

## 論文

극저온에서 우레탄과 에폭시 접착제로 접착된 트리플렉스의  
전단강도와 박리 강도 평가손민영<sup>\*+</sup>**Evaluations of lap shear and peel strength for epoxy and polyurethane adhesive bonded Triplex sheets at cryogenic temperatures**MinYoung Shon<sup>\*+</sup>**ABSTRACT**

Adhesive joints are widely used for structural joining applications in various fields and environmental conditions. Polyurethane (PU) and Epoxy adhesives are now being used for liquefied natural gas (LNG) carriers at cryogenic temperatures. This paper presents a comprehensive evaluation of epoxy and PU adhesive bonds between Triplex sheets at normal and cryogenic temperatures. The most significant result of this study is that for all adhesives tested, there is a significant decrease in peel strength at cryogenic temperatures. However, the reasons for the decrease in peel strength for epoxy and PU adhesives differ. Consequently, PU adhesives can be considered better suited for use in applications requiring high bonding performance at cryogenic conditions, such as in LNG carriers.

**초 록**

접착제에 의한 접합은 일반적으로 구조물의 접합에 널리 사용되고 있다. 폴리우레탄 접착제와 에폭시 접착제는 현재 극저온에서 운항되고 있는 LNG 선박의 화물창에 적용되고 있다. 본 연구에서는 화물창용 소재인 트리플렉스와 폴리우레탄 및 에폭시 접착제와의 상온과 극저온에서의 접착강도를 평가하였다. 연구결과 모든 접착시스템에서 극저온에서 박리강도의 감소가 있었으며 그 원인은 접착제마다 다르게 검토되었다. 결과적으로는 폴리우레탄 접착제와 트리플렉스가 극저온에서의 강도 값이 에폭시에 비해 우수하였으며 LNG 선박 같은 극저온 환경에 접합한 것으로 평가되었다.

**Key Words** : 에폭시(Epoxy), 폴리우레탄(Polyurethane), 접착제(Adhesive), 박리강도(Peel strength), 극저온(Cryogenic temperature)

**1. Introduction**

Fiber-reinforced plastic composites have been applied in many fields due to their advanced engineering properties such as high specific strength and modulus. Their general applications for industrial fields have been reported in many papers [1-5]. The joining method for composite materials is a

very important determiner of stress concentration in the bond region. Adhesive joining is a widely used technique for composites in various fields; it permits the joining of composite material with uniform stress distribution across the bond region and without the mechanical damage caused by bolting or riveting [6].

Epoxy and polyurethane adhesives are very common materials

\*+ Department of Industrial Chemistry, Pukyong National University, Corresponding author(E-mail:myshon@pknu.ac.kr)

for industrial adhesive joining applications. Epoxy adhesives are used mainly in the construction, automotive, and electronics industries due to their high bonding strength, low shrinkage, and good durability. However, its use is generally restricted for cryogenic temperature conditions due to their brittleness [7]. On the other hand, polyurethane (PU) adhesives have expanded their applications to the bonding of various substrates, such as glass, wood, plastics, and composites. PU adhesives are considered a high-performance adhesive due to their high reactivity, high flexibility, and good mechanical properties; they especially exhibit excellent adhesive properties at low temperatures [8,9,10].

Experiments on the peeling of laminates and adhesive joints have a long history because peeling is very important parameter in many industrial joining products. The evaluation of adhesive performance through peel tests is a natural extension of this situation, and analysis of such tests is highly developed. Some researchers have analyzed the peel test by considering the stress distribution around the peel, or crack front [10-18]. Kinloch et al. studied failures in peel tests according to the peel angle, thickness of the peel arm [19], test rate, and temperature [20-23]. They found that the adhesive fracture energy is a function of the thickness of adhesive layer when the thickness of the adhesive layer is relatively low. Furthermore, such energy dissipation leads to the value of the adhesive fracture energy being dependent upon the rate and temperature at which the peel test is conducted.

Liquefied natural gas (LNG) carriers-natural gas liquefies at  $-163^{\circ}\text{C}$  have cargo containment systems composed of primary and secondary barriers, as shown in Fig. 1. The primary barrier is composed of corrugated stainless steel, and the secondary barrier is composed of an adhesively bonded glass fabric sandwich construction. The function of the secondary barrier is to maintain the pressure of LNG containment systems for a minimum of 15 days when the primary barriers have failed. When the LNG is loaded into the cargo containment system, the temperature of the bond region of the secondary barrier reaches approximately  $-110^{\circ}\text{C}$ . As a result, complex stresses, including shear and peel stresses, develop in the bond region.

In this work, epoxy and PU adhesives were used because they are already being used in the secondary barrier bonding of LNG carriers. In order to evaluate the suitability of bonding performance for secondary barrier bonding of LNG carriers, glass fiber reinforced plastic (GFRP) samples bonded with epoxy and PU adhesives were prepared, and the lab shear strength and peel strength of the adhesives were evaluated at normal and cryogenic temperature conditions.

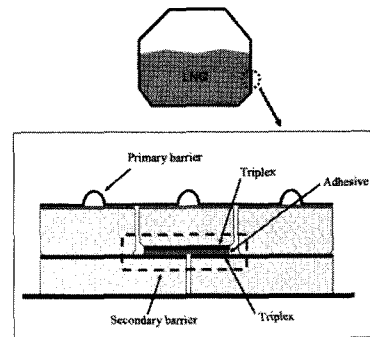


Fig. 1 Structure (cross-section) of an LNG containment system with dual barriers.

## 2. Experimental

### 2.1 Materials

Two types of adhesive materials-epoxy and PU adhesives were used in this study. Diglycidyl ether bisphenol-A (DGEBA)/amine-based two-component epoxy adhesive and polyol/toluene di-isocyanate(TDI)-based two-component PU adhesive were used. The adherend used in this study was a sandwich structure composite sheet called Triplex; it is composed of two glass fabric faces impregnated by an epoxy resin (600  $\mu\text{m}$  thickness) with aluminum foil (10  $\mu\text{m}$  thickness) in the centre, as shown in Fig. 2.

### 2.2 Mechanical properties of adhesives

The tensile strength tests for the epoxy and PU adhesives were performed using an Instron 8801 universal testing machine with a crosshead speed of 5 mm/min as per the ASTM D638 standard. The shear and compressive properties of epoxy and PU adhesives were tested using an Instron 8561 universal testing machine with a crosshead speed of 1.3 mm/min according to the ASTM D-732 and D-659 standard test methods, respectively. Liquid nitrogen was used to cool down the test temperature from  $23^{\circ}$  to  $-170^{\circ}\text{C}$ .

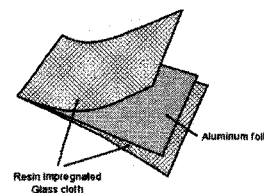


Fig. 2 Structures of Triplex glass fabric composites.

### 2.3 Preparation of single lap shear and peel specimens

Figure 3 shows the schematic diagram of the specimen preparation process. Two sheets of Triplex were bonded using an epoxy and PU adhesive, respectively. The Triplex surface was cleaned by acetone and dried before the bonding process. The epoxy and PU adhesives were evenly spread on the surface of the bottom Triplex with a spatula; the top Triplex was then attached to the spread adhesive layer. A pressing board was then placed on the top of the Triplex surface with a pressure of 250 mbar. The Triplex bonded with epoxy was cured at temperature conditions of 23°C for 12 h (epoxy A) and 60°C for 6 h (epoxy B), respectively. On the other hand, PU-bonded Triplex was only cured at 60°C for 6 h. The controlled thickness of the adhesives was approximately 500-600 μm.

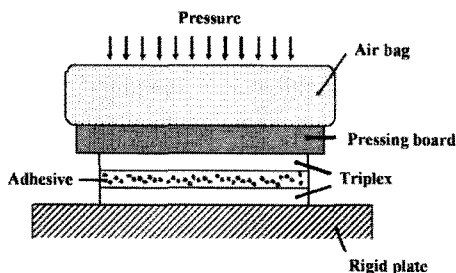


Fig. 3 Manufacturing process for specimens: pressurization by air bag.

In order to prepare the single lap shear specimens, bonded Triplex samples were prepared with 50 mm × 50 mm dimensions and adhered to an aluminum support using PU adhesives. The prepared specimens were kept for seven days at room temperature to cure the PU adhesive bonding the aluminum support and bonded Triplex. Figure 4 shows the dimension details for a single lap shear specimen.

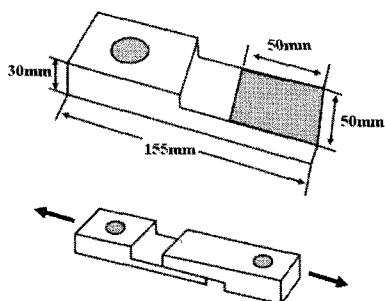


Fig. 4 Dimensions of a single lap shear specimen.

Peel specimens were prepared using bonded Triplex according to the ISO 4578 standard. The width of the specimen was 25 mm, and the length was 240 mm. The prepared bonded Triplex was adhered to a GFRP plate with a thickness of 3 mm using PU adhesive [24]. Figure 5 shows the dimensions for a peel specimen.

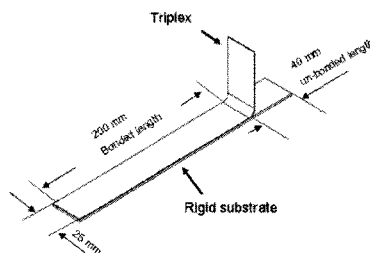


Fig. 5 Dimensions of a peel specimen.

### 2.4 Peel test, single lap shear test and surface analysis

The bonding performances of Triplex bonded by epoxy and PU adhesives were evaluated by the peel and single lap shear tests. The floating roller peel test (ISO-4578) was carried out using an Instron 3367 universal testing machine with a crosshead speed of 10 mm/min. Liquid nitrogen was used to cool the test temperature down from 23° to -170°C. Ten specimens were prepared for each adhesive and temperature condition (23° and -170°C).

A modified thick adherend single lap shear test was carried out using an Instron 8802 universal testing machine with a crosshead speed of 1.3 mm/min. Liquid nitrogen was used to cool down the test temperature from 23° to -170°C. Ten specimens were prepared for each adhesive and temperature condition (23° and -170°C). After the peel test, the fractured surface of the Triplex was examined with a scanning electron microscope (SEM, LEICA S-430).

All specimens were placed in a cryogenic chamber which was manufactured to keep the constant temperature of -170°C by temperature sensor.

## 3. Results and discussion

### 3.1 Effects of test temperature on the mechanical properties of adhesives

The mechanical performance of the epoxy and PU adhesives at cryogenic temperatures was compared with their mechanical

performance at room temperature. The tensile properties of the epoxy and PU adhesives are described in Table 1 with respect to the test temperature. The tensile strength and modulus of the epoxy adhesive was higher than for the PU adhesive at the test temperature of 23°C. This result might be due to the high flexibility and elongation of PU adhesives at this temperature compared with the epoxy. However, the tensile properties showed the opposite result at the test temperature of -170°C-i.e., the PU adhesive had a higher tensile strength and modulus than epoxy adhesive. This seems to be due to the increase in toughness of PU against the increase in brittleness of the epoxy at cryogenic temperatures.

Table 1 Tensile properties of epoxy and PU adhesives.

| Adhesive | Young's modulus, E(GPa) |        | Tensile strength, $\sigma$ (MPa) |        | $\nu$ |        |
|----------|-------------------------|--------|----------------------------------|--------|-------|--------|
|          | 23°C                    | -170°C | 23°C                             | -170°C | 23°C  | -170°C |
| Epoxy    | 3.85                    | 8.33   | 38.89                            | 58.49  | 0.48  | 0.32   |
| PU       | 0.03                    | 9.14   | 17.10                            | 87.83  | 0.40  | 0.29   |

The shear and compressive properties of the epoxy and PU adhesives are described in Table 2 with respect to the test temperature. The shear strength of the epoxy was slightly lower than that of the PU adhesive independent of test temperature. On the other hand, the compressive strength of the PU adhesive was not measured because of its high softness at 23°C. The compressive strength of PU increased in accordance with the decrease in test temperature to -170°C, but the compressive strength of the epoxy adhesive was slightly higher than that of the PU adhesive. Consequently, it is clearly indicate that the mechanical properties of epoxy and PU adhesives such as tensile and shear strength were increased as the temperature decreases because of modulus and strength increase of epoxy and PU adhesives at cryogenic temperature while the ductility decreases. Also, PU adhesive provides a better mechanical performance than epoxy adhesives at cryogenic temperatures. It was reported that the Polyurethane adhesives have the best low temperature properties [25] because Polyurethane adhesives containing the polyether backbone were found to give superior adhesives performance at cryogenic temperatures as compared to epoxy resins [26].

Table 2 Shear and compressive properties of epoxy and PU adhesives

| Adhesive | Shear strength, $\tau$ (MPa) |        | Compressive strength, $\sigma_c$ (MPa) |        |
|----------|------------------------------|--------|--|--------|
|          | 23°C                         | -170°C | 23°C                                   | -170°C |
| Epoxy    | 39.23                        | 75.29  | 85.96                                  | 340.00 |
| PU       | 46.17                        | 82.50  | -                                      | 271.31 |

### 3.2 Effects of the test temperature on the lap shear strength of epoxy- and PU-bonded Triplex

Figure 6 shows the results for the test on single lap shear strength of epoxy- and PU-bonded Triplex at test temperatures of 23° and -170°C.

At a test temperature of 23°C, the shear strength of high temperature-cured epoxy-bonded Triplex (Epoxy B) was similar in shear strength to low temperature-cured epoxy-bonded Triplex (Epoxy A). On the other hand, the shear strength of PU-bonded Triplex was lower than that of the Epoxy A and B systems. These results indicate that the shear strength of epoxy-bonded Triplex is higher than that for PU-bonded Triplex at the test temperature of 23°C regardless of the curing temperature for the epoxy adhesive. In addition, these results agree well with the respective material properties of the adhesives at 23°C.

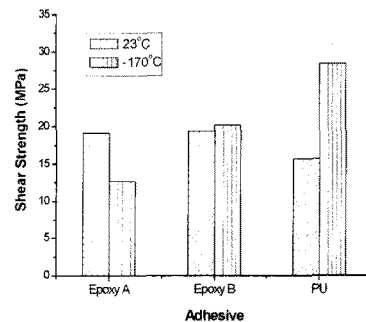


Fig. 6 Results for the single lap shear strength of epoxy- and PU-bonded Triplex with respect to test temperatures of 23° and -170°C.

At a test temperature of -170°C, the shear strength of Epoxy A decreased compared to its strength at the test temperature of 23°C. However, the shear strength of Epoxy B remained almost the same compared to its performance at 23°C. The failure mode of Epoxy A and Epoxy B at -170°C was adhesive and cohesive failure, respectively. The relatively lower shear strength of Epoxy A was based on the fact that the bonding strength between Triple-X and Epoxy adhesive was not developed enough by room temperature and it gave lower shear strength at -170°C.

On the other hand, the shear strength of PU-bonded Triplex increased when the test temperature was decreased to -170°C. Consequently, the shear strength of PU-bonded Triplex was higher than that of epoxy-bonded triplex at cryogenic temperatures. These results agree well with the material properties for PU adhesives at the test temperature of -170°C.

### 3.3 Effects of test temperature on the peel strength of epoxy- and PU-bonded Triplex

Figure 7 shows the results for the peel strength of epoxy- and PU-bonded Triplex at the test temperature of 23°C.

At 23°C, the peel strength of Epoxy B was 1.3 times higher than that of Epoxy A. On the other hand, the peel strength of PU-bonded Triplex was 3.3 times higher than that of Epoxy B. These results indicate that the increase of peel strength of Epoxy B with the increase in curing temperature is associated with the increase in bonding strength of the interface between the epoxy adhesive and Triplex. Furthermore, the peel strength of PU-bonded Triplex was much higher than that of the epoxy-bonded Triplex at 23°C regardless of the epoxy curing temperature. This seems to be caused by the high bonding strength and high reactivity of the PU adhesive on the Triplex surface.

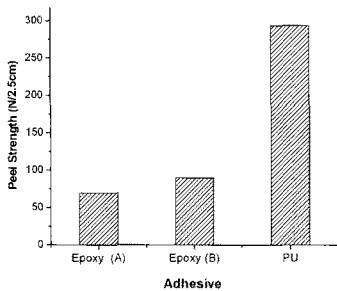


Fig. 7 Results for the peel strength of epoxy- and PU-bonded Triplex with respect to a test temperature of 23°C.

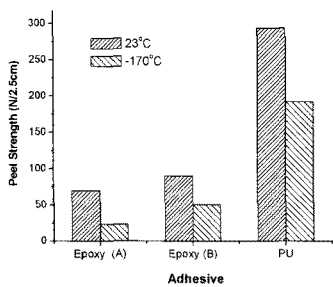


Fig. 8 Comparison of peel strength for epoxy- and PU-bonded Triplex at 23° and -170°C.

Figure 8 shows a comparison of the peel strength of epoxy- and PU-bonded Triplex at 23° and -170°C. At -170°C, the peel strength of Epoxy A decreased from 69.8 to 23.2 N/2.5 cm as the temperature decreased. A similar tendency for the change in peel strength was observed in

Epoxy B, which decreased from 90.0 to 50.3 N/2.5 cm in accordance with the decrease in test temperature. On the other hand, the peel strength of PU-bonded Triplex greatly decreased from 294.4 to 192.5 N/2.5 cm in accordance with the decrease in test temperature.

In conclusion, the peel strength of PU-bonded Triplex is higher than Epoxies A and B, even if the decrease in peel strength rate of PU-bonded Triplex is much higher than that of the epoxy adhesives at -170°C.

### 3.4 Effects of test temperature on failure mode of epoxy and PU bonded Triplex

Figure 9 shows the three failure modes observed in the peel test, which are classified as follows:

1. Partial cohesive and adhesive failure. Failure occurred both at the interface and bonding layer, as shown in Fig. 9(a).
2. Cohesive failure. Failure occurred at the bonding layer, as shown in Fig. 9(b).
3. Substrate failure. Failure occurred at the substrate, as shown in Fig 9 (c).

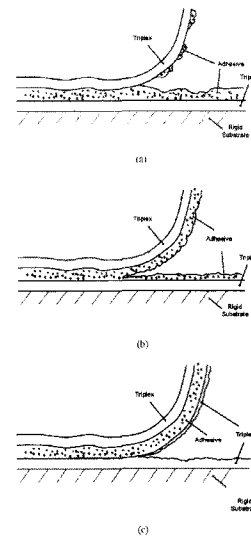


Fig. 9 Failure modes observed in the peel test.

Figure 10 shows the SEM images of the fractured surface of the Triplex after the peel test at 23°C. The failure mode of Epoxy A, as shown in Fig. 10(a), was partial cohesive and adhesive failure. The thickness of the failed epoxy adhesive in cohesive mode was very thin. On the other hand, cohesive failure within the epoxy adhesive was the main

culprit in Epoxy B, as shown in Fig. 10(b), but very small area with the adhesive failure mode was also observed. The thickness of the failed epoxy adhesive in cohesive mode was relatively thicker than that for Epoxy A. Figure 10(c) shows that the PU-bonded Triplex had cohesive failure. These results of failure mode agree well with the results of peel strength. That is to say, cohesive failure mode shows the higher peel strength than the adhesive failure mode at 23°C.

Figure 11 shows the SEM images of the fractured surface of the Triplex after the peel test at -170°C. The failure mode of Epoxy A, as shown in Fig. 11(a), was cohesive and adhesive failure. As the test temperature changed, the failure mode changed from partial cohesive and adhesive failure to less cohesive and more adhesive failure, and the thickness of the failed epoxy adhesive in cohesive mode was thicker than after the peel test at 23°C. The failure mode of Epoxy B, as shown in Fig. 11(b), was cohesive failure. The failure mode did not change with the temperature. However, the morphology of the failed epoxy adhesive in cohesive mode was sharper and larger than that after the peel test at 23°C. On the other hand, the failure mode of the PU-bonded Triplex, as shown in Fig. 11(c), was substrate failure. The failure mode changed from cohesive failure to substrate failure as the temperature changed.

The peel strength of all adhesive system was decreased compared to the peel strength at 23°C. In Epoxy A, the main reason of peel strength decrease seems to be the increase of brittleness of epoxy adhesive and decrease the bonding strength at -170°C. In Epoxy B, the main reason of peel strength decrease seems to be the increase of brittleness of epoxy adhesive at -170°C.

On the other hands, the main reason of peel strength decrease in PU bonded Triplex may be caused by the increase of brittleness of resin of substrate (Triplex) at -170°C because the failure occurred by substrate itself.

These results clearly indicate that the decrease in peel strength of epoxy-bonded Triplex as the test temperature decreased to -170°C is associated with the increase in brittleness of the epoxy adhesive. This agrees well with the observed failure modes for Epoxies A and B. On the other hand, the decrease in peel strength of PU-bonded Triplex at the test temperature decreased to -170°C is associated not with the decrease in bonding performance of the PU adhesive but with the decrease in strength of the Triplex resin. This agrees well with the observed failure modes of the PU-bonded Triplex in peel strength at cryogenic temperatures. This held true regardless of adhesive.

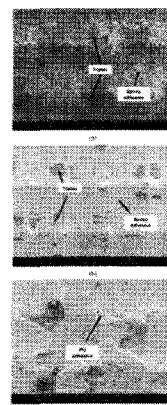


Fig. 10 SEM images of the fractured Triplex surface after the peel test at 23°C. (a) Epoxy A, (b) Epoxy B and (c) PU.

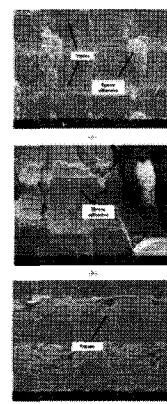


Fig. 11 SEM images of the fractured Triplex surface after the peel test at -170°C. (a) Epoxy A, (b) Epoxy B and (c) PU.

#### 4. Conclusions

A comprehensive evaluation of epoxy- and PU-bonded Triplex was performed at normal and cryogenic temperatures. In general, PU-bonded Triplex showed better bonding performance than the epoxies regardless of the epoxy curing temperature. The most significant result of this work is that for all adhesives tested, there was a significant decrease in peel strength at cryogenic temperatures. This held true regardless of adhesive. However, the reasons for the peel strength decrease in the epoxy- and PU-bonded systems were different. Therefore, when designing the adhesive joining of composite parts at cryogenic conditions, PU adhesives are a suitable material for use in applications requiring high bonding performance at cryogenic conditions, such as in LNG carriers.

References

- 1) J.F. Bonacci and M. Maalej, "Externally bonded FRP for service-life extension of RC infrastructure," *J. Infrastruct. Sys. ASCE* 6, 2000, pp. 7-33.
- 2) H.R. III Hamilton and C.W. Dolan, "Durability of FRP reinforcements for concrete," *Prog. Struct. Eng. Mater.* 2, 2000, pp. 45-139.
- 3) V.M. Karbhari and F. Seible, "Fiber reinforced composites - advanced materials for the renewal of civil infrastructure," *Appl. Compos. Mater.* 7, 2000, pp. 95-124.
- 4) K.W. Neale, "FRPs for structural rehabilitation: a survey of recent progress," *Prog. Struct. Eng. Mater.* 2, 2000, pp. 8-133.
- 5) M.A. Shaw and J.F. Drewett. "Case studies of carbon fibre bonding worldwide," In: L.C. Hollaway and M.B. Leeming (eds), *Strengthening of Reinforced Concrete Structures Using Externally-Bonded FRP Composites in Structural and Civil engineering.* Woodhead Publishing, Cambridge, UK, 1999.
- 6) D.F. Atiken, "Engineer's Handbook of Adhesives," The Machinery Publishing Company, London, 1972.
- 7) S.M. Kumar, N. Sharma and B.C. Ray, "Mechanical behavior of glass/epoxy composites at liquid nitrogen temperature," *J. Reinf. Plast. Compos.* 27, 2008, pp. 937.
- 8) K. Frisch and S.L. Reegen, "Advances in Polyurethane Science and Technology," Vols. 1-9. Echnomic, Westport 1984.
- 9) Z. Wirpsza, "Polyurethanes-Chemistry, Technology and Applications," PTR Prentice Hall, London 1993.
- 10) 손민영, 이재광, 홍정락, 한국복합재료학회지, 제22권 제4호, 2009, pp. 13-19.
- 11) D.H. Kaelble, "Theory and analysis of peel adhesion: mechanisms and mechanics," *Trans. Soc. Rheol.* 3, 1959, pp. 161.
- 12) D.H. Kaelble, "Theory and analysis of peel adhesion: bond stress and distributions," *Trans. Soc. Rheol.* 4, 1960, pp. 45.
- 13) D.H. Kaelble, "Peel adhesion: micro-fracture mechanics of interfacial unbonding of polymers," *Trans. Soc. Rheol.* 9, 1965, pp. 135.
- 14) D.H. Kaelble and C.L. Ho, "Biaxial bond stress analysis in peeling," *Trans. Soc. Rheol.* 18, 1974, pp. 219.
- 15) J.J. Bikerman, "Theory of peeling through a Hookean solid," *J. Appl. Phys.* 28, 1957, pp. 1484.
- 16) J.L. Gardon, "Peel adhesion I: some phenomenological aspects of the test," *J. Appl. Polym. Sci.* 7, 1963, pp. 625.
- 17) J.L. Gardon, "Peel adhesion II: a theoretical analysis," *J. Appl. Polym. Sci.* 7, 1963, pp. 643.
- 18) G.J. Spies, "The peeling test on redux-bonded joints," *Aircraft Eng.* 30, 1953, pp. 2.
- 19) J. Jouwersma, "On the theory of peeling," *J. Appl. Polym. Sci.* 45, 1960, pp. 253.
- 20) A.J. Kinloch, C.C. Lau and J.G. Williams, "Small scale aluminium/epoxy peel test specimens and measurement of adhesive fracture energy," *Int. J. Fract.* 66, 1994, pp. 45.
- 21) A.N. Gent and A.J. Kinloch, "Adhesion of viscoelastic materials to rigid substrates III: energy criterion for failure," *J. Appl. Polym. Sci.* 9, 1971, pp. 659.
- 22) E.H. Andrews and A.J. Kinloch, "Mechanics of adhesive failure I," in: *Proc. R. Soc. Lond. A* 332, 1973, pp. 385.
- 23) E.H. Andrews and A.J. Kinloch, "Mechanics of adhesive failure II," in: *Proc. R. Soc. Lond. A* 332, 1973, pp. 401.
- 24) ISO 4578, Adhesives - Determination of peel resistance of high-strength adhesive bonds - Floating roller method.
- 25) Stanley R. Sandler, Florence R. Berg, "Polyurethanes as cryogenic adhesives," *Journal of Applied Polymer Science*, Vol 9, 1965, pp. 3909-3916.
- 26) Edward M. Petrie, "Handbook of adhesives and sealants," pp. 705.