CHARACTERIZATION OF PROTECTIVE FILMS AND ADHESIVE LINERS USED IN BACKEND MANUFACTURING

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ABSTRACT

Foreign materials (FMs) management under the cleanroom environment is one of the top ordeals in the semiconductor industry, especially in processing optical wafers. One of the top contributors of these FMs are adhesive tapes and protective films. However, some layers in the protective films have been disclosed due to proprietary rights and has been one of the limitations in analyzing the materials.

To have a better insight into the behavior of these films, three protective adhesives were considered from different suppliers, namely, Adwill, Furukawa, and Sumitomo. Difference in morphology in both fresh and cured tapes was explored using optical and SEM imaging techniques. Compositional fingerprints were examined using EDS and FTIR. Thermoanalytics, including TGA-MS and DSC, has been carried out to explore the thermal gradation of the samples.

SEM images showed that the morphology of Adwill and Sumitomo tapes changes after UV curing. Decrease in the reflectance at 500cm^{-1} - 1000cm^{-1} present in all samples were observed attributed to the conversion of C-O to C-H, C=C to C-C due to polymerization after curing. This decrease is also observed in the carbon content of the cured films in the EDX plot. The TGA plots of the films showed the onset temperature of outgassing for each film with the fresh samples have faster outgassing rate compared to the cured ones. Significant outgassing was observed around 200C. At higher temperatures, some of the curves vanish in the DSC plot of the cured films are represented by one curve with greater area. This suggests that the amount of heat required to increase the temperature is higher in the cured films. Finally, specific m/z species trends were plotted with respect to temperature to show hints of possible thermal defragmentation.

1. 0 INTRODUCTION

Adhesives and protective films are used in a wide range of applications such as dicing of wafers (crystalline silicon, silicon glass etc.), singulation of packages and substrates, or to keep dies intact during wafer reconstruction, protecting sensitive surfaces from foreign materials (FMs), corrosion, or physical damages during the sawing process. This has become the preference among semiconductor manufacturers due to the easy removal of the singulated units from wafer after the dicing process.

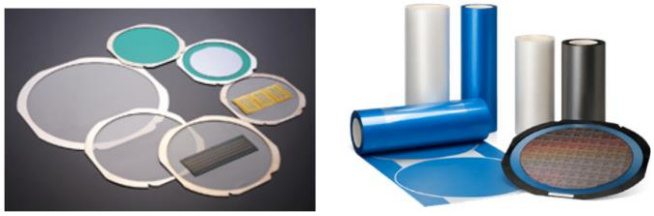


Fig. 1. Samples of adhesive liners and protective films used in the semiconductor industry.

During the processing of the metalens wafers for optical diffuser and time-of-flight (ToF) applications, FMs has become one of the top reject contributor detected at the automatic optical inspection (AOI) stations. The process shown in Fig 2. includes 3 AOI stations to inspect the wafer post electrical wafer sort (EWS), post-debond, and after wafer reconstruction. The shredded remains of the tapes and the sticky adhesive reacting with other particles has become one of the top contributors of the AOI rejects. With the usage of the multiple tapes for specific processes, accurate identification of the tapes and their decomposition fragments should be properly established.

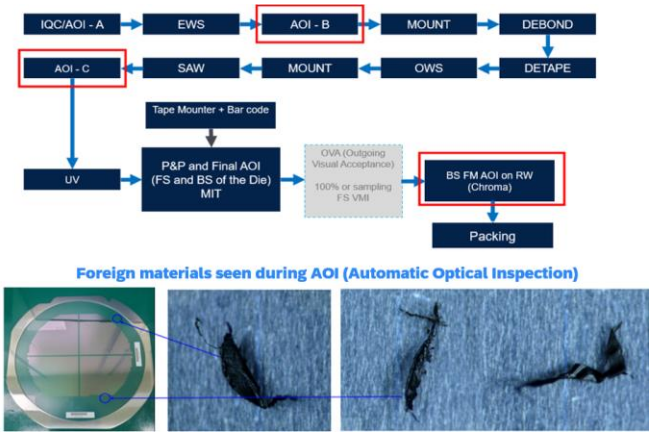


Fig. 2. Adhesive residues are seen as the top contributor of foreign material during dicing and backgrinding process.

In this literature, 3 protective films from different suppliers were characterized based on their morphology, composition, thermal behaviors, and elemental decomposition at higher elevations. The comparison between these 3 films were discussed and

2. 0 REVIEW OF RELATED WORK

The basic layering of an adhesive film comprises the topmost layer as the base film, followed by the adhesive layer, finally the release layer. In most cases, the based layer material and the release film are disclosed while the adhesive material is protected the proprietary rights.

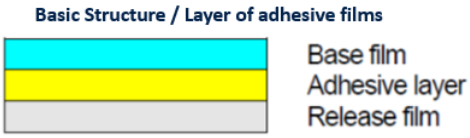


Fig. 3. Basic structure/layer of the adhesive films.

To improve the adhesion, ultra-violet (UV) curing was used as a rapid and practical route for conversion of a fluidic monomer to a solid polymer after UV irradiation. The curing can be described in two phases: 1) photoinitiated polymerization; and 2) photopolymerization or photo crosslinking of functionalized oligomers to form a solid cross-linked film. This technique has been widely utilized due to its straightforwardness, can be carried-out under ambient temperature hence lower energy consumption and does not require wide space for equipment footprint[1].

UV curing, often termed as light-curing or photocuring, is a process irradiation of adhesives usning UV-A or "blue-light" with wavelengths ranges from 365nm to 405nm. The typical UV curable adhesive consists of photoinitiators that are responsible for light absorption instead of solvent as polymerization catalyst. This phenomenon promotes polymerization of oligomers and monomers to form a more robust cross-linked network, hence, better adhesion strength. Additionally, the monomer/oligomers chemical structure is a critical structure in adjusting the crosslinking properties of the adhesives. Notable structure variations include aliphatic, aromatic, and hydrocarbon, polyether, polyester, polyurethane, fluorochemical, or siloxane chains resulting in significant differences in mechanical, chemical resistance, weatherability, and optical properties. One of the most widely used monomer/oligomer in photopolymerization were acrylic and methacrylate. Also, low molecular weight monomers has been prevalent in the market, and functionalization of prepolymers such as epoxies, polyethers, polyesters, and polyurethane, with compounds containing with -OH, NH2, NCO groups has been widely used. Specifically, these prepolymers are often processed with acrylic XR-OCO-CH=CH2 or methacrylic XR-OCO-C(CH3) = CH2 compounds to meet market demands for UV light curing materials [2]. Some of these prepolymers were used in the adhesives discussed in the succeeding sections.

3.0 METHODOLOGY

Three protective films/adhesive liners from different suppliers, namely, Furukawa, Sumitomo and Adwill were characterized during their fresh and cured state. The optical images of both the base film and the adhesive side were taken as the initial reference of the tapes respective morphologies. The bright and dark field photos were used to further elucidate the tapes surface morphologies at 100x and 1000x magnification comparing the fresh and UV cured conditions. Furthermore, the scanning electron microscopy (SEM) images using Hitachi FESEM SR400 at 5kV accelerating voltage at 2.5kx magnification was used to peek into the adhesive sticky surface. For elemental composition analysis, energy dispersive spectroscopy (EDS) and Bruker Fourier transform infrared spectroscopy at 600cm^{-1} to 4000cm^{-1} was used. The thermal behavior of the films was characterized using thermogravimetric analysis coupled with mass spectra and differential scanning calorimetry.

4.0 RESULTS AND DISCUSSION

Optical photos for each protective film as shown on Fig 4. were taken using brightfield and darkfield illumination at 100x and 1000x magnification to differentiate the surface morphology of each adhesive liner. This was done for both the fresh and cured state.

Based on the optical photos taken at 1000x magnification, there is no significant difference on the grain structure of the different adhesive liners of fresh and UV-cured tapes. Among the three adhesive liners, Sumitomo has the smoothest grain structure as compared to the other two liners.

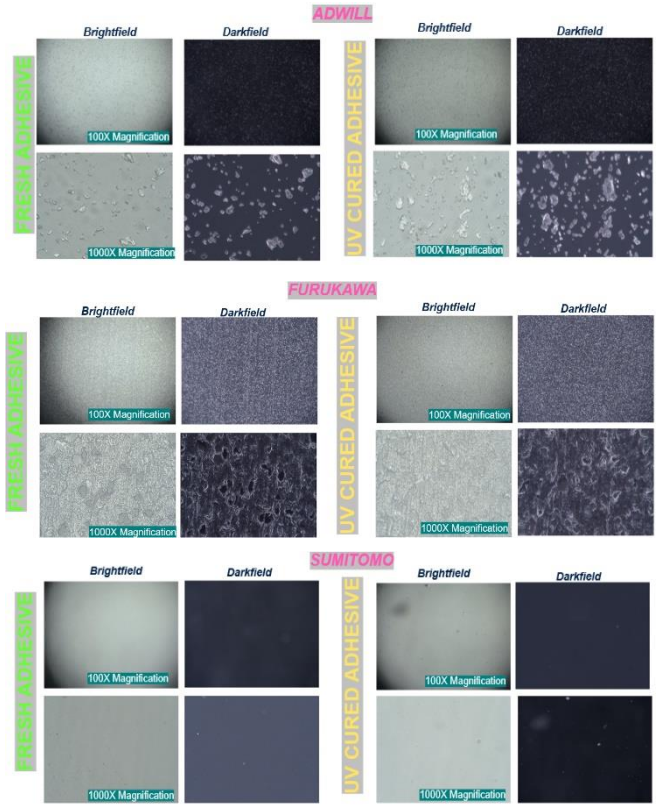


Fig. 4. Surface morphology of the fresh and cured state of Adwill, Furukawa and Sumitomo adhesive liner.

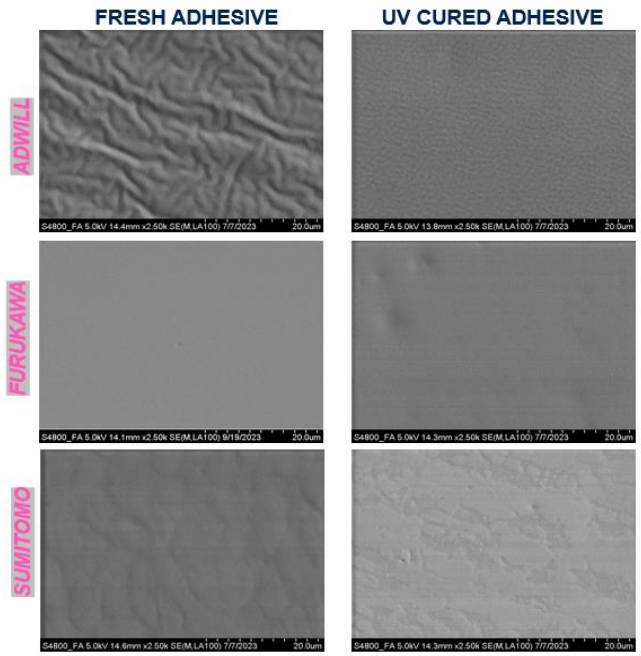


Fig. 5. SEM images showing the surface morphology of the fresh and cured state of ADWILL, FURUKAWA and SUMITOMO adhesive liners.

SEM imaging as shown in Fig 5. showed that the UV cured adhesive has a smoother morphology compared to its fresh state. This is due to the cross-linking enhanced through the UV curing. This is a common observation for the three suppliers.

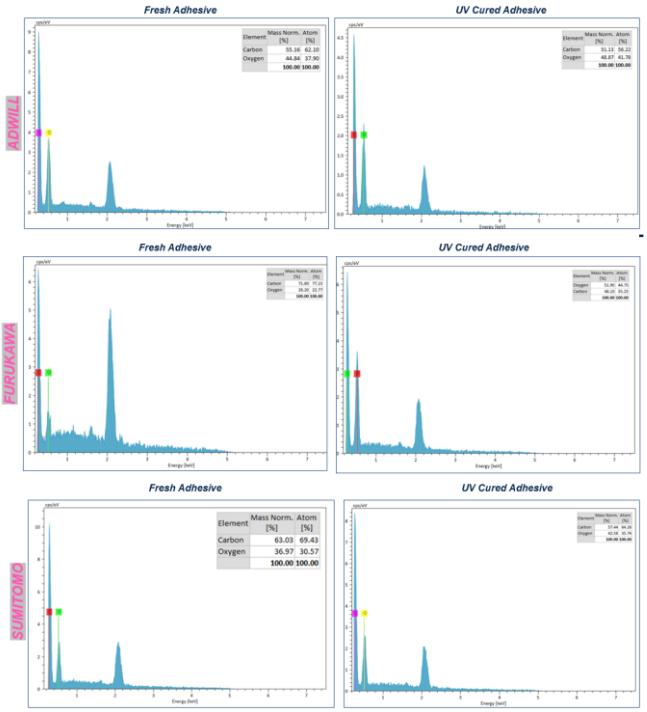
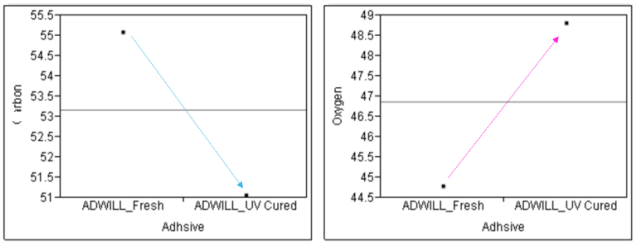


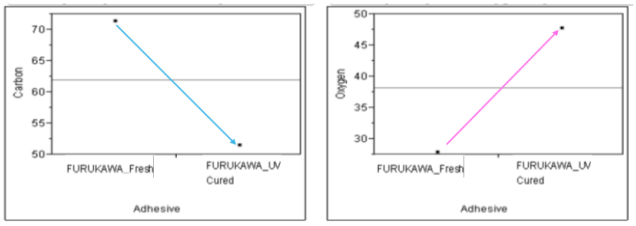
Fig. 6. EDX spectrum of the fresh and cured state of ADWILL, FURUKAWA and SUMITOMO adhesive liner

Elemental analysis through EDX at 10 keV accelerating voltage showed that for both fresh and cured state, all adhesive liners from different suppliers are composed of Carbon and Oxygen. The effects of the UV curing on the elemental composition between the fresh and UV-cured films showed a decrease in carbon content while increase in the oxygen content. The decrease in the carbon content is due to the polymerization of the adhesive or further cross-linking while increasing the oxygen content. This is observed in all samples.

	Carbon	Oxygen
ADWILL_Fresh	55.16	44.84
ADWILL_UV Cured	51.13	48.87



	Carbon	Oxygen
FURUKAWA_Fresh	71.8	28.2
FURUKAWA_UV Cured	51.9	48.1



	Carbon	Oxygen
SUMITOMO_Fresh	63.03	36.97
SUMITOMO_UV Cured	57.44	42.56

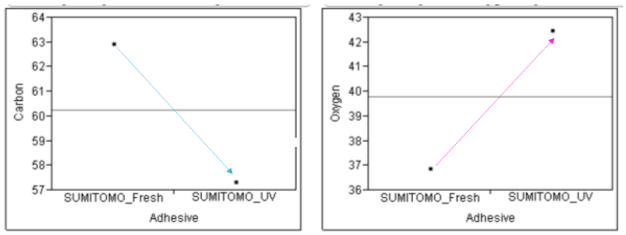
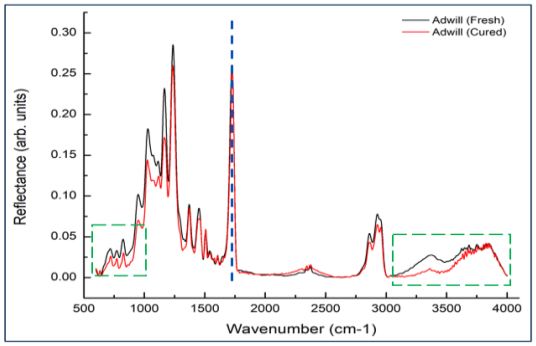
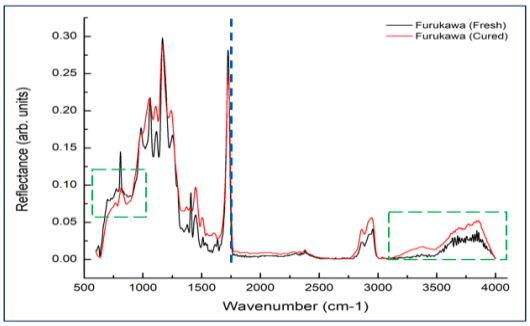


Fig. 7. Comparison of Atomic Percentage Values of Carbon and Oxygen between Fresh state and UV cured State.

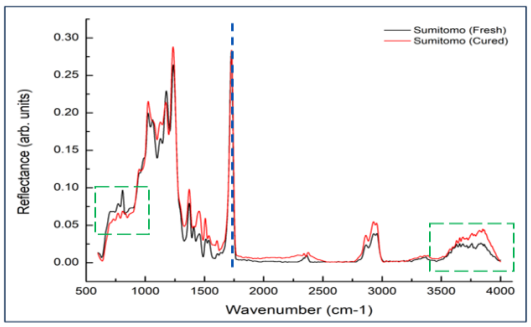
The FTIR was used to obtain the molecular/chemical fingerprint of the adhesive film for each manufacturer. Individual spectrum for fresh and cured state of the adhesive liners were taken as shown on Fig 8. When these spectrums are overlapped, you could see an almost identical spectrum for both fresh and UV cured adhesive despite the difference in the material used during manufacturing. Looking deeper into the spectrum, a sharp peak at 1750cm^{-1}, which is assigned to C=C vibrations. Material from the three suppliers showed that UV curing does not change the structure of the material, only conversion to C-O to C-H, C=C to C-C, which are all due to polymerization.



Release Sheet: Polyester
Adhesive Layer: Acrylic
Base Film: Polyolefin



Release Sheet: PET
Die Attach Film: Epoxy Adhesive
Adhesive Layer: Unknown Material
Base Film: Polyolefin



Release Sheet: PET
Die Attach Film: Epoxy Adhesive
Adhesive Layer: Unknown Material
Base Film: Unknown Material

Fig. 8. FTIR spectrum of the fresh and cured state of ADWILL, FURUKAWA and SUMITOMO adhesive liner.

The thermal stages on the TGA curve are shown on Fig 9. TGA curves of the Fresh and Cured ADWILL tapes showed that the transition from point 1 to point 2 of the fresh Adwill tape has a faster mass loss rate compared to cured Adwill tape. Differential Scanning Calorimetry plots between fresh and UV cured tapes showed that Area 1 on the DSC plots have comparable enthalpy values between fresh and cured Adwill tapes. Cured Adwill tapes in the exothermic region around 200C have higher enthalpy compared to the Fresh tape. This suggests that there is still residual curing on the cured tapes or the exothermic activity is due to the outgassing of tapes due to thermal degradation

Enthalpy values

Category	Area 1	Area 2
Fresh	-59.37384	10.0696
Cured	-50.7746	26.14592

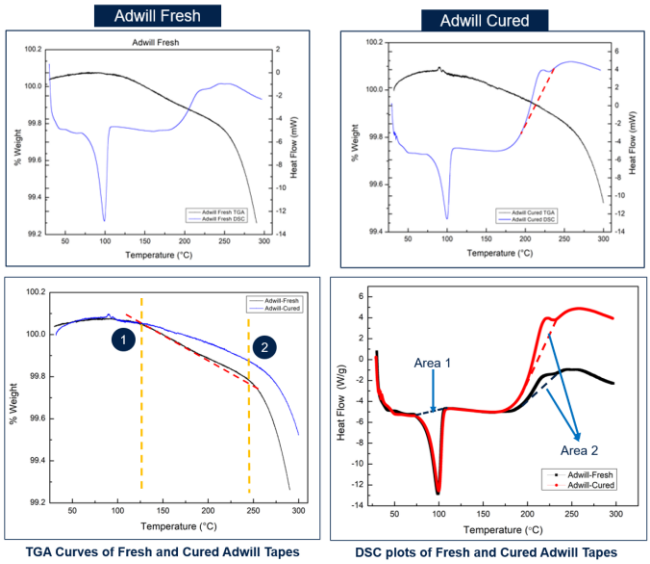
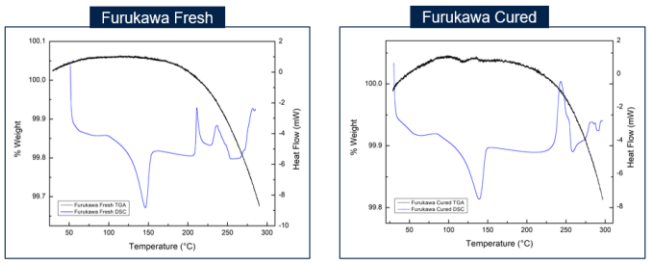


Fig. 9. TGA and DSC plots of the fresh and cured state of Adwill tape.

TGA curves of the Fresh and Cured Furukawa on Fig 10. showed onset of the thermal degradation is early on fresh Furukawa tape compared to UV cured tape. Also, the percentage loss due to thermal effects is lessened on the cured tape. Differential Scanning Calorimetry plots between fresh and UV cured tapes showed both fresh and cured Furukawa tape has the same moisture content suggested by the value of its enthalpy on Area1. Fresh tape has 2 exothermal spikes around 200 to 250C. The first exothermic spike has vanished in the cured tape, however the enthalpy corresponding to Area is almost tripled compared to the fresh tape.

Enthalpy values

Category	Area 1	Area 2	Area 3
Fresh	-39.61865	37.23974	11.07159
Cured	-35.99934		27.25926



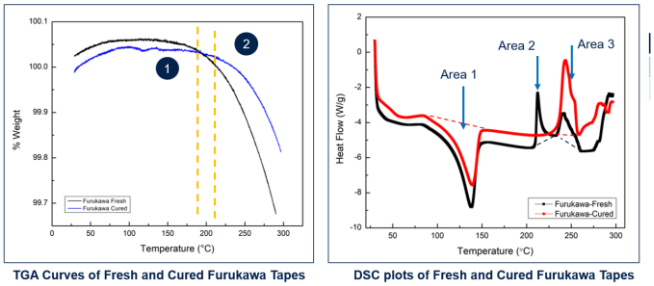


Fig. 10. TGA and DSC plots of the fresh and cured state of Furukawa tape.

TGA curves of the Fresh and Cured Sumitomo in Fig 11. showed that the cured Sumitomo tape have a low percentage weight even temperature below 200C, however, reaching beyond 200C, thermal degradation rate is faster on fresh adhesive compared to cured Sumitomo. Differential Scanning Calorimetry plots between fresh and UV cured tapes showed the enthalpy on the endothermic dips around 150C is comparable between cured and fresh. There are 2 exothermic peaks of the fresh Sumitomo tape. The shoulder exothermic peak vanished on the cured suggesting further polymerization. The enthalpy value for area 3 is greater than of the cured adhesive.

Enthalpy values

Category	Area 1	Area 2	Area 3
Fresh	-38.35664	2.82891	14.73636
Cured	-40.04069		95.44771

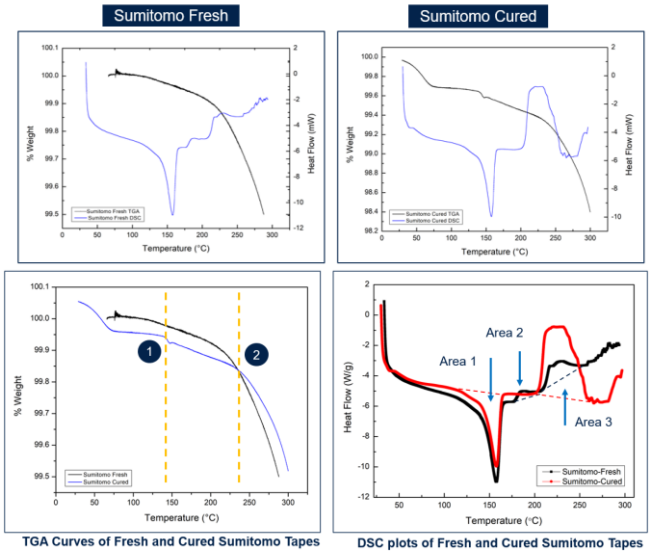


Fig. 11. TGA and DSC plots of the fresh and cured state of Sumitomo tape.

There are several distinct behavior between fresh and cured Adwill adhesive when looking at the mass spectra data corresponding to specific m/z. For Fig 12 a., m/z species continuous increase with temperature, the cured outgassing is greater than the fresh adhesive. Fig 12b: Abrupt outgassing of cured tape around 200C. Fig 12c., iIncrease of m/z outgassing with a shoulder peak starting from 150C and

increases at 200C. Fig 12d, Abrupt increase from downtrend with two step out gassing of cured tape.

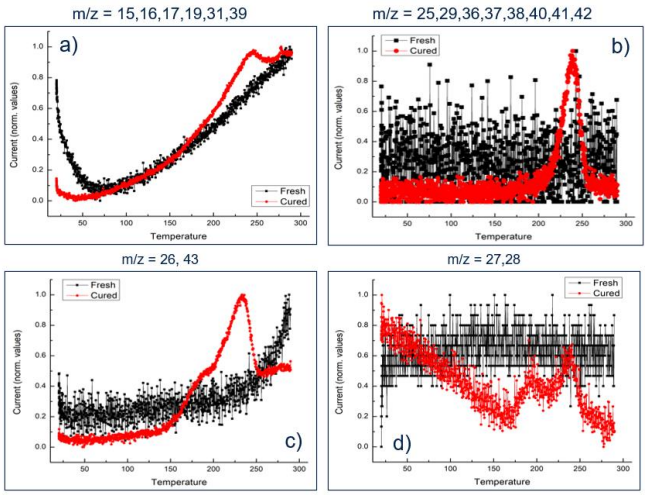


Fig. 12. Mass Spectra of the fresh and cured state of ADWILL tape

Mass spectra data for Furukawa tape showed that there are two trend behaviors observed. Figure on the left showed abrupt decrease in the current of the fresh tape, while increased behavior is observed in the cured tape. The right figure showed the opposite trend with cured tape in decreasing trend, while abrupt increase is observed in the fresh.

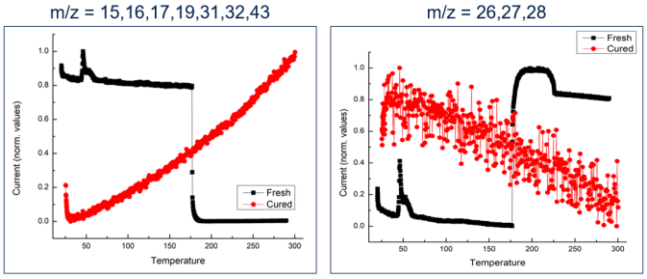


Fig. 13. Mass Spectra of the fresh and cured state of FURUKAWA tape

Mass spectra data for SUMITOMO tape showed that the figure on the left has a greater rate of outgasing of cured tape vs. fresh, with partial outgasing of fresh around 200C. The right graph showed more decreasing ion current trend in fresh tape compared to cured tape.

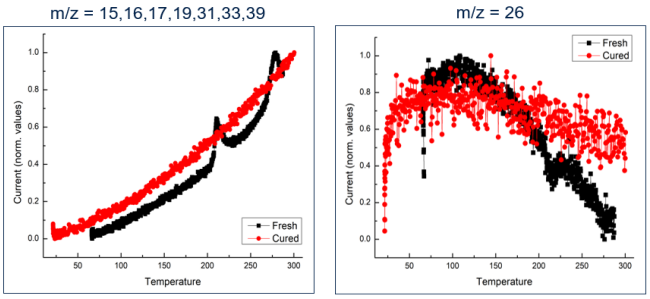


Fig. 14. Mass Spectra of the fresh and cured state of SUMITOMO tape

5.0 CONCLUSION

The optical photos of the fresh Sumitomo, Adwill and Furukawa tapes showed no significant difference compared to their cured counterparts at 1000x magnification, both in bright and dark field illumination conditions. However, changes in morphology were observed in Adwill and Sumitomo at 5kV and 2.5kx magnifications. The FTIR spectra of the tapes showed a decrease in the intensity in the 500cm^{-1} to 1000cm^{-1} fingerprint region of the cured tapes due to the conversion of C-O to C-H, C=C to C-C as the result of further polymerization due to UV curing. This is also manifested in the decrease in the atomic percentage of carbon in the EDX of the cured tapes compared to the fresh ones. The thermal degradation of the fresh films was faster compared to the cured ones, hence stronger bonds due to the cross linking of polymers upon UV curing. The onset of outgassing is different for each tape. The DSC curves has is also unique for each tape. However, in higher temperatures, some of the curves vanish in the cured plot and are represented as one curve with greater area. This suggests that the amount of heat required to increase the temperature is higher in the cured films. Finally, the m/z with respect to temperature gives hint for the possible reaction if contamination occurs after the films were subject to elevated temperatures. However, this is subject to further analysis of the possible chemical reaction.

6.0 RECOMMENDATIONS

The outgassing of each material relates to the thermal degradation or further polymerization of the tapes, thus it is recommended to further analyze the fragmentation of these tapes.

7.0 ACKNOWLEDGMENT

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8.0 REFERENCES

1. Seung-Woo Lee et al, **Adhesion Performance of U-V curable Debonding Acrylic PSAs with Different Thickness in Thin Si-Wafer Manufacture Process** , Journal of Adhesion and Interface, Vol 11, No 3, 2010

2. PROSTECH., "**UV Adhesive, A comprehensive Overview**" https://prostech.vn/a-comprehensive-overview-of-uv-adhesive/#1_What_is_UV_Adhesive

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