 2004;45:211–234.
- [3] Doiphode SV, Reneker DH, Chase GG. Nanofibers and spheres by polymerization of cyanoacrylate monomer. *Polymer.* 2006;47:4328–4332.
- [4] Algaier D, Baskaran D, Dadmun M. The influence of temperature on the polymerization of ethyl cyanoacrylate from the vapor phase. *React Funct Polym.* 2011;71:809–819.
- [5] Dossi M, Storti G, Moscatelli D. Synthesis of poly(alkyl cyanoacrylates) as biodegradable polymers for drug delivery applications. *Macromol Symp.* 2010;289:124–128.
- [6] Senchenya NG, Guseva TI, Gololobov YG. Cyanoacrylate-based adhesives. *Polymer Sci.* 2007;49:235–239.
- [7] Guthrie J, Otterburn MS, Rooney JM, et al. The effect of heat on the molecular weight of poly(ethyl 2-cyanoacrylate) adhesive. *J Appl Polym Sci.* 1985;30:2863–2867.
- [8] Chorbadjiev KG, Novakov PCH. Study of the thermal degradation of poly(alkyl  $\alpha$ -cyanoacrylate)s. *Eur Polym J.* 1991;27:1009–1015.
- [9] Robello DR, Eldridge TD, Swanson MT. Degradation and stabilization of polycyanoacrylates. *J Polym Sci A Polym Chem.* 1999;37:4570–4581.
- [10] Ryan B, McCann G. Novel sub-ceiling temperature rapid depolymerization-repolymerization reactions of cyanoacrylate polymers. *Macromol Rapid Comm.* 1996;17:217–227.
- [11] Pepper DC. Zwitterionic chain polymerizations of cyanoacrylates. *Makromol Chem M. Symp.* 1992;60:267–277.
- [12] Johnston DS, Pepper DC. Polymerisation via macrozwitterions, 2. Ethyl and butyl cyanoacrylates polymerised by pyridine and polyvinylpyridine. *Makromolekul Chem.* 1981;182:407–420.
- [13] Denchev Z, Tomanova M, Lederer A. On the anionic homo- and copolymerization of ethyl- and butyl-2-cyanoacrylates. *J Polym Sci A Polym Chem.* 2008;46:5142–5156.