

RESEARCH ARTICLE

A quantitative determination of the polymerization of benzoxazine thin coatings by time-of-flight secondary ion mass spectrometry

Eva Pospisilova¹ | Alexis Renaud² | Marc Poorteman² | Marjorie Olivier² | Ludovic Dumas³ | Philippe Dubois³ | Leila Bonnaud⁴ | Konstantin Moshkunov¹ | Bernard Nysten¹ | Arnaud Delcorte¹ 

¹Bio and Soft Matter Division, Université catholique de Louvain, Institute of Condensed Matter and Nanoscience, Louvain-la-Neuve, Belgium

²Department of Materials Science, Materials Engineering Research Center (CRIM), University of Mons, Mons, Belgium

³Laboratory of Polymeric and Composite Materials, Center of Innovation and Research in Materials and Polymers (CIRMAP), University of Mons, Mons, Belgium

⁴Materia Nova Research Center, Materia Nova asbl, Mons, Belgium

Correspondence

Arnaud Delcorte, Université catholique de Louvain, Institute of Condensed Matter and Nanoscience, 1 Place Louis Pasteur, 1348 Louvain-la-Neuve, Belgium.
Email: arnaud.delcorte@uclouvain.be

Phenol-paraphenylenediamine (P-pPDA) benzoxazines exhibit excellent barrier properties, adequate to protect aluminum alloys from corrosion, and constitute interesting candidates to replace chromate-containing coatings in the aeronautical industry. For the successful application of P-pPDA coatings, it is necessary to decrease the curing temperature to avoid the delamination of the coating while preserving the mechanical properties of the alloy, as well as the barrier properties of the coating. However, decreasing the curing temperature leads to less polymerized films, the extent of which requires a quantitative assessment.

While the conversion rate of the polymerization reaction is commonly evaluated for bulk samples using differential scanning calorimetry (DSC), a tool for its evaluation in thin films is missing. Therefore, a new approach was developed for that matter using time-of-flight secondary ion mass spectrometry (ToF-SIMS). The relation between the SIMS data integrated from inside thin films and the DSC results obtained on bulk samples with the same curing cycle allowed to calibrate the SIMS data. With this preliminary calibration of the technique, the polymerization of P-pPDA coatings can be locally determined, at the surface and along the depth of the coating, using dual-beam depth profiling with large argon cluster beam sputtering.

KEYWORDS

benzoxazine, crosslinking, polymerization, thin polymer coatings, ToF-SIMS

1 | INTRODUCTION

Aluminum alloys commonly used in aeronautical industry are sensitive to localized corrosion. At the industrial scale, several pretreatments are currently developed to enhance the anticorrosion properties: anodized layers,¹ conversion coatings,² and organic coatings.³ However, the anodization protection pretreatment usually involves highly biotoxic chromates, which are progressively banned since September

2017. Therefore, new ecological friendly materials and technologies are needed to replace hazardous chromates.

Presently, protective organic coatings for aluminum alloys are mostly epoxy resins, but these have several limitations. The most problematic property of epoxy resins is the water uptake, which can cause blistering, delamination, and even corrosion.⁴ Another disadvantage of epoxy resins is their limited thermal stability that prohibits applications for engine parts. On the contrary, polybenzoxazine

coatings possess the necessary properties.⁵ Indeed, they are known for their low water uptake, high glass transition temperature, and good dielectric properties.⁶ Another advantage is the relative simple and high yield synthesis of benzoxazine precursors following a Mannich-like condensation of a phenol, a primary amine, and formaldehyde.⁷

Benzoxazine precursors with desired properties can be synthesized using an adequate selection of reactants. Benzoxazine precursors based on phenol and phenol-paraphenylenediamine (P-pPDA) are composed of a mixture of monomers and few oligomers when synthesized from a fine mixing of p-phenylene diamine, paraformaldehyde, and phenol in a stoichiometric ratio of 1: 4: 2 following a robust bulk procedure at 140°C for 30 minutes (described elsewhere⁸). The reaction is schematically summarized in Figure 1A, and the detailed precursor characterization was previously reported.⁸ Interestingly, the resulting precursor is thermally stable and nonflammable, which makes it a good candidate for applications in an aircraft as well as for anticorrosion coatings.

However, one of the possible issues in the applications of benzoxazine for aluminum alloy protection can be the fact that P-pPDA coatings are cured at relatively high temperatures (up to 220°C/230°C) while some aluminum alloys can be very sensitive to thermal treatments.⁹ In particular, alloys from series 2xxx (according to the nomenclature for wrought aluminum alloys, where the first digit indicates the main alloying element and the mechanical resistance; in this case, the main alloying element is Cu, and the achieved mechanical resistance is 170–520 MPa), that are commonly used in aircraft applications cannot be exposed to high temperatures without suffering changes in their mechanical properties due to the modification of their microstructure.¹⁰ Therefore, curing has to be performed at temperatures lower than 170°C. To assess that the desired film properties can be obtained in such conditions, an evaluation of the degree of conversion of the polymerization and crosslinking reaction is required.

Polybenzoxazines were studied in the last few years because of their simple ring opening polymerization upon thermal curing (Figure 1B) and their outstanding properties.^{11,12} The desired properties of the coating are acquired by thermal curing that induces polymerization. Different curing cycles and their effect on the elastic modulus, fracture toughness, impact resistance, and glass transition temperature of resins were studied by Wu et al.¹³ Other authors dealt with the polymer network formation kinetics and the partial

crosslinking of epoxies used in industrial applications.^{14,15} Techniques used for epoxy processing can also be applied to polybenzoxazines.

The chemical properties of polymers are usually characterized for the bulk samples, and there are several methods that are well suited for this task: nuclear magnetic resonance spectroscopy (NMR), differential scanning calorimetry (DSC), Fourier-transform infra-red spectroscopy (FTIR), or swelling experiments. The limit of FTIR is the penetration depth of 1 to 2 μm . In the case of DSC, only bulk samples can be used, and the method is destructive. When it comes to thin polymer films or organic layers, only surface sensitive methods are applicable.

Combined with principal component analysis (PCA), secondary ion mass spectrometry (SIMS) has proven to be a powerful method to determine the structure of plasma polymers¹⁶ and, in particular, to determine their crosslinking degree.¹⁷ Plasma polymers form very thin layers (<1 μm) with a complex crosslinked structure,¹⁸ and therefore, SIMS is one of the few tools able to access the chemical information.^{19,20}

In this study, a conventional polymerization process takes place, also leading to a crosslinked molecular network (Figure 1B). After confirming the nature of the polymerization reaction in the investigated benzoxazine samples by means of DSC and FTIR, time-of-flight secondary ion mass spectrometry (ToF-SIMS) can be successfully used to locally evaluate the conversion degree of the reaction in very thin coatings, unlike the other methods at hand.

2 | EXPERIMENTAL

2.1 | Samples

A first series of samples consisted in aluminum alloys (AA1050) coated with P-pPDA following the procedure explained in a previous publication⁹ and exposed to thermal curing. The measured density of the dry P-pPDA monomers is 1.25 g/cm³. The solution of P-pPDA was prepared by dissolving P-pPDA precursors composed of monomers and few oligomers in chloroform (200 g/l). This solution was spin coated (3000 rpm for 30 s) on aluminum alloy sheets. The samples were then dried at 100°C in order to remove the residual solvent. After drying,

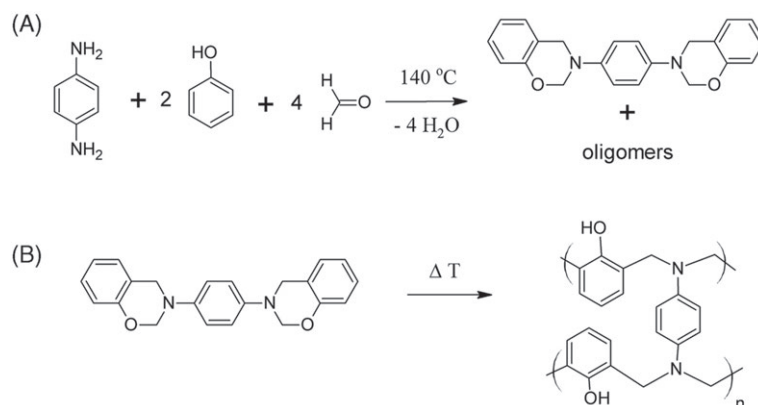


FIGURE 1 One pot synthesis of phenol-paraphenylenediamine (P-pPDA) (a) and P-pPDA polymerization via ring opening mechanism upon thermal curing (b). From reference 9

TABLE 1 Curing cycles applied on phenol-paraphenylenediamine (P-pPDA) coatings in order to obtain different polymerization degrees and the conversion degree χ obtained from the differential scanning calorimetry (DSC) measurements conducted on bulk P-pPDA samples

Curing Procedure Index	Drying at 100°C (min)	Curing at 140°C (min)	Curing at 160°C (min)	Curing at 180°C (min)	Curing at 200°C (min)	Curing at 220°C (min)	Curing at 230°C (min)	χ (%)
1	60	-	-	-	-	-	-	21
2	60	300	-	-	-	-	-	48
3	60	60	240	-	-	-	-	70
4	60	60	-	240	-	-	-	93
5	-	60	-	120	120	30	30	100

samples were cured by successive thermal curing steps described in Table 1.

A second series of five samples was simply cured for a shorter time of 30 minutes at different temperatures, from 100°C to 180°C by steps of 20°C (Table 2). The solution preparation and spin coating process were similar to the samples in Table 1, however the substrate was changed to a silicon wafer.

2.2 | Analysis methods

The chemical composition of the films was analyzed by time of flight secondary ion mass spectrometry (TOF-SIMS 5; Ion-tof GmbH) using Bi_5^+ clusters at 30 keV as an analysis beam, the analysis beam current was typically 0.06 pA. The repetition rate was 5 kHz (for a m/z range 0–3500). In the case of the subsurface characterization, ToF-SIMS was used in dual-beam molecular depth-profiling mode, where Ar_{1500}^+ at 10 keV with beam current 10 nA, used as a sputter beam, eroded the material, and Bi_5^+ was employed to analyze the bottom of the sputtered volume. The size of the area eroded by the sputter beam was $450 \times 450 \mu\text{m}^2$. To avoid edge effects, the analysis raster size was $150 \times 150 \mu\text{m}^2$. An automated electron beam (energy: 20 eV) compensated the charge build up in the polymer layer. Each sample was probed at three different places in order to ensure reproducibility of the analysis. The mass spectra were obtained in both ion polarities.

The thickness of the polymer layer was determined with a Stylus profiler (Bruker DektakXT) measuring the depth of the volume etched by ToF-SIMS. The Stylus tip radius was $0.7 \mu\text{m}$ and the applied Stylus force 1 mg. In addition to the Al substrates, the depth-profiling and profilometry measurements were also conducted on similar P-pPDA samples spin coated on flat silicon wafers in order to accurately determine the sputter yield volumes obtained upon 10 keV Ar_{1500}^+ bombardment. These sputter yield volumes are reported in Figure S1.

TABLE 2 Second series of curing cycles applied on phenol-paraphenylenediamine (P-pPDA) samples for 30 minutes and the conversion degree χ obtained from the differential scanning calorimetry (DSC) measurements conducted on bulk P-pPDA samples

Curing Procedure Index	A	B	C	D	E
T (°C)	100	120	140	160	180
χ (%)	21	21	24	32	43

FTIR measurements were carried out in the 650 to 4000 cm^{-1} range using a Nexus 870 spectrometer (Thermo Electron Company).

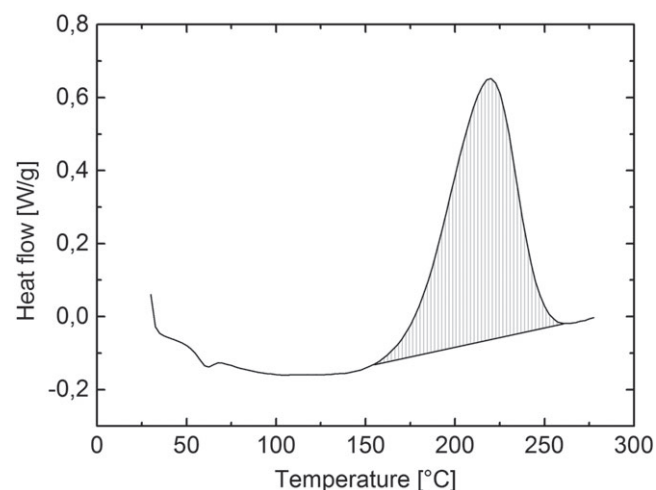
DSC measurements were carried out on a Q200 calorimeter from TA instrument under N_2 flow (50 mL/min). An indium standard was used for calibration.

2.3 | Results and discussion

DSC was used as a reference for the quantification of the conversion degree χ of the polymerization reaction for bulk P-pPDA samples cured with the same thermal curing protocols as the coatings (Tables 1 and 2). A typical DSC thermogram of reference P-pPDA bulk sample is shown in Figure 2. From the thermogram, the glass transition temperature of the precursor (T_g) can be determined at around 55°C and the start of the polymerization reaction around 160°C. The polymerization process produces a large exothermic peak. The potential of a material to polymerize is characterized as the reaction enthalpy ΔH , and its value is obtained by integrating the polymerization peak.

The conversion degree was then evaluated according the Equation 1

$$\chi[\%] = \frac{\Delta H_0 - \Delta H_{\text{residual}}}{\Delta H_0} \times 100, \quad (1)$$

**FIGURE 2** Differential scanning calorimetry (DSC) thermogram of phenol-paraphenylenediamine (P-pPDA) reference sample. The integral of the polymerization peak is marked by gray lines

where ΔH_0 corresponds to the total theoretical reaction enthalpy (392 J.g^{-1}) and $\Delta H_{\text{residual}}$ corresponds to the enthalpy measured after a given curing cycle. The DSC-obtained conversion degrees for bulk samples of P-pPDA are also given in Tables 1 and 2.

The effect of the thermal curing on the chemical composition of the P-pPDA layers was investigated by ToF-SIMS. To help the spectral interpretation, the scheme in Figure 1B indicates the most probable polymerized structure that forms according to the ring opening mechanism.⁹ In order to verify the vertical homogeneity of the chemical structure of the coatings, ToF-SIMS was used in the dual beam depth-profiling mode, as explained in the experimental section. Typical positive secondary ion mass spectra of two films with very different values of χ , reconstructed from the middle section of the P-pPDA layer, are presented in Figure 3, while a characteristic depth profile, obtained on a sample cured with cycle 1, is shown in Figure 4. The middle section of the depth profile of the P-pPDA layer, used to reconstruct the bulk-like SIMS spectra, is identified by the rectangle drawn in Figure 4. To have an accurate image of the bulk of the film, comparable with DSC, this section was chosen far from both the air benzoxazine and the benzoxazine aluminum interfaces, thereby avoiding their influence. In Figure 4, the bulk-like region is characterized by a wide plateau, between 20 and 160 seconds of sputtering. In order to have a good signal-to-noise ratio, we averaged the intensities over approximately 50 seconds of sputtering, in the middle of the coating. However, the results are insensitive to the exact limits of the integration region, provided that the interfaces are excluded. For the sake of clarity, a table with the identification of the main secondary ions observed in the positive and negative SIMS spectra of the P-pPDA samples is available as supplementary information (Table S1).

Figure 4 demonstrates that the ion intensities are significantly different in the very beginning of the profile (left side). Major chemical modifications induced by the ion beam can be excluded given that $10 \text{ keV Ar}_{1500}^+$ ions are used for the erosion of the sample.²⁰ Therefore, it is reasonable to suggest that the observed variation is caused by a difference in chemistry, such as the presence of surface contamination or the segregation of low mass benzoxazine oligomers towards the surface. In any case, the profiles justify that mass spectra taken

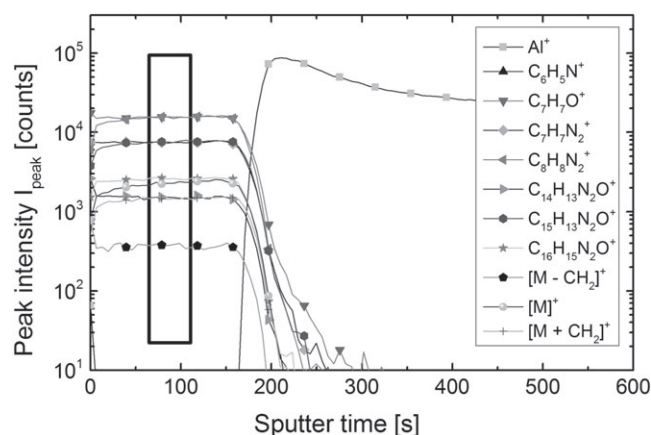


FIGURE 4 Molecular depth profile of phenol-paraphenylenediamine (P-pPDA) coating cured with procedure 1 in Table 1. The evolution of a series of characteristic P-pPDA fragments is represented

from the bulk of the coating were considered in order to compare them with results obtained from bulk analysis techniques such as DSC and IR. The bulk-like mass spectra of the noncured and fully cured samples (Figure 3) show that the SIMS intensity of large molecular fragments representing the P-pPDA precursor decreases with the polymerization of the coating. In contrast, the fragments with low molecular mass (below 100 a.m.u.) appear in the mass spectra of polymerized P-pPDA as well as in the mass spectra of the noncured coating (curing procedure index 1). The small molecular fragments cannot be used as the characteristic markers for the P-pPDA monomer because they do not contain the characteristic benzoxazine C—O—C bond.

In general, an increase of the curing temperature also results in a decrease of the total intensity of the mass spectra, as shown in Figure 5. The sample cured with procedure 5 (230°C) is expected to be the most polymerized ($\chi = 100\%$), and it has the lowest spectrum intensity. This is in agreement with the fact that highly crosslinked materials require more bond scissions to produce secondary ions and are therefore harder to sputter. In addition, a linear correlation is observed between the decrease of the total intensity of the mass

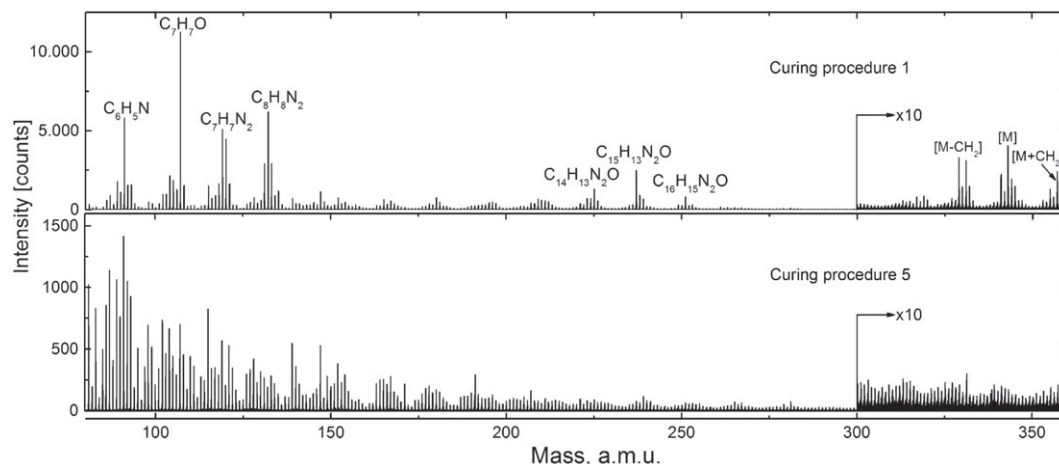


FIGURE 3 Comparison of the positive secondary ion mass spectra obtained for curing procedures 1 and 5

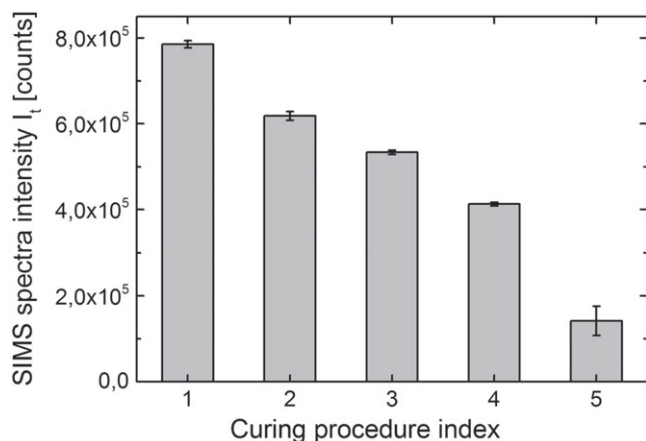


FIGURE 5 Total intensity of the positive secondary ion mass spectra of coatings prepared according to curing procedures of Table 1

spectra and the sputter yield volumes of the differently cured P-pPDA coatings (see Figure S1), demonstrating that, indeed, the evolution of the total ion intensity mirrors the relative ease to sputter the material.

To address polymerization of P-pPDA in more details, the intensities of large molecular species containing the benzoxazine function C—O—C were followed (precursor $[M]^+$ at 343 a.m.u and $C_{15}H_{13}N_2O^+$ at 237 a.m.u, see Table S1). As shown in Figure 6, the intensity of both fragments decreases monotonically as the polymerization becomes more extensive (from 1 to 5).

In order to confirm the ring opening mechanism via C—O—C bond, FTIR-attenuated total reflectance (ATR) was also employed. Coatings were scraped off and put on a support, and FTIR spectra of the pieces of the coatings were obtained. On the basis of the literature, the characteristic absorption of benzoxazine appears at 1223 cm^{-1} (asymmetric stretching of C—O—C) and 1035 cm^{-1} (symmetric stretching of C—O—C).^{8,21} Figure 7A shows the FTIR spectra of the coatings and Figure 7B the ratio between the characteristic absorption of benzoxazine and benzene ($C=C$ at 1612 cm^{-1}). The benzene absorption was chosen for the normalization because it is representative of the

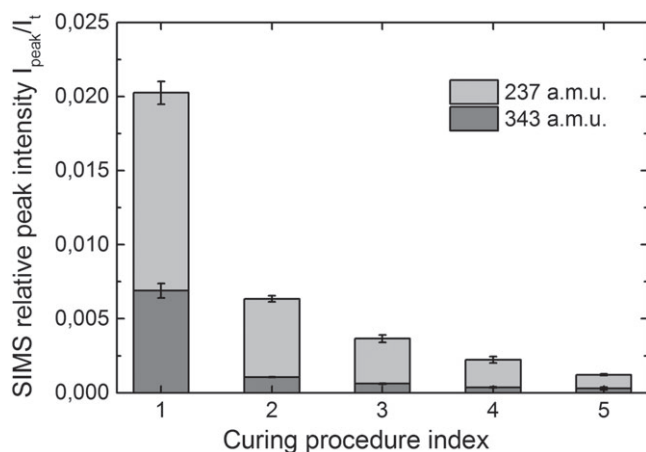


FIGURE 6 Evolution of phenol-paraphenylenediamine (P-pPDA) molecular fragments with benzoxazine bonds (C—O—C) after the thermal curing procedures listed in Table 1

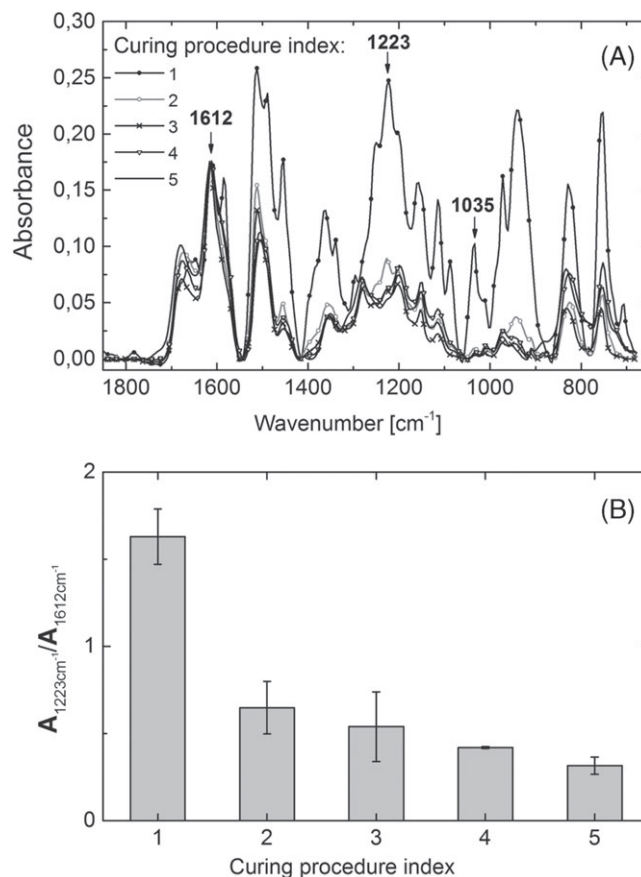


FIGURE 7 (a) Fourier-transform infra-red spectroscopy (FTIR) spectra and (b) evolution of the characteristic benzoxazine C—O—C bond for phenol-paraphenylenediamine (P-pPDA) coatings thermally cured according to Table 1

precursor as well as the polymer structure of P-pPDA and does not vary during the polymerization.

The evolution of the benzoxazine bond is similar to the decreasing intensity of SIMS molecular fragments (Figure 6) and confirms the ring opening mechanism of the polymerization of the coatings. Figures 6 and 7 confirm that the evolution of large P-pPDA molecular fragments is linked to the polymerization of the material.

On the basis of these results, a relation between DSC and SIMS data can be established that will allow to use SIMS for the determination of the conversion degree χ of any P-pPDA coating and thereby provide quantitative information on the polymerization state of the films. The SIMS signal is represented with an intensity ratio R (2) between small P-pPDA fragments and large molecular fragments. The denominator includes the protonated molecule of P-pPDA, $[M-H]^+$ at 343 a.m.u. and other intense fragments containing at least one C—O—C function (see Table S1). They are therefore representative of the unreacted molecule and should not be observed anymore after reaction. In contrast, the small unsaturated ions selected for the numerator ($C_3H_2^+$, $C_3H_3^+$, $C_4H_3^+$, $C_4H_4^+$) are expected to be produced with a similar probability from the reacted and the unreacted benzoxazine molecule. Indeed they are most likely formed from the three aromatic rings of the molecule, which do not participate in the

polymerization reaction. Our data show that they exhibit similar intensities in the mass spectra regardless of the curing procedure applied to the coatings.

$$R = \frac{\sum_{\text{intensity}} [M_{38} + M_{39} + M_{52} + M_{51}]}{\sum_{\text{intensity}} [M_{225} + M_{237} + M_{251} + M_{329} + M_{343}]} \quad (2)$$

The SIMS signals used in the ratio R (2) were taken from the middle part of the depth profile (Figure 4), where surface and interface effects are eliminated and bulk behavior of the material is the major contribution (a sum of five successive mass spectra for each sample, as indicated in Figure 4). Considering the homogeneous material in the middle part of the depth profile ensures similar properties as the bulk P-pPDA measured by DSC, it gives sufficient confidence to calibrate R by χ .

The intensity ratio between the sum of small fragments and molecular fragments characteristic for the P-pPDA precursor R was plotted as a function of the conversion degree χ determined by DSC in the bulk P-pPDA material cured with the same curing procedures (Figure 8).

In order to obtain a calibration curve that can be used to estimate the conversion degree of unknown P-pPDA samples, a linear fit was applied to nine out of 10 experimental points in Figure 8. The last point, with the highest χ , corresponds to the curing procedure 5, which includes a period of 30 minutes at 230°C. For this curing procedure, other processes, including degradation of the material because of the high temperature, may dominate. Therefore, this point was excluded from the fit. In turn, the linear regression of Figure 8 safely covers a range of χ comprised between 20% and 90%. Using the relationship established in Figure 8, ToF-SIMS can be used to locally determine the conversion degree χ of P-pPDA in thin films, for samples that can be micrometric in lateral dimensions and as thin as a few nanometers.

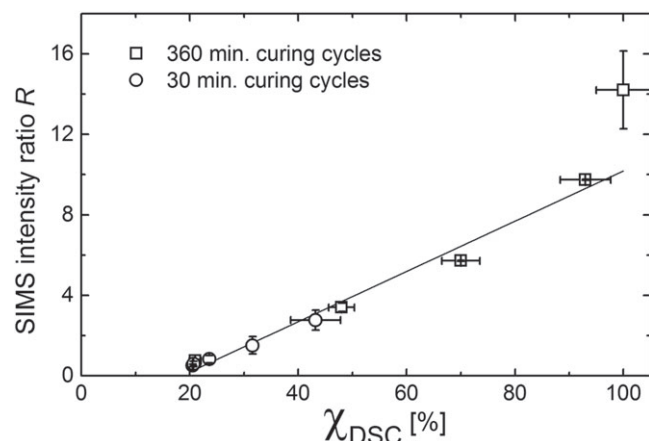


FIGURE 8 Calibration curve for the evaluation of polymerization of phenol-paraphenylenediamine (P-pPDA) coatings based on the ratio of molecular fragment intensities R and conversion χ determined in bulk P-pPDA material by differential scanning calorimetry (DSC). The error bars represent standard deviation based on five DSC measurements (x axis) and standard deviation based on three to five time-of-flight secondary ion mass spectrometry (ToF-SIMS) measurements (y axis)

3 | CONCLUSIONS

A novel method is proposed to evaluate the degree of polymerization of a thin polymer layer (P-pPDA in our case) by ToF-SIMS. This method is based on calibrating specific SIMS signal ratio by the conversion degree χ of the reaction, obtained using DSC for bulk P-pPDA samples. This enables the determination of the local conversion degree χ of thin organic layers that was previously inaccessible to the standard techniques, providing a quantitative measure of the level of polymerization in the films. Such approach may only be valid if no significant secondary reactions accompany the polymerization process. Taking advantage of the 3D analysis capability of SIMS, our method can also be used to access lateral or in-depth inhomogeneities of the polymerization in the films, with a micrometric lateral resolution and a nanometric depth resolution.

ACKNOWLEDGEMENTS

The authors wish to thank the Wallonia Region and the European Community for the financial support in the framework of the Programme d'Excellence: "OPTI²MAT" and "FLYCOAT," INTERREG V program (BIOCOMPAL project), and FEDER 2014-2020 (MACOBIO and HYBRITIMESURF projects). A.D. is a research director of the FNRS.

ORCID

Arnaud Delcorte  <https://orcid.org/0000-0003-4127-8650>

REFERENCES

- Harscoet E, Froelich D. Use of LCA to evaluate the environmental benefits of substituting chromic acid anodizing (CAA). *J Clean Prod.* 2008;16(12):1294-1305.
- Katzman HA, Malouf GM, Bauer R, Stupian GW. Corrosion-protective chromate coatings on aluminum. *Appl Surf Sci.* 1979;2(3):416-432.
- Campestrini P, van Westing EPM, Hovestad A, de Wit JHW. Investigation of the chromate conversion coating on Alclad 2024 aluminium alloy: effect of the pH of the chromate bath. *Electrochim Acta.* 2002;47(7):1097-1113.
- Foyet A, Wu TH, van der Ven L, Kodentsov A, de With G, van Benthem R. Absorption of water and corrosion performance of a clear and pigmented epoxy coating on Al-2024 alloy. *ECS Trans.* 2010;29:31-39.
- Ishida H, Allen D. Physical and mechanical characterization of near-zero shrinkage polybenzoxazines. *J Polym Sci B.* 1996;34(6):1019-1030.
- Liu HC, Su WC, Liu YL. Self-assembled benzoxazine-bridged polysilsesquioxanes exhibiting ultralow-dielectric constants and yellow-light photoluminescent emission. *J Mater Chem.* 2011;21(20):7182-7187.
- Ghosh NN, Kiskan B, Yagci Y. Polybenzoxazines-new high performance thermosetting resins: synthesis and properties. *Prog Polym Sci.* 2007;32(11):1344-1391.
- Dumas L, Bonnaud L, Olivier MG, Poorteman M, Dubois P. High performance benzoxazine/CNT nanohybrid network – an easy and scalable way to combine attractive properties. *Eur Polym J.* 2014;58:218-225.
- Poorteman M, Renaud A, Escobar J, et al. Thermal curing of Paraphenylenediamine benzoxazine for barrier coating applications on 1050 aluminum alloys. *Prog Org Coat.* 2016;97:99-109.

10. Renaud A, Poorteman M, Escobar J, et al. A new corrosion protection approach for aeronautical applications combining a phenol-paraPhenyleneDiAmine benzoxazine resin applied on sulfo-tartaric anodized aluminum. *Prog Org Coat*. 2017;112:278-287.
11. Nair CPR. Advances in addition-cure phenolic resins. *Prog Polym Sci*. 2004;29(5):401-498.
12. Ishida H, Agag T. *Handbook of benzoxazine resins*. Amsterdam: Elsevier; 2011.
13. Wu WL, Hu JT, Hunston DL. Structural heterogeneity in epoxies. *Polym Eng Sci*. 1990;30(14):835-840.
14. Moosburger-Will J, Greisel M, Sause MGR, Horny R, Horn S. Influence of partial cross-linking degree on basic physical properties of RTM6 epoxy resin. *J Appl Polym Sci*. 2013;130:4338-4346.
15. Moosburger-Will J, Greisel M, Horn S. Physical aging of partially crosslinked RTM6 epoxy resin. *J Appl Polym Sci*. 2014;131:41121-41129.
16. Cristaudo V, Collette S, Tuccitto N, et al. Molecular surface analysis and depth-profiling of polyethylene modified by an atmospheric Ar-D2O post-discharge. *Plasma Processes Polym*. 2016;13(11):1106-1119.
17. Ligot S, Bousser E, Cossement D, et al. Correlation between mechanical properties and cross-linking degree of ethyl lactate plasma polymer films. *Plasma Processes Polym*. 2015;12(6):508-518.
18. Zarshenas M, Moshkunov K, Czerwinski B, Leyssens T, Delcorte A. Molecular dynamics simulations of hydrocarbon film growth from acetylene monomers and radicals: effect of substrate temperature. *J Phys Chem C*. 2018;122(27):15252-15263.
19. Delcorte A, Cristaudo V, Zarshenas M, Merche D, Reniers F, Bertrand P. Chemical analysis of plasma-treated organic surfaces and plasma polymers by secondary ion mass spectrometry. *Plasma Processes Polym*. 2015;12(9):905-918.
20. Mouhib T, Poleunis C, Wehbe N, et al. Molecular depth profiling of organic photovoltaic heterojunction layers by ToF-SIMS: comparative evaluation of three sputtering beams. *Analyst*. 2013;138(22):6801-6810.
21. Agag T, Takeichi T. Synthesis and characterization of novel Benzoxazine monomers containing allyl groups and their high performance thermosets. *Macromolecules*. 2003;36(16):6010-6017.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

How to cite this article: Pospisilova E, Renaud A, Poorteman M, et al. A quantitative determination of the polymerization of benzoxazine thin coatings by time-of-flight secondary ion mass spectrometry. *Surf Interface Anal*. 2019;51:674-680. <https://doi.org/10.1002/sia.6639>