DOI: https://doi.org/10.24425/amm.2024.151430

R.R.P. KUPPUSAMY[1*], A. ZADE[1], B. SRIDHAR BABU[2]

EVALUATION OF PEEL PLY EFFECTIVENESS IN CONTROLLING MOULD RELEASE AGENT CONTAMINATION OF EPOXY / CARBON FIBRE COMPOSITE LAMINATE SURFACES

The peel-ply effectiveness in controlling the mould release contaminations of resin transfer molded (RTM) RTM6/G0926 epoxy-carbon fibre composite laminate surfaces have been examined. X-ray photoelectron spectroscopy (XPS) was employed to evaluate the extent of transfer of mould release agents and other surface contaminants of RTM composite laminates at semi-cured and fully cured states. Fully cured and 55% semi-cure degree of RTM composite laminates were prepared using polyester and diatex peel plies. The effectiveness of polyester and diatex peel plies were evaluated by comparing the amount of Frekote mould release contaminants present in the laminate surfaces processed with and without peel plies. The XPS results shows that the composite laminates processed without peel plies at different cured states exhibit uniform contamination with Freakote calcium metal ions. At the comparisons of polyester and diatex peel plies, the diatex peel ply performs better in controlling the surface contaminations.

Keywords: RTM6 Resin; Resin Transfer Moulding; Mould Release Agent; Surface Contaminations; X-Ray Photoelectron Spectroscopy

1. Introduction

In Liquid Composite Moulding applications, mould releasing agents are externally coated on the mould surface to ease the extraction of moulded products from the metal part. The usage of mould releasing agents during moulding process leads to the contaminations on the surface of the moulded parts [1-6]. The limitations of surface contaminations become more vital, when the moulded products are required to post process with its surface applications. The above situations are specifically true to the higher end applications such as aerospace structures, manufactured with specially designed resin matrix and reinforcement fibres that are required to fabricate the part with minimal surface contaminations [7-12]. These minimal contaminations will degrade the surface physiochemical properties, which is significant in the post product processing, e.g. adhesive bonding of pre-cured composite laminates [1,3-6,9,13-16].

The application of peel-plies between the mould release coat and reinforcement fibres are often seen as the solution to avoid the contact of mould releasing agents on the moulding products. But, the efficiency of the peel-plies solely depends on its compatibility to the process raw materials, mould release and moulding conditions. Hence, it is important to evaluate the peel-plies effectiveness on controlling surface contaminations. These surface analyses facilitate the right choice of the peel-ply to the prevailing process conditions. The peel-ply effectiveness can be evaluated by testing the presence of species of mould release on the part surfaces. Hence, lesser the presence of mould release elements on the mould part during surface analysis is greater the effectiveness of the peel ply [1,4-9,16].

The present work is the compliment to the research held in the development of adhesive bonding of semi-cured composite panels manufactured through using Resin Transfer Moulding (RTM) Process. Therefore, it is required to test the RTM composite laminates for mould release surface contaminations for the better adhesion during epoxy adhesive co-curing of semi-cured composite laminates. The main objectives of the present work are:

1. To evaluate the epoxy/carbon fibre composite laminates [16-19] surface contaminations induced by the application of mould release during RTM process.
2. To measure the degree of surface contaminations at the different product cure stages of RTM processing, i.e. semi and fully cured states of RTM composite laminates
3. To check the effectiveness of different peel plies in controlling the surface contaminations

[1] CHEMICAL ENGINEERING, NATIONAL INSTITUTE OF TECHNOLOGY WARANGAL, TELANGANA, INDIA
[2] MECHANICAL ENGINEERING, MALLA REDDY ENGINEERING COLLEGE, INDIA

* Corresponding author: raghuraj@nitw.ac.in

2. Materials

RTM6 resin supplied by Hexcel, is a degassed mono-component epoxy resin, specifically developed to fulfill the requirements of the aerospace and space industries in advanced liquid composite moulding processes, was used as the resin matrix. Carbon fibre fabric G0926 with 5H satin weave, supplied by Hexcel was used as reinforcement. A proprietary mould release “Locatite Frekote 700 NC” from Henkel Technologies was used as the mould releasing agent during RTM processing. EA 9895 Polyester peel ply and 1500EV6 diatex peel ply supplied by Henkel, were the two different peel plies tested in controlling the surface contaminations.

3. Experimental methods

3.1. Resin Transfer Moulding Process

The semi cured and fully cured composite laminates with different peel ply conditions were manufactured through RTM process using respective cure cycles. A perfect pre-cure degree of semi cured laminates is required to enable perfect adaptability and co-curing during adhesive bonding and physical consistency during cold storage until post processing. The under cured composite laminates facilitates the adaptability and co-curing during adhesive bonding but the increased tackiness due to sub-cure risks the handling. On the other hand, the over cured composite laminates becomes rigid which makes tougher for better adaptability and co-curing at the adhesive bonding process. An offset between tackiness and rigidity in terms of desired cure is often preferred for the better performance of semi cured laminates in both adaptability in adhesive bonding and storage handling. Hence, a targeted laminate cure of 55% using cure cycle 160°C was utilized to prepared semi-cured composite laminates through RTM process.

A hit and trial method was used to prepare semi-cured RTM laminates of targeted cure. Also, to test surface contaminations at the fully cured condition, a cure cycle of 180°C was employed at the RTM process. With the combinations of laminate cure states and peel plies, there were six different case studies reported to the surface analyses, which are listed TABLE 1 with their respective RTM cure cycles. The peel plies were allowed to remain with the composite laminates under storage until the laminates were utilized for the surface analysis. The arrangement of peel ply, RTM processing and manufactured composite laminates are shown in Fig. 1. A carbon fibre mat architecture of 6 layers at 45° / 45° / 45° / 45° / 45° / 45° with dimensions 600 mm × 300 mm was used to prepare RTM composite panels.

TABLE 1

Manufacturing of RTM Composite Laminates for Surface Analysis

Case Study	Cure State	Peel Ply	Cure Cycle
1	Semi Cured	No Peel Ply	160°C – 45 Minutes
2	Semi Cured	Polyester Peel Ply	160°C – 50 Minutes
3	Semi Cured	Diatex Peel Ply	160°C – 50 Minutes
4	Fully Cured	No Peel Ply	180°C – 2 Hours
5	Fully Cured	Polyester Peel Ply	180°C – 2 Hours
6	Fully Cured	Diatex Peel Ply	180°C – 2 Hours

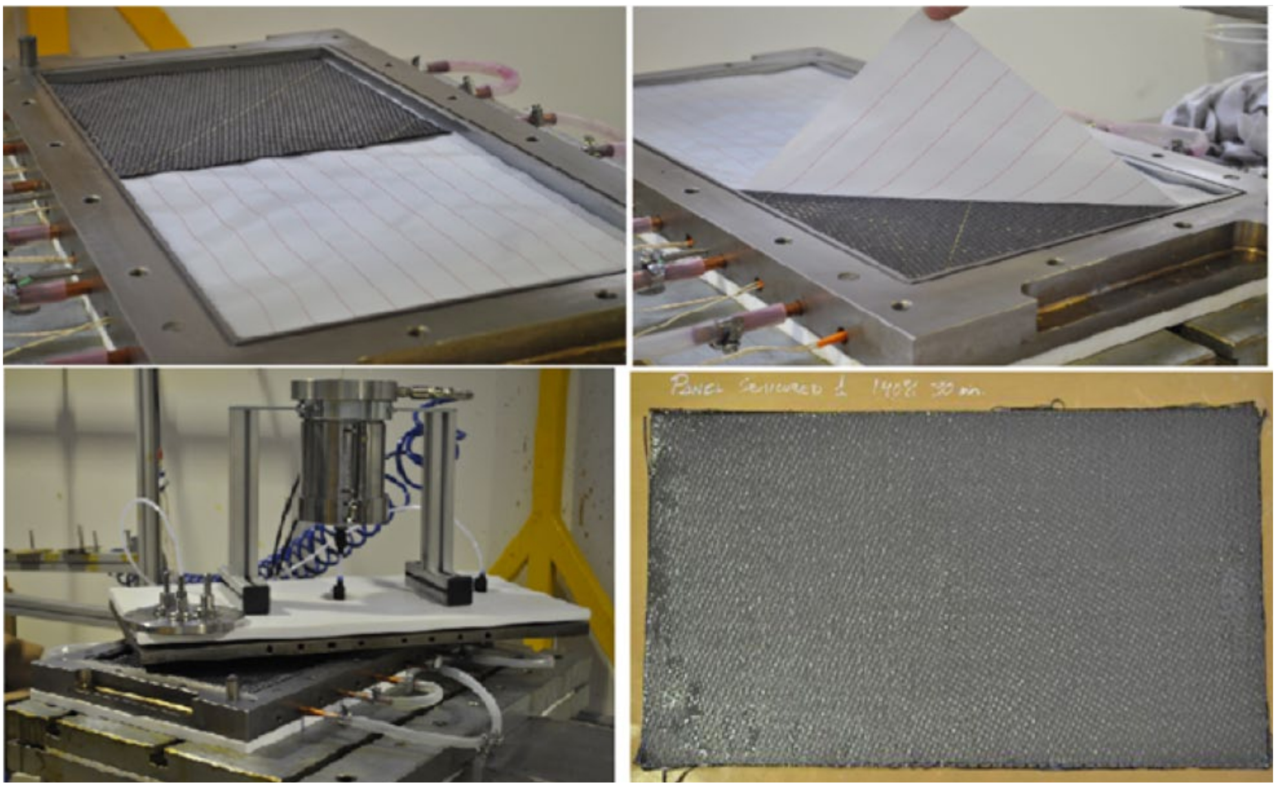

Fig. 1. Resin Transfer Moulding Process with Peel Ply

3.2. Dynamic Heating Differential Scanning Calorimetry (DSC) Experiments

The degree of cure of hot press composite laminates were studied by measuring the residual heat through dynamic DSC runs at a heating rate 10°C/min. DSC Q200 model of TA instruments was used to measure the residual of RTM composite laminates through the temperature ramp. The degree of cure of the laminates were obtained from the DSC residual heat using Eq. (1).

$$\alpha\left(Degree\,of\,\,Cure\right) = 1 - \frac{\begin{array}{c}Residual\,Heat\,of\,\,Resin\,Flakes\\ from\,Semi-Cured\,Laminate\end{array}}{RT\,M6\,Total\,Heat\,of\,\,Reaction} \quad (1)$$

3.3. X-ray Photoelectron Spectroscopic Analysis

The XPS analyser with the specifications "PHOIBOS HSA3500 150 R6 [HWType 30:100] MCD-9" was used in the surface analysis. The XPS analyser yields the electron intensity as a function of binding energies. The peak and binding energies range helps to identify the elements whereas the peak area helps to identify the relative elemental composition on the analysed surface. A sensitivity factor is empirically derived to each element according to the efficiency in absorbance of electrons emitted from the specified element. Hence, the relative elemental composition on any surface analysis is given as:

$$Relative\ elemental\ composition = [\Delta_i/S_i]\,/\,[\Sigma\Delta_i/\Sigma S_i] \quad (2)$$

Where, Δ_i and S_i are the peak area and sensitivity factor of the individual element and $\Sigma\Delta_i$ and ΣS_i are the total peak area and sensitivity factors. Finally, the relative elemental compositions are normalized to 100 to represent as percentage elemental composition [2,3,13,17-25].

In each case study, samples for the XPS analysis were prepared to the dimensions 10 mm × 15 mm. The samples were cut and stored in such a way that the surfaces should not get affected by any physical means of handling. Importantly, the case studies with the use of peel plies, the composite laminate samples were cut with the peel plies and the final peel off were made at the time of surface analysis. These were followed to avoid the surface damages during handling of the samples.

4. Results and discussions

4.1. RTM Composite Laminate Cure

The degrees of cure of the RTM laminates were examined using dynamic DSC heating at 10°C/min. The cured resin flakes were extracted from the centre of the cured laminates and it was used for the DSC analysis. The dynamic DSC heat flow curves of raw RTM6 resin and RTM semi-cured composite laminates at different case studies are presented in Fig. 2. The area under each dynamic DSC heat flow curve gives the heat of reaction of respective case studies. The degree of cure of RTM composite laminate is calculated from Eq. (1) and it is tabulated in TABLE 2. From DSC residual heat, it was found case studies 1, 2, 3 cures to 53%, 56% & 55%, respectively for the applied RTM cure cycles. Since there is no preprocessing / thermal treatment performed for the raw resin prior to DSC analysis, the enthalpy of reaction is higher due to exothermal heat evolved during crosslinking. Whereas, the RTM moulded composite panels were partially cured at mentioned cure cycles and the samples were DSC analyzed to obtain the residual heat. Moreover, carbon fibers at the composite panel are thermally resistive and hence, the enthalpy of reaction is decreasing with increase in cure % and also found with huge enthalpy difference between raw resin and composite panels.

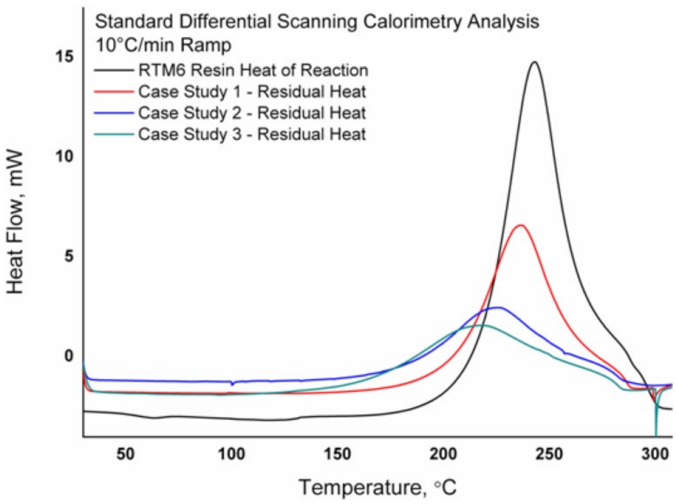

Fig. 2. Dynamic DSC Heat Flow Curves of RTM6 Resin & RTM Composite Laminates

TABLE 2

Degree of Cure of RTM Composite Laminates

Case Study	Heat of Reaction, J/gm	RTM Composite Panel Cure
Raw RTM6 Resin	512	—
1	242	Semi-Cured 53%
2	222	Semi-Cured 56%
3	231	Semi-Cured 55%
4	—	100% (Hexcel Data Sheet – Degree of Cure for Cure Cycle 180°C – 2 Hours
5	—	100% (Hexcel Data Sheet – Degree of Cure for Cure Cycle 180°C – 2 Hours
6	—	100% (Hexcel Data Sheet – Degree of Cure for Cure Cycle 180°C – 2 Hours

4.2. Constituting elements

RTM6 resin, carbon reinforcement fibres, peel ply and mould releasing agent were the ingredients used in the manufacturing of RTM composite laminates. Mono-component RTM6 resin is manufactured from the derivation of tetra glycidyl (di-amino di-phenyl) methane [TGDDM] and di-amino di-phenyl sulfone [DDS]. Hence, the RTM6 resin has carbon, nitrogen, oxygen and sulphur as the elemental constituents. In carbon reinforcement's fibres, carbon is the dominating element. Organic silicones are used as the sizing material for the carbon fibres and hence forth, some traces of silica takes in the reinforcement elemental composition. The polyester peel ply has carbon, oxygen and nitrogen elemental composition. Diatex peel ply is also a form of polyamide nature which means the elemental composition is same as the polyester peel ply. Diatex peel plies are standard polyamide based peel plies specifically designed for applications in high temperature epoxy resin systems. Basically, the mould release "Locatite Frekote 700 NC" is composed of heavy naptha and proprietary resin which are dissolved in dibuty ethyl solvent. In addition, calcium sterates are mixed to form a oxide coating over the mould surface at the time of application. Therefore, calcium is very important element identification for the presence of mould release contaminations over the composite laminate surfaces.

4.3. Case Studies XPS Spectra

The results obtained from the XPS analyser is presented as spectra having counts per second as a function of binding energies as shown in Figs. 3-8 for the case studies 1-6.

4.4. Elemental Peak Range, Area and Composition

From Figs. 3-8, having different cure state and peel ply conditions, primarily identification of elements and its ranges were held. Then, the identified zones were scanned in detail to obtain a clear XPS spectrum of the individual element. The peak

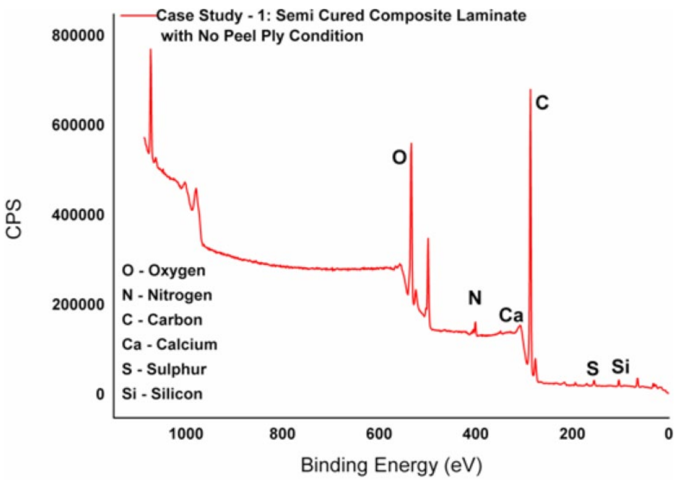

Fig. 3. XPS Elemental Scan Spectra of Case Study 1: Semi Cured Composite Laminate with No Peel Ply Condition

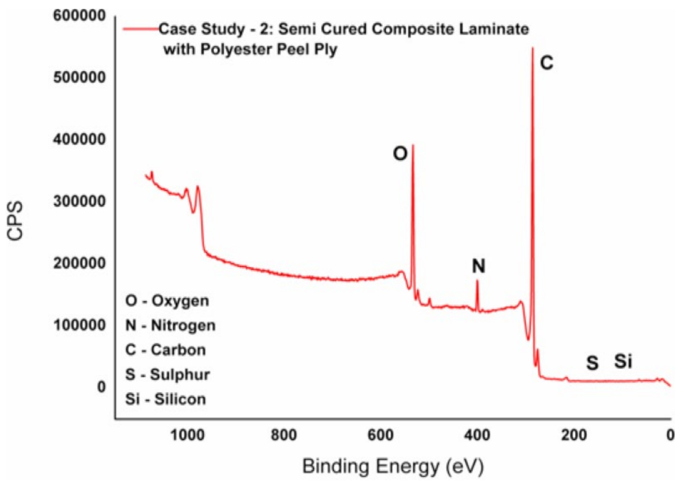

Fig. 4. XPS Elemental Scan Spectra of Case Study 2: Semi Cured Composite Laminate with Polyester Peel Ply

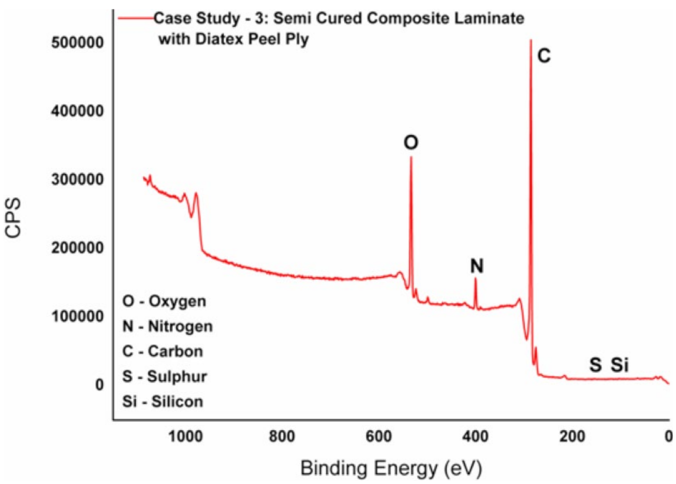

Fig. 5. XPS Elemental Scan Spectra of Case Study 3: Semi Cured Composite Laminate with Diatex Peel Ply

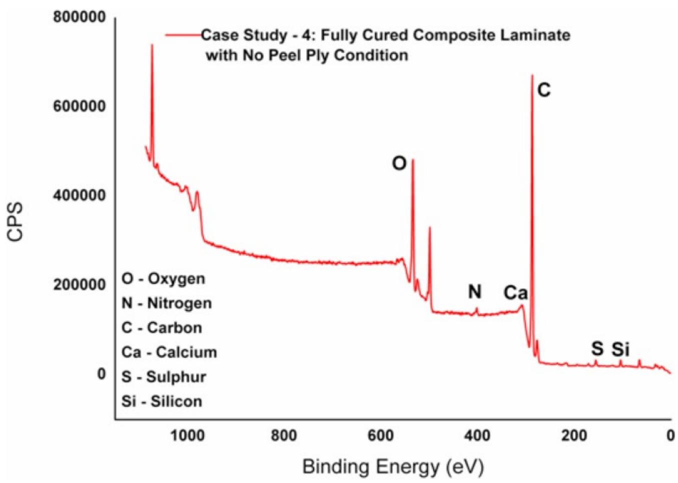

Fig. 6. XPS Elemental Scan Spectra of Case Study 4: Fully Cured Composite Laminate with No Peel Ply Condition

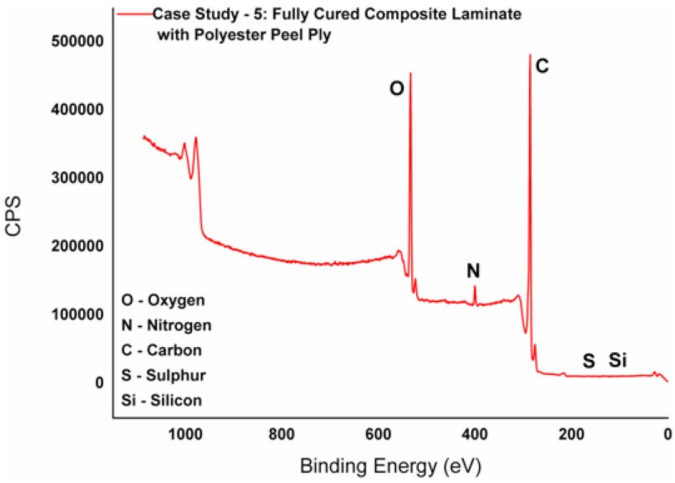

Fig. 7. XPS Elemental Scan Spectra of Case Study 5: Fully Cured Composite Laminate with Polyester Peel Ply

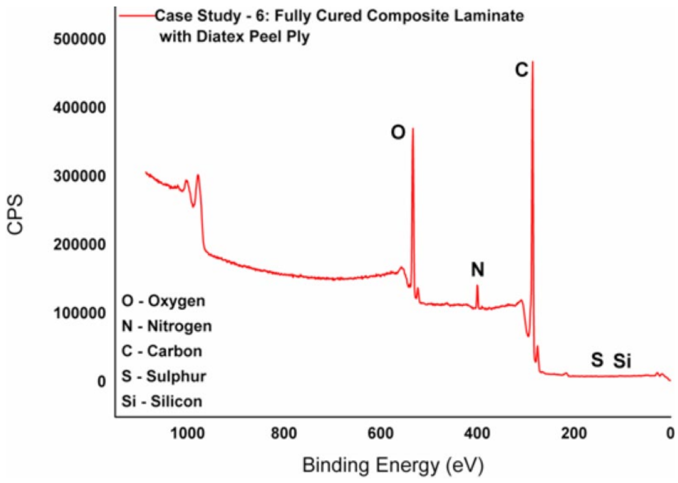

Fig. 8. XPS Elemental Scan Spectra of Case Study 6: Fully Cured Composite Laminate with Diatex Peel Ply

range and peak area of the individual elements were analysed and tabulated in TABLES 3-9. The sensitivity factors for the individual elements were obtained from free online source and the relative elemental composition was computed using Eq. (1). The relative elemental composition and normalized percentage elemental composition at different case studies are tabulated below.

The effectiveness of the peel plies are evaluated with the quantity measurement of mould release specimens on the composite laminates. In the present work, "Locatite Frekote 700 NC" was used as the mould releasing agent. This is a proprietary mould release where the exact element constituents and their compositions are not known. From the Henkel data sheet, it was reported that the Frekote 700 NC contains heavy naptha mixed with dibuty ether solvent and graded resin to an unresolved proportions. Importantly, it contains a portion of calcium sterate which forms the metal oxide film during air dried – open coat application of releasing agent over the metal mould surface.

In this work, there are three different ways in identifying the degree of surface contaminations and the effectiveness of peel plies in controlling it.

1. The presence of organic solvent dibutyl ether on the surface of the composite laminates ensures a contaminated surface. This can be measured as the quantification of carbonyl form of carbon (C=O, ether form) which are readily supplied by solvent form dibutyl ether. More the presence of carbonyl form of carbon is greater the surface contamina-

TABLE 3

Elemental Peak Range, Area and Composition of Case Study 1: Semi Cured Composite Laminate with No Peel Ply Condition

Element	Peak Range, eV	Peak Value, eV	Peak Area, eV-CPS	Elemental Sensitvity Factors	Relative Elemental Composition	% Elemental Composition
Carbon	293-282	287	400986	0.25	2.98	42.24
Oxygen	540-529	534	709309	0.66	2.00	28.31
Nitrogen	408.5-397.5	401	271823	0.42	1.20	17.05
Sulphur & Others	198-189, 168-173, 160-150	193.5, 170.5, 155	84550	0.54	0.29	4.12
Silicon	108-100	104	26628	0.27	0.18	2.60
Calcium	355.5-346	353.5, 348.5	224676	1.05	0.40	5.64

TABLE 4

Elemental Peak Range, Area and Composition of Case Study 2: Semi Cured Composite Laminate with Polyester Peel Ply

Element	Peak Range, eV	Peak Value, eV	Peak Area, eV-CPS	Elemental Sensitvity Factors	Relative Elemental Composition	% Elemental Composition
Carbon	293-282	285.5	374117	0.25	2.73	50.71
Oxygen	540-528	534	527894	0.66	1.46	27.10
Nitrogen	405-395	400.5	244990	0.42	1.06	19.77
Sulphur & Others	169-160	164.5	14569	0.54	0.05	0.91
Silicon	108-100	104	12260	0.27	0.08	1.54
Calcium	—	—	—	—	—	—

tions. In addition, the presence of carbonyl form of carbon (C=O) decreases the percentage of C-H form of carbon contributed from resin matrix and reinforcement fibres. In the XPS spectra, carbonyl form of carbon (C=O, ether form) peaks at a value greater than 286.5 eV whereas C-H form of carbon peaks at value lesser than 285.5 eV. Hence, the shift of carbon peaks from 285.5 eV to the greater values indicates the increased surface contaminations.

2. The presence of increased concentration of oxygen on the surface of the composite laminates, contributed from the metal oxide film formed during coating of release agents over the mould metal surface.
3. The presence of calcium metal elements contributed from the calcium sterate which is the major source to form metal oxide film to enhance the release properties.

The results of this surface analysis were derived from the aforementioned three senses by correlating to XPS spectra and percentage elemental composition. From TABLE 9, comparing semi and fully cured composite laminates, it was evident that the composite laminate surfaces at the both cured states are highly contaminated with the presence of calcium metal concentration, increased oxygen concentration and carbonyl form of carbon (C=O). Additionally, it can been seen from the TABLES 3 & 6, the carbon peeks at a value more than 286.5 showing an increased concentrations of ether bonds (C=O) contributed by the presence of dibutyl ether, a possible source of contaminant to the laminate surface. At the comparison of peel ply conditions, it was inferred that the use of peel plies at both the cure states controls the calcium metal concentrations drastically. The peak of calcium vanishes at XPS spectra with use of both peel plies.

At the comparisons of polyester and diatex peel plies, the diatex peel ply performs better in controlling the surface contaminations. From TABLE 9, it can been seen that the diatex peel ply performs marginally better than polyester peel ply in terms of controlling carbonyl form of carbon and oxygen concentrations rose from ether bonds and metal oxides contributed from the mould release. At the use of diatex peel ply, there is an increased C-H form of carbon composition contributed from resin matrix and carbon fibres. This is even proven by referring carbon peek values (285.5) from TABLES 5 & 8, which shows a shifting towards C-H form of carbon.

TABLE 5

Elemental Peak Range, Area and Composition of Case Study 3: Semi Cured Composite Laminate with Diatex Peel Ply

Element	**Peak Range, eV**	**Peak Value, eV**	**Peak Area, eV-CPS**	**Elemental Sensitvity Factors**	**Relative Elemental Composition**	**% Elemental Composition**
Carbon	293-282	285.5	332749	0.25	2.81	52.03
Oxygen	540-528	534	455292	0.66	1.46	26.96
Nitrogen	405-396	400.5	201177	0.42	1.01	18.72
Sulphur & Others	170-161	165	13077	0.54	0.05	0.95
Silicon	107-100	104	9702	0.27	0.08	1.40
Calcium	—	—	—	—	—	—

TABLE 6

Elemental Peak Range, Area and Composition of Case Study 4: Fully Cured Composite Laminate with No Peel Ply Condition

Element	**Peak Range, eV**	**Peak Value, eV**	**Peak Area, eV-CPS**	**Elemental Sensitvity Factors**	**Relative Elemental Composition**	**% Elemental Composition**
Carbon	294-279	287.5	420493	0.25	2.94	41.96
Oxygen	541-528	534	710471	0.66	1.88	26.86
Nitrogen	408-397	406, 402	274171	0.42	1.14	16.29
Sulphur & Others	206-190, 176-166, 162-148	203, 193, 171, 155	126763	0.54	0.41	5.86
Silicon	110-100	104	30260	0.27	0.20	2.80
Calcium	356-345	353, 349	261848	1.05	0.44	6.22

TABLE 7

Elemental Peak Range, Area and Composition of Case Study 5: Fully Cured Composite Laminate with Polyester Peel Ply

Element	**Peak Range, eV**	**Peak Value, eV**	**Peak Area, eV-CPS**	**Elemental Sensitvity Factors**	**Relative Elemental Composition**	**% Elemental Composition**
Carbon	295-281	285.5	380023	0.25	2.51	48.83
Oxygen	543-527	534	684571	0.66	1.72	33.32
Nitrogen	404-395	400.5	197687	0.42	0.78	15.12
Sulphur & Others	170-160	164.5	16056	0.54	0.05	0.96
Silicon	110-100	104	15320	0.27	0.09	1.82
Calcium	—	—	—	—	—	—

TABLE 8

Elemental Peak Range, Area and Composition of Case Study 6: Fully Cured Composite Laminate with Diatex Peel Ply

Element	Peak Range, eV	Peak Value, eV	Peak Area, eV-CPS	Elemental Sensitvity Factors	Relative Elemental Composition	% Elemental Composition
Carbon	295-281	285.5	347856	0.25	2.59	49.66
Oxygen	543-527	534	585739	0.66	1.65	31.68
Nitrogen	404-395	400.5	188129	0.42	0.83	15.99
Sulphur & Others	170-160	165	13733	0.54	0.05	0.91
Silicon	110-100	104	13170	0.27	0.09	1.74
Calcium	—	—	—	—	—	—

TABLE 9

Comparisons of Case Studies Percentage Elemental Composition

Case Study	Carbon	Oxygen	Nitrogen	Sulphur & Others	Silicon	Calcium
Semi Cured Composite Laminate with No Peel Ply Condition	42.24	28.31	17.05	4.12	2.60	5.64
Semi Cured Composite Laminate with Polyester Peel Ply	50.71	27.10	19.77	0.91	1.54	—
Semi Cured Composite Laminate with Diatex Peel Ply	52.03	26.96	18.72	0.95	1.40	—
Fully Cured Composite Laminate with No Peel Ply Condition	41.96	26.86	16.29	5.86	2.80	6.22
Fully Cured Composite Laminate with Polyester Peel Ply	48.83	33.32	15.12	0.96	1.82	—
Fully Cured Composite Laminate with Diatex Peel Ply	49.66	31.68	15.99	0.91	1.74	—

5. Conclusion

Epoxy/Carbon RTM composite laminates of 100% and 55% cure states were prepared using respective cure cycle with the application of polyester and diatex peel plies. The composite laminate surfaces are characterized by X-ray photoelectron spectroscopy to evaluate the mould release contaminants. From the results, it was found that the mould release Frekote contaminant calcium metal ions at both cure states are equally contaminated when no peel ply was applied. With the use of peel plies, at both cure states, diatex peel ply blocks more percentage of mould release contaminants than polyester peel ply.

Acknowledgements

This research was supported by Extra Murral Research (EMR) Scheme" of Science & Engineering Research Board (SERB), Department of Science and Technology (DST), India. File No.: EMR / 2016 / 005562

REFERENCES

[1] M. Kanerva, O. Saarela, The Peel Ply Surface Treatment for Adhesive Bonding of Composites: A Review. Int. J. Adhes. Adhes. **43**, 60-69 (2013).

[2] D.A. Cole, L. Zhang, Surface Analysis Methods for Contaminant Identification, 585-652 (2008).

[3] B.M. Parker, R.M. Waghorne, Testing Epoxy Composite Surfaces for Bondability. Surf. Interface Anal. **17**, 471-476 (1991).

[4] M.E. Sarlin, M. Hoikkanen, K. Rämö, O. Saarela, J. Vuorinen, Interface Modification of Glass Fibre–Polyester Composite–Composite Joints using Peel Plies. Int. J. Adhes. Adhes. 40-52 (2015).

[5] M. Phariss, B. Flinn, The Effect of Peel-Ply Surface Preparation Variables on Bond Quality. In: DOT/FAA/(AR)-06/2 (2006).

[6] B.D. Flinn, B.K. Cark, J. Satterwhite, P.J. Van Voast et al., Influence of Peel Ply Type on Adhesive Bonding of Composites, In: SAMPE, Baltimore, MD (2007).

[7] Q. Bénard, M. Fois, G.M. Peel et al., Ply Surface Treatment for Composite Assemblies: Chemistry and Morphology Effects. Compos. Part A, **36** (11), 1562-1568 (2005).

[8] J.M. Gardner, J.P. Wolbert, L.R. Holmes Jr, D.D. Pappas, Evaluation of Alternative Peel Ply Surface Preparation Methods of SC-15 Epoxy / Fiberglass Composite Surfaces for Secondary Bonding. In: ARL-TR-6781 (2010).

[9] Q. Bénard, M. Fois, M. Grisel et al., Influence of Fibre Reinforcement and Peel Ply Surface Treatment towards Adhesion of Composite Surfaces. Int. J. Adhes. Adhes. **25** (5), 404-409 (2005).

[10] V.J. Law, J. Mohan, F.T. O'Neill, A. Ivankovic, D.P. Dowling et al., Air Based Atmospheric Pressure Plasma Jet Removal of Frekote 710-NC Prior to Composite-to-Composite Adhesive Bonding. Int. J. Adhes. Adhes. **54**, 72-81 (2014).

[11] G.W. Critchlow, R.E. Litchfield, I. Sutherland, D.B. Grandy, S. Wilson et al., A Review and Comparative Study of Release Coatings for Optimised Abhesion in Resin Transfer Moulding Applications. Int. J. Adhes. Adhes. **26** (8), 577–599 (2006).

[12] B. Goss, The Effective use of Mould Release Agents. Reinforced Plastics **48** (8), 24-26 (2004).

[13] T.A. De Vilbiss, D.L. Messick, D.J. Progar et al., SEM/XPS Analysis of Fractured Adhesively Bonded Graphite Fibre-Reinforced Polyimide Composites. Composites **16** (3), 207-219 (1985).

[14] J.R.J. Wingfield, Treatment of Composite Surfaces for Adhesive Bonding. Int. J. Adhes. Adhes. **13** (3), 151-156 (1993).

[15] N. Encinas, B.R. Oakley, M.A. Belcher, K.Y. Blohowiak, R.G. Dillingham, J. Abenojar, A.A. Martinez, Surface Modifi-

cation of Aircraft used Composties for Adhesive Bonding. Int. J. Adhes. Adhes. **550**, 157-163 (2014).

[16] A. Nick, B. Nick, F.J. Wortmann, Peel Testing of Adhesively Bonded Joints of Carbon Fibre Reinforced Epoxy Resin. ESIS, Elsevier **27**, 261-271 (2000).

[17] S.K. Ryu, B.J. Park, S.J. Park, XPS Analysis of Carbon Fibre Surfaces – Anodized and Interfacial Effects in Fibre Epoxy Composites. J. Colloid Interface Sci. **215** (1), 167-169 (1999).

[18] C.L. Weitzsacker, M. Xie, L.T. Drzal, Using XPS to Investigate Fiber/Matrix Chemical Interactions in Carbon-Fiber-Reinforced Composite. Surf. Interface Anal. **25** (2), 53-63 (1997).

[19] F. Awaja, P.J. Pigram, Surface Molecular Characterisation of Different Epoxy Resin Composites Subjected To UV Accelerated Degradation Using XPS and Tof-SIMS. Polym. Degrad. Stab. **94** (4), 651-658 (2009).

[20] O. Aires, P.F.D. Silva, F.R.S. Nunes, V.C. Jesus, R. França, Description of Six Nanofilled Composite Resin According to Degree of Conversion. Contact Angle, XPS, Dent. Mater. **29** (1), 31-32 (2013).

[21] Y. Nakayama, F. Soeda, A. Ishitani, XPS Study of the Carbon Fiber Matrix Interface. Carbon **28** (1), 21-26 (1990).

[22] W. Śmiszek-Lindert, A. Bajorek, J. Kubacki, Analysis of the Composite Materials having a Structure of the Mineral Fibers Based on the Non-Invasive Spectroscopic Methods. Chemik **69** (7), 411-418 (2015).

[23] S. Ohno, M.H. Lee, K.Y. Lin, F.S. Ohnchi, Thermal Degradation of IM7/BM15260 Composite Materials: Characterization by X-Ray Photoelectron Spectroscopy. Mater. Sci. Eng. **293** (1-2), 88-94 (2000).

[24] C. Jeenjitkaew, Z. Luklinska, F. Guild et al., Morphology and Surface Chemistry of Kissing Bonds in Adhesive Joints Produced by Surface Contamination. Int. J. Adhes. Adhes. **30** (7), 643-653 (2010).

[25] J. Kovac, Surface Characterization of Polymers by XPS and SIMS Techniques. Mater. Technol. **45** (3), 191-197 (2011).