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Segregation and crosslinking in urea formaldehyde/epoxy resins: a study by high-resolution XPS

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Abstract

The segregation of minor components such as flow agents, in an industrial coil coating based on epoxy resins crosslinked with a urea formaldehyde resin and applied to a hot-dipped galvanized steel (HDGS) substrate, has been investigated by high resolution XPS. The addition of a low amount of flow agent in the coating formulation leads to changes in the surface elemental composition. High-resolution monochromated XPS C1s spectra can be peak-fitted taking into account all functionalities of the respective components of the formulation. The examination of both the elemental and chemical surface compositions clearly demonstrates that the use of flow agent in the process leads to its preferential segregation towards the air–film interface. This result is interpreted in terms of minimisation of the surface free energy of the final coil coating. It is also possible to monitor the extent of crosslinking undergone within the coil coating system, using the peak-fitting in the same manner as above, and it was concluded that the system is fully crosslinked. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: High resolution XPS; Epoxy resins; Urea formaldehyde resin

1. Introduction

Polymeric materials are conveniently and traditionally divided into two groups: thermoplastic and thermosetting materials. In the study of polymers by XPS it is the thermoplastic materials that have received by far the most attention. This is not surprising as preparation of these materials for

standards purposes is relatively simple, as one merely prepares a solution in an appropriate solvent and casts the solution on to a suitable substrate. Once the solvent has evaporated, a thin film of the thermoplastic material, with identical chemistry to the bulk polymer remains. The case with thermosetting resins, however, is not so straightforward as a result of the irreversible crosslinking process required to form the end product. For this reason, many of the investigations concerning these materials have been undertaken on the individual components or the dry, but uncured formulation.

Thermosetting resins are widely used as organic

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coatings and adhesives as they are readily applied in the liquid state and then cured (crosslinked) by the simple expedient of heating or the use of ultra-violet or visible light. Such formulations are complex and contain many individual components and the tacit assumption is that all components are distributed homogeneously throughout the product. This is clearly the case at the manufacturing stage, and one would hope, at the point of application; but following application, minor components may be enhanced at the substrate/polymer and/or the polymer/ambient interfaces. This may be beneficial to adhesion, as in the case of organosilane adhesion promoters, or it may have a deleterious effect as work from this laboratory has demonstrated in the case of UV photoinitiators [1] and reactive diluents [2]. The logical extension of this concept is seen in self-stratifying decorative paints that are now commercially available.

In previous work, coil coatings components were initially characterised in terms of surface composition by XPS and thermodynamic properties by inverse gas chromatography [3]. It was shown that an hydroxylated acrylic copolymer exhibited a dispersive contribution to the surface free energy of 32.3 mJ/m^2 . In subsequent studies, we have undertaken research on segregation and crosslinking phenomena in a model primer based on those used for coil coating applications [4]. This paper showed that, with proper charge management, peak fitting of the high resolution (i.e. monochromated Al $K\alpha$) C1s XPS spectra was able to account for all carbon functionalities within the melamine formaldehyde/epoxy formulation.

In the current work a study is made, by high resolution XPS, of individual components of a model clear coat system based on a commercial coil coating and of the cured coating itself. This includes the main component of the coating, an epoxy resin, the crosslinking agent (a urea formaldehyde resin) and also the flow agents. In this manner, the extent of surface segregation of a minor component (one of several commercially relevant flow agents) will be studied. The cure mechanism, previously investigated by ToF-SIMS [4], will also be studied by the consideration of the relative intensities of the various functionalities identified within the C1s spectrum.

2. Experimental section

2.1. Materials and methods

The main components contained in the coil coating formulation are two epoxy resins and a urea formaldehyde. The flow agents used in the coating process are as follows: two acrylic types based on different pendant chains and one based on a silicone material. The corresponding structures of the commercial resins and flow agents employed, when known, are reported in Fig. 1.

The study of each individual component was performed as follows: thin films of each component were prepared by spin-casting from solutions at a concentration of 5% (w/v), prepared in either ethanol (urea formaldehyde resin) or chloroform (epoxy resin and the flow agents). The substrate used was high purity (99.9%) aluminium sheets as provided by Goodfellow Cambridge Ltd.

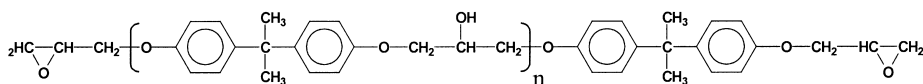
Coated HDGS panels of some model unpigmented primer formulations were prepared by applying solutions of the resins, crosslinker and flow agents to the substrate, using a wire wound bar (K3 RK Print Coat Instruments, Royston). A reference formulation was included which contained no flow agent. The panels were baked in an oven at 270°C for 40 s in order to achieve a peak metal temperature (PMT) of 232°C , and were then quenched in a bucket of clean water. This ensures crosslinking takes place and, as has been suggested previously, improved paint substrate adhesion is achieved by the chemical reaction of the epoxy resin with the pretreatment of the substrate [5]. The coating formulation is described in Table 1. The flow agents were added to the formulation in a proportion of 0.2% for the acrylate flow agents and 0.1% for the silicon-based product. The dry film thickness was approximately $10 \mu\text{m}$.

To perform surface analysis, discs of 10 mm diameter were punched from the prepared HDGS sheets coated with the various films.

2.2. Surface analysis by XPS

All the XPS analyses were performed on a Thermo VG Scientific ESCALAB 250 spectrometer. The instrument is equipped with a microfocusing

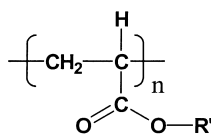
Epoxy resin:



Type 7: average number of repeat units equal to 9

Type 9: average number of repeat units equal to 12

Acrylic flow agent:



Polydimethylsiloxane polyether (polypropylene glycol) modified structure:

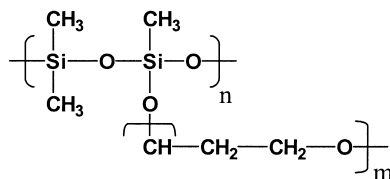


Fig. 1. The model resins and flow agent components.

monochromator and a charge compensation system [6]. A monochromatic Al K α X-ray source was used with a spot size of 500 μ m diameter at an electron take-off angle of 90°. The pass energy was set at 100

eV for the survey spectra and at 10 eV for high-resolution spectra of all elements of interest. High-resolution spectra were recorded for all core levels of interest: C1s, O1s, N1s as well as Si2p in case of the silicon-based flow agent. Peak fitting was performed using the supplier's software (PC-based Eclipse 3.1 running on OS/2). Quantitative surface analyses were calculated for each specimen using the peak areas of the high-resolution spectra, after background subtraction (Shirley baseline) and using Scofield sensitivity factors, which have been corrected for instrumentation transmission function. For all specimens, the reference CC/CH component is centred at 285.0 eV.

Table 1

Formulation of the thermally cured coatings used in this investigation

Component	Wt. %
Mixture of 7+9 type epoxy resins	24.0
Urea formaldehyde resin	12.5
Non-reactive solvents	61.8
Flow control agent	0.1–0.2

Table 2
Elemental surface composition of all samples (at.%)

Sample	C	O	N	Si
UF	62.8	17.3	19.9	NA
Epoxy ^a	85.0	14.8	0.2	NA
FA1	82.3	17.7	NA	NA
FA2	76.8	23.2	NA	NA
FA3	63.3	26.4	NA	10.3
Clear coat	75.9	15.0	9.1	NA
CC+FA1	79.5	16.2	4.4	NA
CC+FA2	77.5	19.4	3.1	NA
CC+FA3	75.3	16.8	6.9	1.0

FAx stands for the flow agent used, as described in the Experimental section and in the same order.

^a The nitrogen in this sample is most likely to originate from cross-contamination.

3. Results

3.1. Study of individual components

Surface compositions determined for the individual components and coil coatings are summarised in Table 2. The chemical shifts in binding energy (eV), the full width at half maximum (FWHM, eV) for all components and relative peak intensities (%) of the high-resolution C1s signals after peak fitting are reviewed in Table 3 for both the individual components and the coil coatings. The reference CC/CH component is centred at 285.0 eV. A consistent approach to peak fitting was achieved by prior knowledge of the chemistry of the components. Comparison of the chemical shifts obtained in the

Table 3
Chemical shifts (eV), full width at half maximum (FWHM, eV) and relative peak intensity (%) of single components involved in the high resolution C1s peak fitting

Sample	C _{ar} /C–Si	C _{al}	C–C=O	C–O _{ar}	C–O _{al}	C–O–C=O	Epoxy	N–C–O	N–C=O	O=C–O	Fig. no.
UF	NA	0 (1.20) 37.8	NA	NA	1.13 (1.20) 12.8	NA	NA	2.25 (1.35) 33.9	3.95 (1.27) 15.5	NA	3
Epoxy ^a	–0.61 (0.92) 50.6	0 (0.91) 18.3	NA	1.02 (1.09) 11.7	1.43 (1.10) 17.1	NA	2.01 (1.10) 2.3	NA	NA	NA	4
FA1	NA	0 (1.02) 59.8	0.48 (0.90) 14.6	NA	NA	1.57 (1.24) 14.6	NA	NA	NA	4.01 (0.83) 11.0	NA
FA2	NA	0 (0.97) 44.1	0.59 (0.88) 20.5	NA	NA	1.56 (1.15) 20.5	NA	NA	NA	4.07 (0.80) 14.9	5
FA3	–0.58 (1.00) 32.5	0 (0.95) 14.0	NA	NA	1.37 (1.05) 53.5	NA	NA	NA	NA	NA	NA
CC	–0.66 (1.05) 44.1	0 (1.00) 14.2	NA	0.82 (1.00) 9.7	1.36 (1.05) 15.8	NA	1.90 (1.05) 1.8	2.18 (1.18) 9.4	3.71 (1.10) 5.0	NA	6
CC+FA1	–0.65 (1.11) 39.7	0 (1.14) 23.7	0.47 (1.00) 2.2	0.88 (1.10) 8.5	1.34 (1.10) 13.4	1.58 (1.10) 2.2	1.88 (1.10) 1.1	2.22 (1.10) 5.1	3.64 (1.12) 2.5	3.96 (0.90) 1.6	NA
CC+FA2	–0.67 (1.13) 35.5	0 (1.10) 22.3	0.52 (1.00) 4.5	0.75 (1.00) 8.4	1.27 (1.05) 12.2	1.49 (1.15) 4.5	1.85 (1.05) 0.7	2.11 (1.15) 5.7	3.66 (1.10) 2.9	3.96 (1.00) 3.3	7
CC+FA3	–0.56 (0.95) 45.2	0 (0.95) 15.6	NA	0.90 (1.00) 6.0	1.40 (1.10) 22.6	NA	2.04 (1.05) 1.1	2.26 (1.13) 6.4	3.85 (0.99) 3.1	NA	8
Ref. [6]	–0.34 ^b	–	–0.4/0.37 ^c		1.45 ^d	1.64 ^e	2.02	2.78	3.84	3.99 ^f	NA
Ref. [4]	–0.40	–	–	1.10	1.50	–	2.10	2.80	–	4.10	NA

Subscripts al and ar identify aliphatic and aromatic species, respectively.

^a Unexpected nitrogen encountered in the survey spectrum.

^b Extreme values are –0.20 and –0.56 eV.

^c Extreme values are 0.21 and 0.52 eV.

^d Extreme values are 1.13 and 1.75 eV.

^e Extreme values are 1.12 and 1.98 eV.

^f Extreme values are 3.64 and 4.23 eV.

literature is also given in Table 3. The full widths at half maximum (FWHM) were set at a value ranging from 0.83 to 1.20 eV according to the type of molecule considered and whether the peak may be assigned to two different components in a formulation. The choice of FWHM was also in good agreement with the values chosen for similar molecules in the High Resolution XPS of Organic Polymers [7]. For example, any peak assigned to the acrylate carbon detected at highest binding energy is very narrow (i.e. ~ 0.85 eV, FWHM).

3.1.1. Components of clear-coat

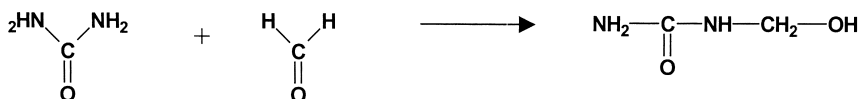
The clear-coat is a mixture of two types of material: urea formaldehyde resin (the crosslinker) and a blend of epoxy resins. These two components have been characterised separately.

Urea formaldehyde resins are prepared by the reaction of formaldehyde with urea in the presence of acid or base. The reaction is shown in Fig. 2. The mono and dimethylol ureas are the most common products, however the trimethylol product has been reported. No evidence of the tetramethylol product has been found [8]. Urea formaldehyde is very reactive and can self-condense and produce structures with methylene ($-\text{CH}_2-$) or ether ($-\text{CH}_2-\text{O}-\text{CH}_2-$) bridges. However, under the influence of acid

and an excess of an added alcohol, an etherification reaction can take place, which suppresses the self-condensation process and blocks the methylol groups so forming latent crosslinking agents. The excess alcohol is often left in situ to act as a solvent. Although self-condensation is suppressed, it is not totally eliminated, consequently alkylated urea formaldehyde resins are polymeric in nature and have complex structures. Neither will they be completely alkylated, hence some alkoxy should still be present in the molecules as well as $(-\text{NH}-\text{CO}-\text{NH}-)$ groups. The peak-fitted carbon signal of urea formaldehyde resin is illustrated in Fig. 3. Not surprisingly, the signal exhibits more than two anticipated components and they are assigned to C–C/C–H aliphatic carbon, ether carbon (chemical shift 1.13 eV), and two carbon types from the urea formaldehyde structure: N–C–O (chemical shift 2.25 eV) and N–CO–N (chemical shift 3.95 eV), respectively.

The other main component of the clear-coat is an epoxy resin of which structure is shown in Fig. 1. The peak fitting of this component is displayed in Fig. 4 and exhibits five components. The main component is assigned to the aromatic carbons present in the rings (chemical shift -0.61 eV). The second one is assigned to C–C/C–H aliphatic carbon. The third (chemical shift 1.02 eV) and fourth

Initiation:



Polymerization:

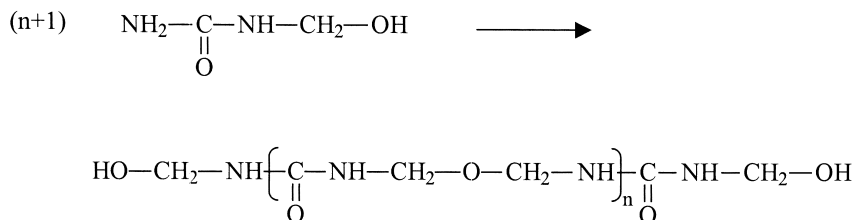


Fig. 2. Synthesis and structure of urea formaldehyde.

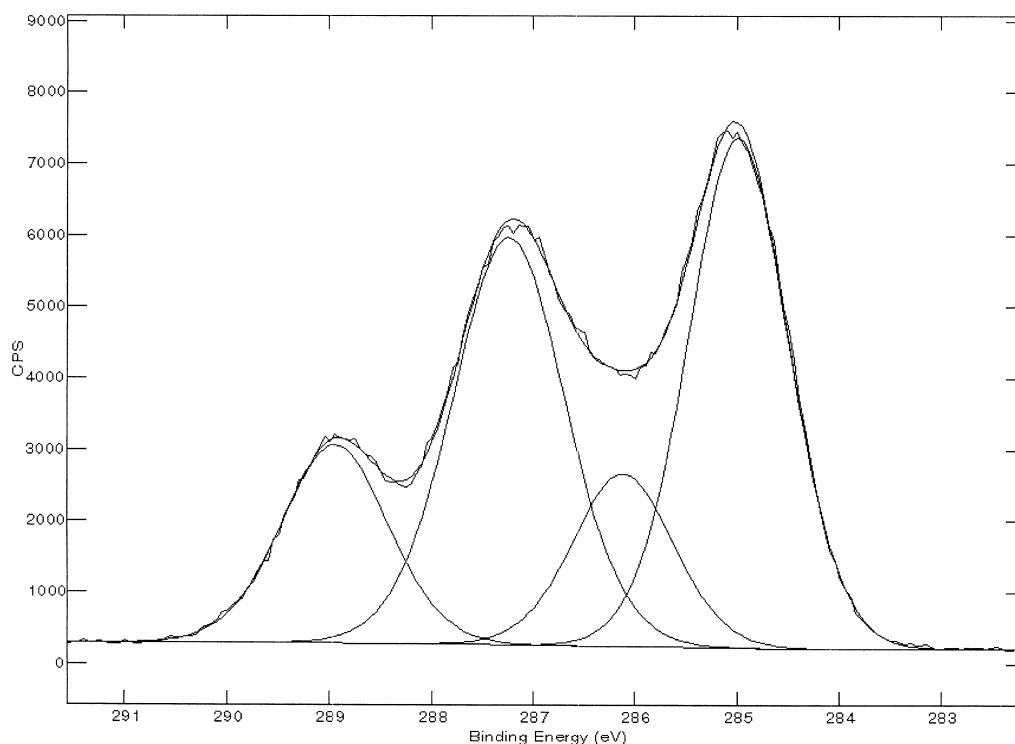


Fig. 3. High resolution C1s peak fitting of urea formaldehyde.

peaks (chemical shift 1.43 eV) are assigned to carbons bound to oxygen either included in a ring or on an aliphatic chain. The last component is assigned to the epoxy end group of the macromolecule (chemical shift 2.01 eV). An extra component (not shown here) is present at high binding energy (chemical shift 6.01 eV) and is due to a shake-up satellite caused by the presence of aromatic rings. The intensity of the shake-up satellite peak to the aromatic carbons is 4.1%.

3.1.2. Flow agents

The three flow agents, used in the other coating formulations, have been characterised individually. The flow agents are labelled as FA x , where x stands for the nature of the flow agent: 1–2 for the acrylic and 3 for the silicon-based flow agents, respectively.

The flow agents FA1 and FA2 are two types of acrylate molecules as illustrated in Fig. 1. Four components can be identified and for clarity only the peak-fitting of the carbon spectrum of FA2 is presented in Fig. 5. The only difference between the

two flow agents is the number of carbons C–C/C–H type included in the pendant acrylate chain, FA1 exhibiting a higher relative C–C/C–H signal. The first component is identified as C–C/C–H type of carbon arising from the pendant chain. The second component is produced by a β -shift induced by the carbonyl group (chemical shifts, 0.48 and 0.59 eV for FA1 and FA2, respectively). The third (chemical shifts, 1.57 and 1.56 eV for FA1 and FA2, respectively) and fourth (chemical shifts, 4.01 and 4.07 eV for FA1 and FA2, respectively) components are assigned to the two carbons of the acrylate functionality. The ratio of the components between C–C/C–H and any of the others is equal to 4 and 2 for FA1 and FA2, respectively.

FA3 is a polyether, polydimethylsiloxane modified structure. Three components are clearly obtained via peak fitting of the carbon signal. They can be easily assigned to a C–Si type (chemical shift -0.48 eV) of carbon, then aliphatic carbon C–C/C–H and the third component (chemical shift 1.37 eV) includes both ether C–O–C and/or alcohol functionalities

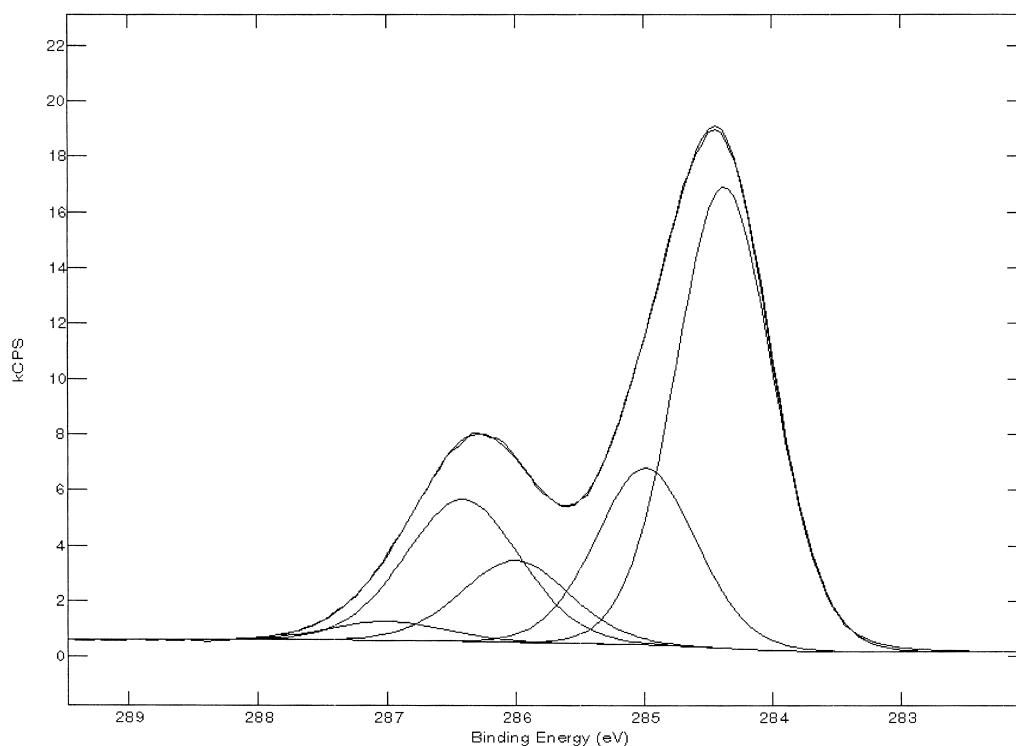


Fig. 4. High resolution C1s peak fitting of epoxy resin.

although the chemical shift probably indicates a higher contribution of the ether type. It is known that the molecule bears a pendant methyl group, which partly explains the intensity of the aliphatic type of carbon.

3.2. Study of coil coating films

3.2.1. Clear-coat

The analysis of the clear-coat without any flow agent in the coating formulation was performed. The peak-fitting was obtained by introducing the same fit as previously observed for the individual components. A variation of ± 0.2 eV was allowed for each peak to obtain the best possible fit, although most of the peaks did not vary by more than 0.1 eV in position compared with the analysis obtained for the single components.

Fig. 6 displays the C1s peak fitting of the clear coat. This signal has been peak-fitted with eight components. To perform the peak fitting, it was first assumed that the aliphatic ether type of carbon (i.e.

CO_{al}) would be obtained at different shifts for the urea formaldehyde component and the epoxy component, 1.13 and 1.43 eV, respectively. Nevertheless, any fit calculation persisted into leading to two components sitting at the same binding energy. It was therefore assumed that all CO_{al} would be fitted with one peak for the two components. The disappearance of the characteristic ether bridge of the urea formaldehyde in the clear coat will be discussed further in Section 3.2.2. The different peaks are assigned to the following carbon structures: aromatic hydrocarbon (chemical shift -0.66 eV), aliphatic hydrocarbon, aromatic ether carbon (chemical shift 0.82 eV), aliphatic ether carbon and hydroxyls (chemical shift 1.36 eV), carbon from epoxy end group (chemical shift 1.90 eV), N-substituted formaldehyde carbon (chemical shift 2.18 eV), diamide carbon atom from urea formaldehyde (chemical shift 3.71 eV) and $\pi-\pi^*$ shake up satellite (chemical shift 6.02 eV, not shown here), respectively. Although both the urea formaldehyde and the epoxy resins contribute to the carbon signal, unambiguous charac-

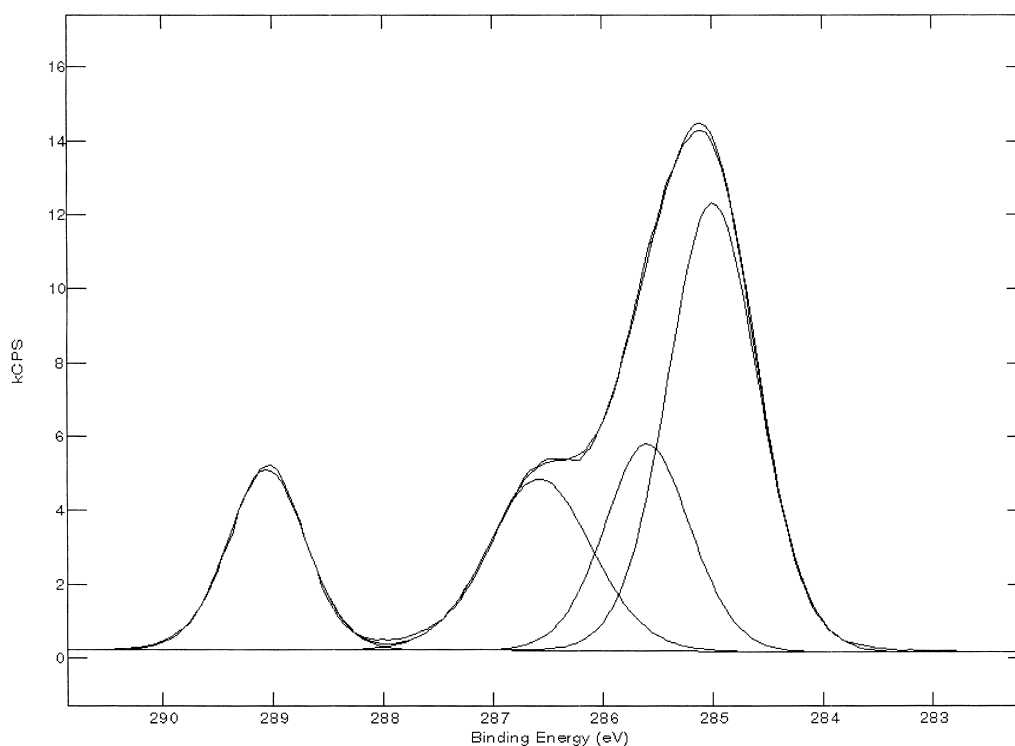


Fig. 5. High resolution C1s peak fitting of flow agent 2 (i.e. FA2).

teristic peaks arising from both components are clearly detected and identified. The intensity ratio (%) of the shake up satellite to aromatic carbon is 2.62, which is lower than previously detected for the epoxy resin due to the presence of urea formaldehyde.

3.2.2. Clear-coat and flow agents formulations

Peak fitting of the carbon spectra was obtained by introducing the same fit as previously observed for the clear coat and for the individual flow agent components. A variation of ± 0.2 eV was allowed for each peak to obtain the best possible fit. This was performed using known information on the composition of the resins as well as the flow agents combined with a study of the shape of the spectra. Comparison of the peak fitting of the C1s high resolution spectra of the clear coat and CC+FAx enables us to observe additional components to the original resin, characteristic of the flow agent used in the coating formulation. The intensities and binding energies of these additional peaks depend on the

nature and the structure of the flow control agent used.

Fig. 7 shows the C1s peak fitting of CC+FA2. The eight peaks arising from the clear-coat are still detected at similar binding energies, and additional peaks assigned to β -shift induced carbon environment (C–COO, chemical shift 0.52 eV), ester carbon component (C–O–C=O, chemical shift 1.49 eV) and a carboxyl carbon component (O=C–O, chemical shift 3.96 eV), respectively are also detected [7]. These components are unambiguous characteristic features of poly(acrylic) nature arising from the flow agent as previously observed. Similar peak fitting is also obtained for CC+FA1, with however slightly different peaks intensities due to a different poly(acrylic) structure of the flow agent.

Peak fitting of the carbon signal of silicon-based flow agent (FA3) shows that the features detected have similar binding energies to those observed for the epoxy resin, thus no characteristic additional feature can be detected for the silicon containing flow agent. The peak fitting of CC+FA3 is shown in

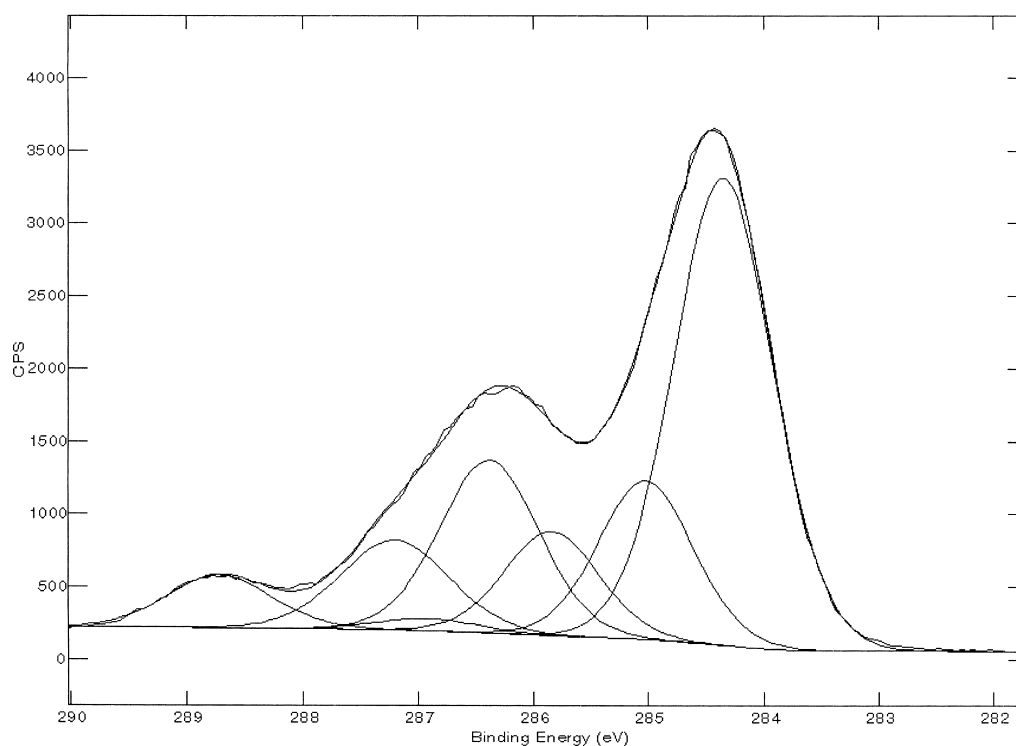


Fig. 6. High resolution C1s peak fitting of clear coat (i.e. CC).

Fig. 8. The peak fitting was mainly based on the peak fitting already obtained for the clear coat. However, more intense peaks are observed in the carbon signal due to contributions from both the clear coat and flow agent. For the silicon-based flow agent, the unambiguous detection of this component is mainly based on the detection of the Si2p peak, arising from the siloxane chain (not shown here).

4. Discussion

4.1. Surface composition

The spectra acquired from the coil coating films indicate carbon, oxygen and nitrogen at their surfaces. Minor elements are representative of the respective flow agents such as silicon (FA3). The surface composition of the films is shown in Table 2. It is clearly seen that the introduction of a low amount of flow agents in the coating formulation results in a variation of the surface composition. In

terms of elemental analysis, the nitrogen originates only from the urea formaldehyde resin within the film and can be used as unique elemental marker. The introduction of 0.1–0.2% flow agent in the coating formulation induces a significant drop of the nitrogen concentration. This is well illustrated by the two survey spectra of the clear coat (Fig. 9a) and the clear coat containing FA2 (Fig. 9b), respectively. Fig. 10 displays the carbon to nitrogen atomic ratio (C/N) calculated from the surface composition for all coatings. Except for CC+FA3 coating, the C/N atomic ratios of CC+FA_x increase by a factor of two to three in comparison to the clear coat and depend on the flow agent. In the case of the silicon containing flow agent, the lower increase in the C/N atomic ratio could be due to the lower carbon content of this flow agent, as demonstrated by the surface composition of the FA3 component (Table 2). This result clearly indicates that the flow agent components segregate at the air–coating surface and thus, the flow agent overlayer masks the underlying clear coat.

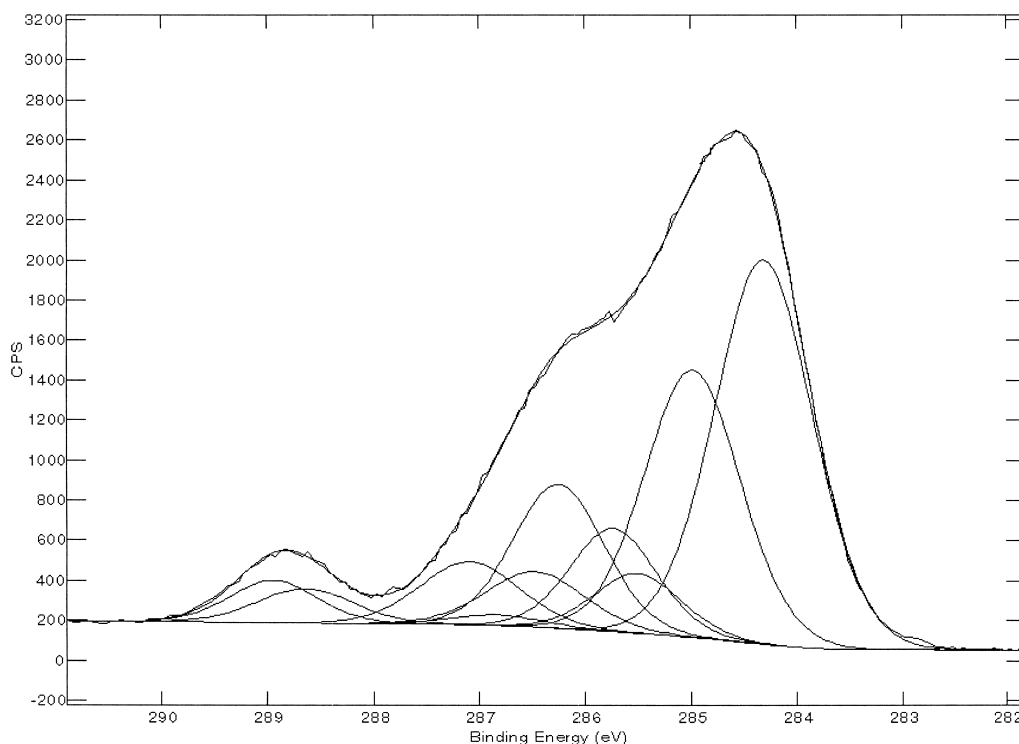


Fig. 7. High resolution C1s peak fitting of clear coat containing flow agent 2 (i.e. CC+FA2).

4.2. Peak fitting

4.2.1. Components of the clear-coat

The peak fitting of the urea formaldehyde resin has indicated that four components or types of carbon were present in the structure. It is known that, during the synthesis of the resin, iso-butanol molecules are present in the medium and that etherification takes place with the forming chains of urea formaldehyde, as shown in Fig. 11. The polymerisation is then terminated and the urea formaldehyde chain end bears one methyl and one ethyl groups. The presence of these alkyl end groups explains the intensity of the CC/CH component in the peak fitting (Fig. 3). To verify this assumption, a theoretical structure was written for which the number of units is equal to n (Fig. 11). This structure contains six aliphatic carbons, two ether carbons, $(2n+2)$ carbons of N–C–O functionality and $(n+1)$ N–CO–N carbon types, respectively. Various ratio calculations can be obtained from this structure as follows: the peak intensity ratio of the aliphatic to the ether

carbon (i.e. $I_{C-C}/I_{C=O}$) is equal to 2.90, close to the theoretical value of three and in good agreement with the assumed end chain structure. In a similar way, the peak intensity ratio (I_{N-C-O}/I_{N-CO-N}) from the urea formaldehyde is equal 2.17, close to the theoretical ratio of 2.0 as calculated from the structure shown in Fig. 11. Finally, ratios from the peak intensities between the number of carbon atoms from the end groups and the number of carbons in the main urea formaldehyde chain, involving the number of units (n), leads to an average value of 1.57 for n . This low value indicates that short urea formaldehyde chains are formed during the synthesis. Moreover, from this unit value and urea formaldehyde structure, we can determine a carbon to nitrogen atomic ratio (C/N) of 3.05. This value is close to the value 3.16 calculated from the surface atomic composition (Table 2). If we removed the contribution of the carbon arising from the iso-butanol end groups to the total carbon content, we can recalculate the surface elemental composition and we determine a carbon to nitrogen atomic ratio of 1.54. This value is

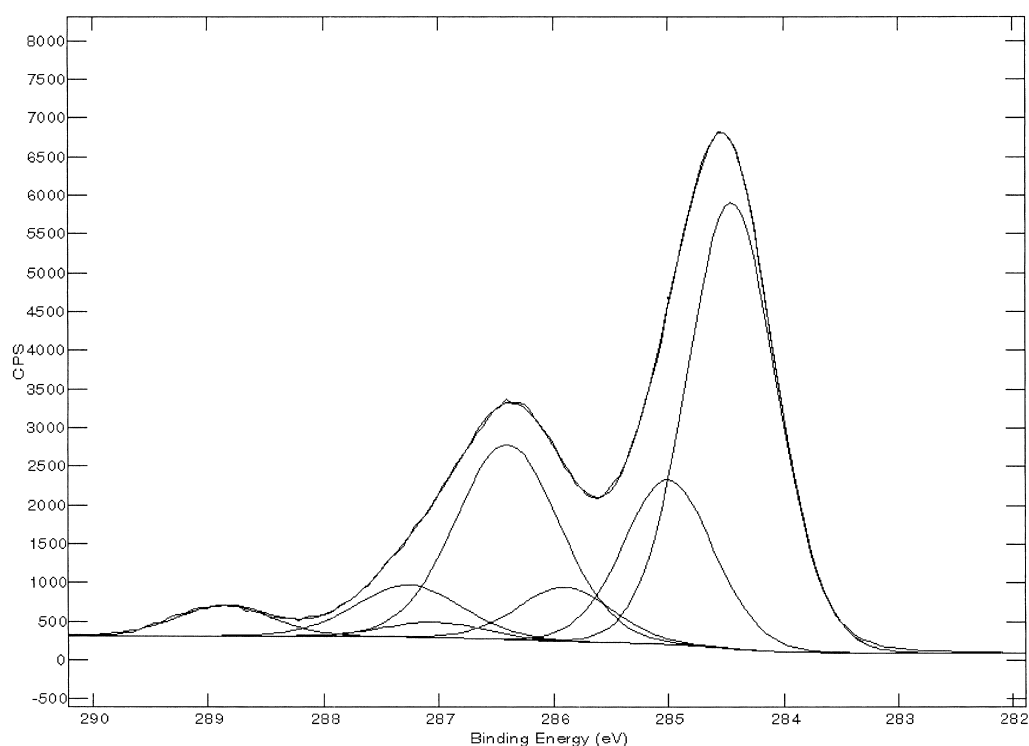


Fig. 8. High resolution C1s peak fitting of clear coat containing flow agent 3 (i.e. CC+FA3).

close to the theoretical value of 1.5 determined from the structure given in Fig. 11.

Following a similar approach for the epoxy structure (Fig. 1), the number of carbons involved in the terminal epoxy groups and in both the aromatic ether and aliphatic ether functionalities can be determined. The ratio will depend on the value of n . The epoxy end group includes four carbons, the aromatic ether groups contain $(2n+2)$ carbons and the aliphatic ether groups incorporate $(3n+2)$ carbons, respectively. These groups can be used as unambiguous functional markers of the epoxy structure. Peak intensity ratios calculated from the carbon peak fitting of the epoxy film allow the determination of the average number of repeat units n of the structure. Peak intensity ratios calculated from $(I_{\text{epoxy}}/I_{\text{C-O}})$ and $(I_{\text{C-Oal}}/I_{\text{C-Oar}})$ give an average n value of 9.2. This value is close to the number of units from a type 7 epoxy ($n=9$) rather than a type 9 epoxy ($n=12$), suggesting that the smaller epoxy molecules segregate to the surface. Another possibility is that the epoxy groups are preferentially oriented towards

the outer surface, leading to a relative increase in the epoxy carbon signal.

4.2.2. Clear-coat and flow agent containing films

Despite the low flow agent content added in the coating formulation, surface analyses of the CC+FAx films allow the detection of the characteristic features of any given flow agent. For example, the two acrylate flow agents are unambiguously detected by their acrylate structure. In case of the silicon containing flow agent, similar binding energy peaks have been observed for the clear coat and FA3 analysed separately. However, the use of the silicon-containing flow agent in the coating formulation leads to an increase in the relative intensity of the components involving both the clear coat and the flow agent as shown in Table 2.

The peak intensity ratios of the CC+FAx, calculated from characteristic peaks of the clear-coat and the flow agent used in the formulation, are in good agreement with those obtained for the components analysed individually. This implies that no chemical

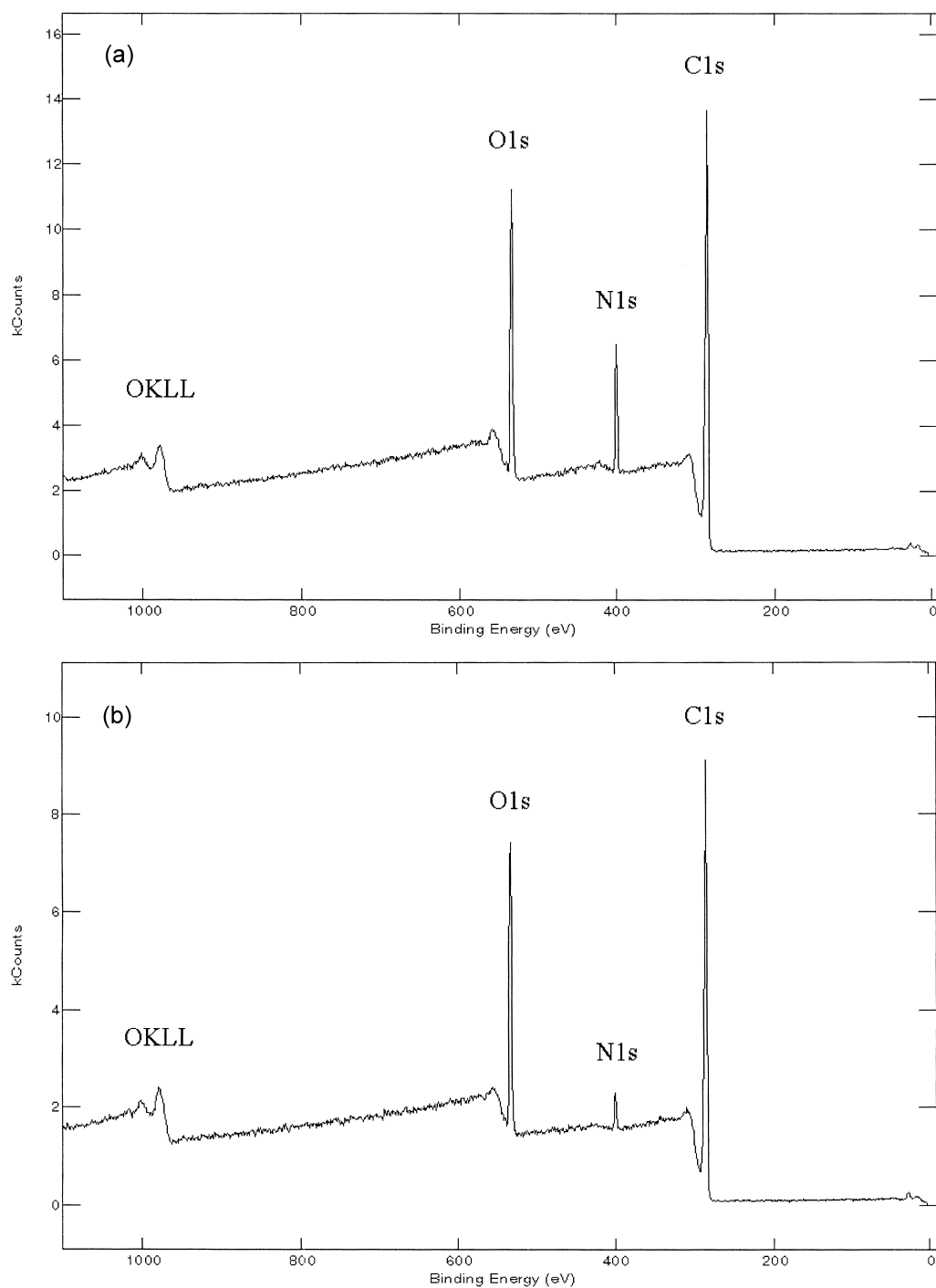


Fig. 9. Survey spectra of clear coat (a) and clear coat containing flow agent 2 (b).

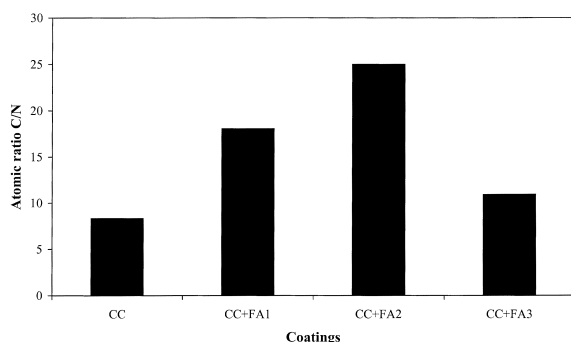


Fig. 10. Plot of carbon to nitrogen atomic ratios (C/N) for clear coat and clear coat containing the flow agents.

reaction has taken place between the resins and the flow agent during the curing treatment as would be expected. The only difference lies in the relative intensity of the aliphatic to aromatic CC/CH carbons. If the signal obtained for the reference sample was an exact superimposition of the relative contributions from the urea formaldehyde and the epoxy resins, the aliphatic CC/CH signal should be more intense as a result of additional contribution from the iso-butanol end groups of the urea formaldehyde, even if this is at lower concentration. The ratio of these two components for the epoxy resin is equal to 2.8 whereas it is 3.1 for the formulated clear-coat. These similar ratios, as well as the persistence of the one ether component, would suggest that only the epoxy resin is present at the surface. However, the

presence of nitrogen indicates that this is not the case. The result can only be explained by the crosslinking process. The reaction between the epoxy and urea formaldehyde resins during the curing is based on a *trans*-etherification between the hydroxyl groups of the epoxy resin and the isobutyl end groups of the urea formaldehyde, which leads to a final cross-linked structure similar to that previously reported [4]. The relevant reaction is given in Fig. 12 and illustrates the loss of CC/CH type of carbon for the urea formaldehyde after crosslinking. The value of the ratio cited above for the clear-coat also seems to imply that the crosslinking reaction has gone to completion. This mechanism does not involve any reaction with the flow agent. Therefore, the carbon signal of the CC+FA_x does not have a different chemical environment in comparison to the clear coat and the flow agent analysed individually.

Comparison of the shape of the carbon signal between the clear coat alone and the clear coat containing a flow agent shows that characteristic features of the flow agent are clearly detected. Due to its low concentration (0.1–0.2 wt.%) in the formulation, the detection of the flow agent can only occur if its preferential segregation towards the air-coating surface takes place. The addition of a flow agent in the coating formulation has two main objectives. First, the flow agent has to improve the wetting properties of the resins solution on to the substrate by reducing the surface free energy. This

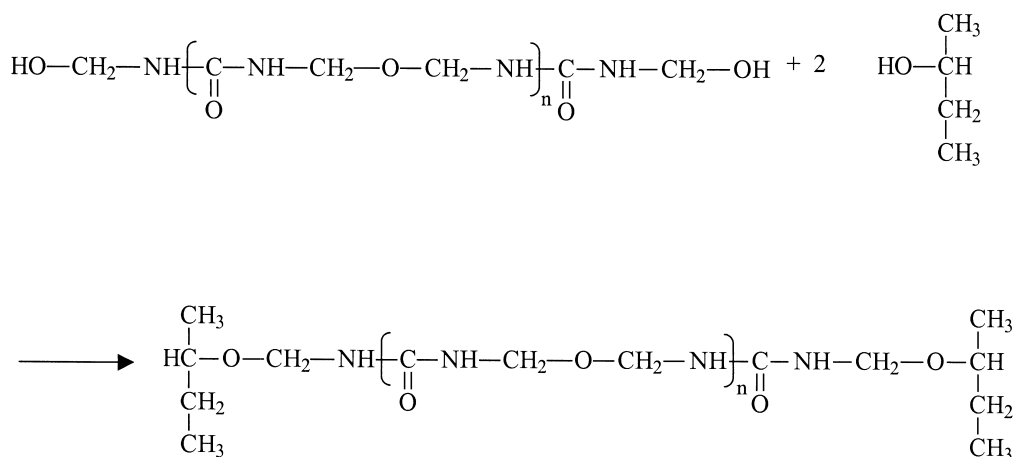


Fig. 11. Etherification reaction of iso-butanol and urea formaldehyde and resulting chemical structure.

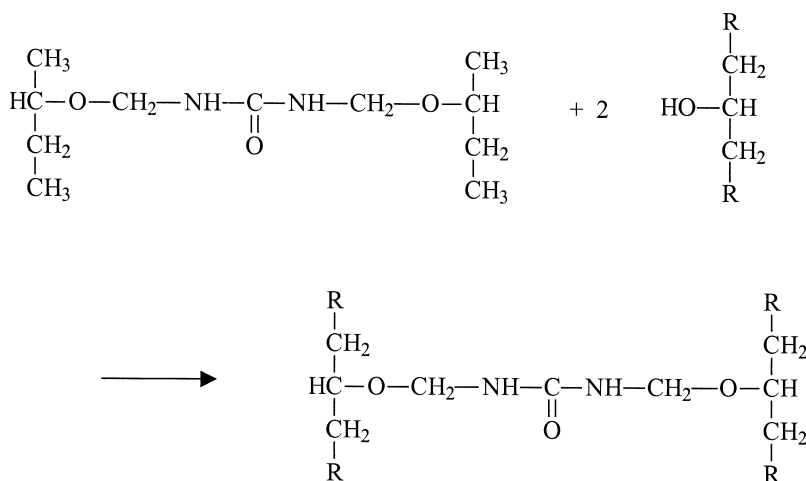


Fig. 12. Crosslinking reaction between the urea formaldehyde and epoxy resins.

results in an improved and quicker wetting of the HDGS surface substrate by the paint film before curing. It must be recalled that the coil coating is a very high speed process, and thus efficient spreading of the coating must take place. Secondly, after application, the flow agent aids levelling of the coating. Good wetting requires the lowest surface free energy component to be segregated towards the air–coating interface (Gibbsian segregation). The analytical evidence presented in this study demonstrates that this occurs. The flow agent segregates to the outer surface of the coating in order to minimise the surface free energy of the final coating. Contact angle measurements and inverse gas chromatography (IGC) [9–11] of polyacrylate and polysiloxane polymers show that these materials exhibit surface free energies, ranging from 29.2 to 42.7 mJ/m² (dispersive contribution 27.0 and 33.7 mJ/m²) and 15.7–25.7 mJ/m² (dispersive contribution 15.0 and 24.6 mJ/m² approximately), respectively.

Examination of the components of the surface of the samples containing flow agents indicates that the concentration of nitrogen characteristic of the clear-coat decreases. Its concentration decreases in the following specimen order: CC>CC+FA3>CC+FA1>CC+FA2 (Table 2). These values show that the segregation is different according to the flow agent employed and probably that the amount segregated towards the outer surface can be ranked in the same order. To reinforce this assumption, the percentage

contribution of characteristic peaks, known to belong only to the acrylate flow agents, to the total carbon signal was calculated, i.e. $(I_{\text{C-C=O}} + I_{\text{C-O-C=O}} + I_{\text{O-C=O}})/I_{\text{CTotal}}$. In the case of CC+FA1, the percentage obtained is equal to 5.4% and, in the case of CC+FA2, 12.2%. This shows unambiguously that FA2 is more highly segregated towards the surface than FA1. This result suggests that FA2 is lower molecular weight than FA1. It is known that FA2 has shorter pendant alkyl chains than FA1 from the carbon signal of the pure material and this may induce an easier diffusion because it is a smaller molecule with lower steric hindrance than FA1. This is also in agreement with the previously quoted C/N ratios.

Peak fitting of the carbon signals of the CC+FAx match that obtained for the clear coat. The relative peak intensities of all the characteristic features of the urea formaldehyde and epoxy resins are lower than those obtained for the clear coat (Table 3). This result confirms that the flow agents segregate towards the air–surface and hence, mask the underlying coating. Nevertheless, the peaks from the epoxy end group from the epoxy and characteristic peaks of the urea formaldehyde are still detected at the expected binding energies and with good peak intensities ratios in all coatings. This is reinforced by the fact that the nitrogen, which only arises from the urea formaldehyde component, is still detected in all the CC+FAx coatings. These results suggest that

either the flow agent does not form a homogeneous layer at the air–surface coating or that the thickness of the flow agent outer layer is lower than the XPS depth analysis (ca. 2–5 nm). These results are in good agreement with those obtained by Leadley et al. [4]. They indeed showed, using time of flight secondary ion mass spectrometry (ToF-SIMS) measurements, that a melamine formaldehyde/epoxy clear-coat containing an acrylic flow agent would exhibit a segregation layer of approximately 2 nm thickness.

5. Conclusions

High resolution XPS has been used in order to investigate the surface composition and chemistry of coil coating primer. To ensure unambiguous subsequent characterisation of the coil coatings containing different flow agents, all components of the coating formulation were first analysed individually. Surface composition and chemistry of coil coating containing a low content of acrylate and silicon-based flow agent in the formulation were compared to a reference coating without any flow agent. The surface composition shows that the addition of a low amount of flow agent in the coating formulation leads to its preferential segregation towards the air–coating surface, thus partially masking the underlayer coating. Peak fitting of the high-resolution carbon signal exhibits characteristic features of each component of the coating formulation. However, the detection of unambiguous peaks relevant to the flow agents confirm that they segregate to the air–surface coating, mainly in order to lower the surface free energy of the resulting coating. Detection of specific features of the underlying coating suggests that the thickness of the overlayer flow agent is lower than the XPS depth analysis or that the surface morphology of the flow agent is patchy. It would be useful to confirm this hypothesis by the use of angle resolved

XPS experiments and/or study the surfaces by time of flight secondary ion mass spectrometry. This work is in hand. It was also concluded from the comparison of the peak fitting of the carbon signal for the pure urea formaldehyde and epoxy resins to the formulated clear-coat that the system is fully cross-linked.

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