Low Cost Per Cycle Silicone Press Pad with Predictable Service Life
(Press Pads for Flex and Rigid Flex PCB Lamination)

Haibing Zhang, Ph.D., Andy Cloud, David Timpe, Art Rayner, Geno Amalfitano
Rogers Corporation / Arlon Silicone Technologies
1100 Governor Lea Road
Bear, DE 19701
United States
www.rogerscorp.com
Phone: 302-834-2100

Abstract

Silicone based press pads provide uniform pressure and temperature during flex and flex-rigid printed circuit board (PCB) lamination. Customer surveys show that cost per cycle, pressure uniformity, surface smoothness with low tack, thermal stability, and thermal uniformity are key properties for silicone based press pads. In this paper, an equation is developed which correlates pressure uniformity to durometer and thickness of a silicone press pad. Pressure sensitive paper confirms the accuracy of the theoretical calculation. The equation is helpful for press pad design, pressure uniformity, and service life determination. It can also be used as a tool to replace expensive pressure sensitive paper used to verify press pad effectiveness in an actual application. A new silicone press pad (UltraPad™) is developed with a low cost per press cycle hour, greater anaerobic thermal stability, predictable service life, smooth low tack surface, and low silicone oil loss.

Content

1. Background

Printed circuit boards (PCB) are made of epoxy, polyimide, fluoropolymer, polyester, and other polymers. PCB lamination is a process to achieve curing or sintering for fabric reinforced polymer composites. The lamination process also bonds the polymer composite to copper foils. A hydraulic press is used to provide pressure and temperature during lamination. Ideally, press pressure is uniform and press plate surfaces are level and smooth, as shown in **Figure 1 (a)**. However, this scenario is unlikely in an actual application. It is almost impossible to design a press system to provide 100% pressure uniformity. As shown in **Figure 1 (b)**, even if the press plate surfaces are smooth, the PCB surface may not be smooth due to design.
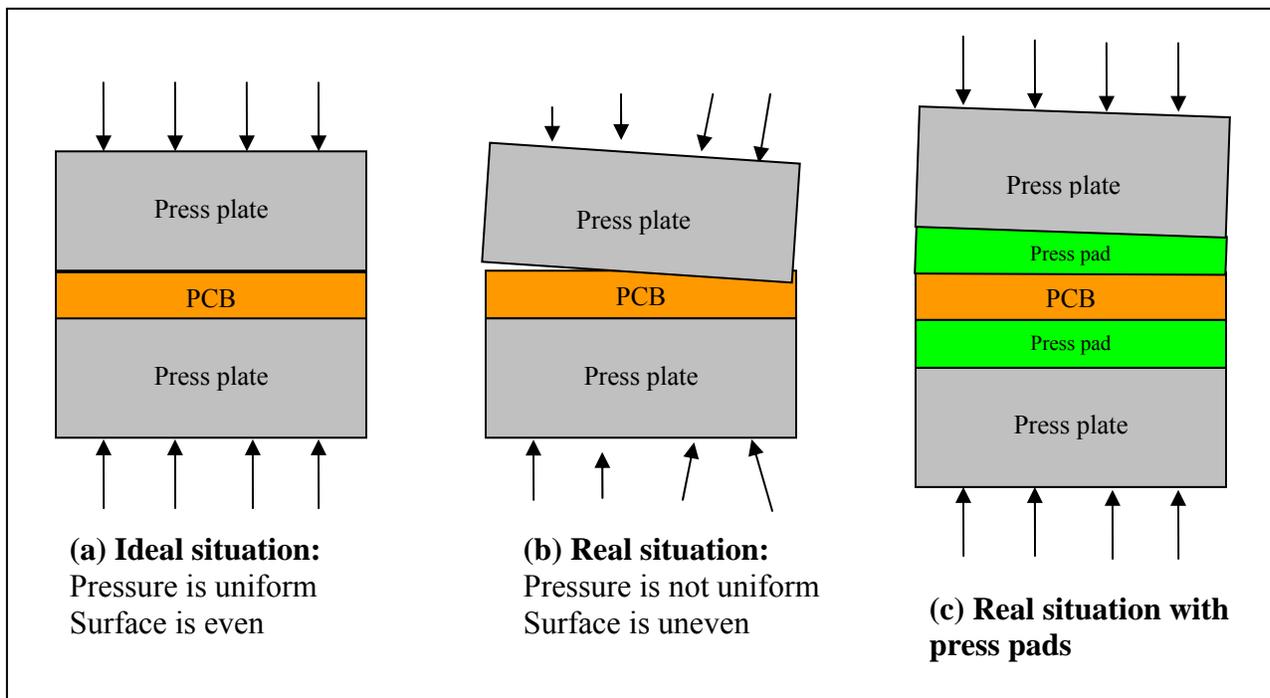

(a) Ideal situation:
Pressure is uniform
Surface is even

(b) Real situation:
Pressure is not uniform
Surface is uneven

(c) Real situation with press pads

Figure 1 Pressure uniformity for PCB lamination in a hydraulic platen press

So press pads are necessary to provide uniform pressure during PCB lamination in a press, as shown in **Figure 1 (C)**. Press pad elasticity balances uneven pressure in the press. Our experience and a customer survey shows that key requirements for a press pad include:

- **Pressure uniformity:** the most important function of press pad. Application pressures range from 0.3 MPa to 3 MPa.
- **Temperature uniformity:** if the temperature across the PCB differs from place to place during lamination, the quality of the final PCB laminate can not be guaranteed.
- **Cost per press cycle hour:** in a competitive environment, low cost combined with high quality is a requirement.

- **Thermal stability:** press pad building blocks must resist high temperature in anaerobic conditions. Press pad degradation results in non uniform pressure and temperature during PCB lamination.

Materials for press pads can be elastomers, papers, metal meshes, etc. Metal mesh is usually used for high temperature lamination (>300°C). Paper is a low temperature option for one time use. An elastomer is the best choice because its elasticity is much better than that of paper or metal mesh. An elastomer provides better pressure uniformity than paper and metal mesh. An elastomeric press pad is usually used when the application temperature is below 300°C. An elastomeric press pad can be used for many cycles so its actual cost per press cycle is competitive with paper products. High elasticity allows elastomeric press pads to conform to uneven surfaces (PCB and press plates) to a high degree. Consequently, they produce better temperature uniformity than paper or metal mesh press pads.

Silicone is an ideal elastomer to be used in the manufacture of press pads due to its high temperature stability. Typical organic elastomers degrade quickly at temperatures less than 150°C [1]. Silicone remains stable up to 300°C [1].

2. Thermal Stability of Silicone

Outstanding thermal and thermal-oxidative stability are two of the most characteristic and technically important properties of silicone rubber. This is a result of inherent strength of a siloxane, Si-O, bond. In general, silicone rubber can withstand much higher temperature than most organic elastomers [2]. The onset temperature of thermal degradation occurs between 300-400°C, while most organic C-C based polymers can rarely exceed 150C-200°C [3].

Higher temperature criteria drove academic and industrial research efforts to push thermal stability of silicone to higher levels [4-25]. Although mechanisms for thermal degradation of silicone have been proposed, there are still questions about the mechanism of silicone degradation at high temperature. These proposed mechanisms include: 1) the "unzipping" mechanism [26, 27], 2) the "random scission" mechanism [28], and 3) the "externally catalyzed" mechanism [29]. These degradation mechanisms all produce elastomer depolymerization. Low molecular weight siloxanes (silicone oil) are byproducts of depolymerization. In a press pad application, the silicone rubber does not contact air so this produces an anaerobic scenario and therefore depolymerization mechanisms are applicable.

If silicone contacts air or oxygen at high temperature, the degradation mechanism is aerobic or thermo-oxidative, and the final degradation by-product is silica. The free radical mechanism was proposed by Andrianov [30].

3. Pressure Uniformity Calculation

A silicone based press pad can be used for many cycles. A press cycle period is dependent on time, temperature, and pressure. These dependent variables will cause degradation of a silicone based press pad, and after a finite period the press pad will not function properly, causing inconsistent PCB lamination. The term service is used to designate a press pad's useful cycling

life. It is critical to determine the service life for a silicone press pad; otherwise the lamination process is not in control.

Pressure uniformity is the most important function of a press pad. It is chosen as the key criteria for this study. Pressure sensitive paper is the direct method to determine the pressure uniformity of a press pad, but is a very expensive tool. An equation in this study is developed to calculate pressure uniformity.

3.1 The equation of pressure uniformity calculation

From a microscopic view, the surface of a press plate is not topographically smooth, even if it appears smooth to the human eye, as shown in **Figure 2**. If the press plate or platen is not positioned parallel to the press pad or PCB, it has the same effect as an uneven surface. After pressure is applied to the press plate, the pressure deforms the press pad surface. The greater the press pad deformation into the press plate surface, the better the press pad conforms to the press plate and therefore pressure uniformity is improved. According to this assumption, pressure uniformity (U_p) is equal to the press pad thickness change (Δt) after applying pressure. The unit of pressure uniformity is distance (mm).

$$U_p = t\text{-}t' = \Delta t \qquad\qquad \textbf{Equation (1)}$$

Where, t is the initial press pad thickness
t' is the press pad thickness under pressure

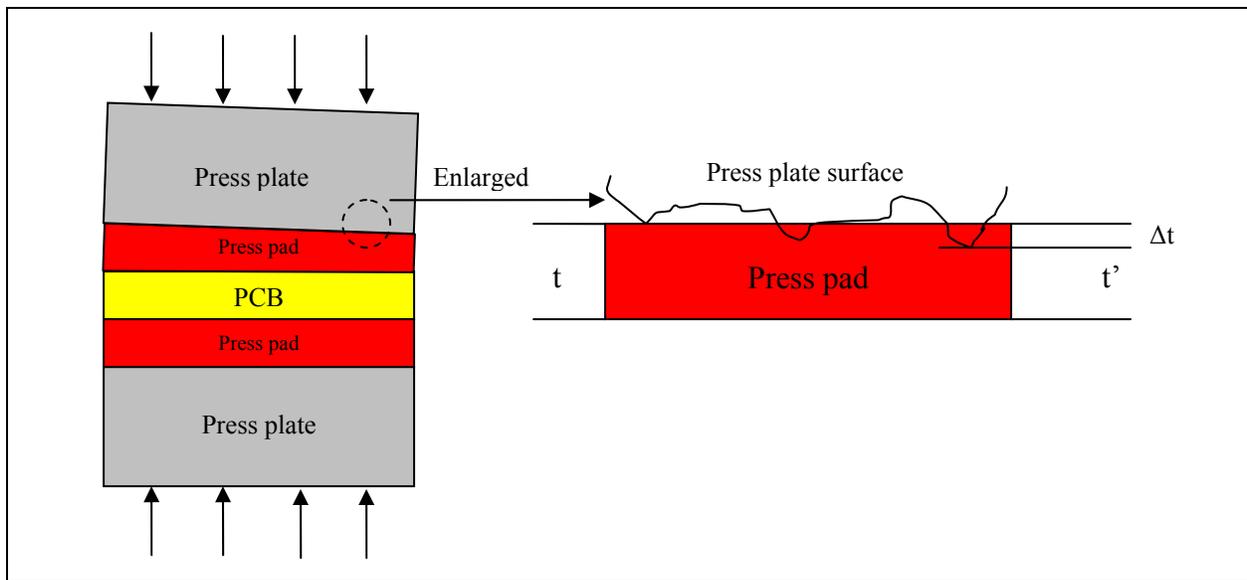**Figure 2 The microscopic schematic of a press plate surface**

The relationship between stress (σ), strain (ε), and modulus (M) can be described by the following equation,

$$M = \sigma/\varepsilon \qquad\qquad \textbf{Equation (2)}$$

In this case,

$$\varepsilon = \Delta t / t \qquad \textbf{Equation (3)}$$
$$\sigma = P \qquad \textbf{Equation (4)}$$

Where, P is the press plate pressure

For elastomeric materials, modulus can be correlated to durometer or hardness [31, 32].

$$M = 10^{0.02D-0.66} \qquad \textbf{Equation (5)}$$

Where, D is the durometer (Shore A Points) of the elastomer
The unit of M is MPa

Substituting **Equations (2)-(5)** into **Equation (1)**, yields pressure uniformity as follows:

$$U_p = \frac{P}{10^{0.02D-0.66}} t \qquad \textbf{Equation (6)}$$

3.2 The verification of the pressure uniformity calculation

Pressure sensitive paper is used to verify the reliability of **Equation (6)**. Arlon's current press pad, 55393R062, is used in the verification experiment. **Figure 3** is the result of pressure sensitive paper after a press cycle without a silicone based press pad, with a silicone based press pad, and with a silicone based press pad after a press cycle of 64 hours at 225°C and 1.03 MPa. In the figure, the red area equates to applied pressure and the white area indicates no applied pressure. A higher percentage of the area in red indicates a higher degree of pressure uniformity. The percentage of red area as a function of the number of press cycles is shown in **Figure 4**. The percentage of red area or pressure uniformity by pressure sensitive paper initially increases and then slowly decreases as a function of increased press cycles. We can see from **Figure 4** that the determination of pressure uniformity from pressure sensitive has limited resolution, which leads to some measurement inaccuracy. Furthermore, pressure sensitive paper is a very expensive option for determining pressure uniformity of a press pad in an actual press application.

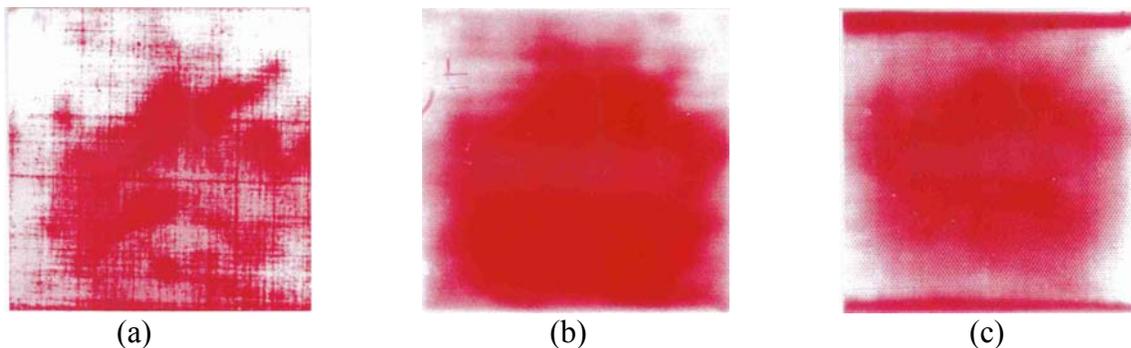(a)   (b)   (c)

Figure 3 Pressure sensitive paper results: (a) without a silicone based press pad, (b) with a silicone based press pad, (c) with a silicone pressure pad after 64 hours at 225°C and 1.03MPa

During the press cycling experiment, the durometer and thickness are measured as a function of time, as shown in **Figure 5**. Press pad durometer initially drops due depolymerization of high polymer. Following depolymerization, the press pad durometer begins to increase. Additionally, the press pad thickness always decreases as a function of time. **Equation (6)** is used to calculate pressure uniformity (U_p), as shown in **Figure 6**. U_p initially increases due to a reduction in durometer, then decreases with time due to durometer increase and a thickness reduction. The trend is the same as that measured by pressure sensitive paper. Relative pressure uniformity is developed as initial pressure uniformity divided by pressure uniformity after a specific number of press cycles, (U_p/U_{p0}). U_p/U_{p0} as a percentage, tells how much pressure uniformity is retained after a certain time period, compared to the initial pressure uniformity. This information will help to determine the service life of silicone press pad, as introduced in the section 4 "Service Life Criteria". U_p/U_{p0} also follows the same trend as U_p, since U_{p0} is a constant.

Data collection resolution is improved, as seen in **Figure 6**., where the data points fluctuate much less than **Figure 4**. This indicates that the calculated pressure uniformity by **Equation (6)** is much more accurate than data collected via pressure sensitive paper. This method of determining pressure uniformity is much less expensive than utilizing pressure sensitive paper. Pressure is easily determined from the hydraulic press output. Press pad durometer (hardness) and thickness can be easily measured by a durometer and micrometer respectively.

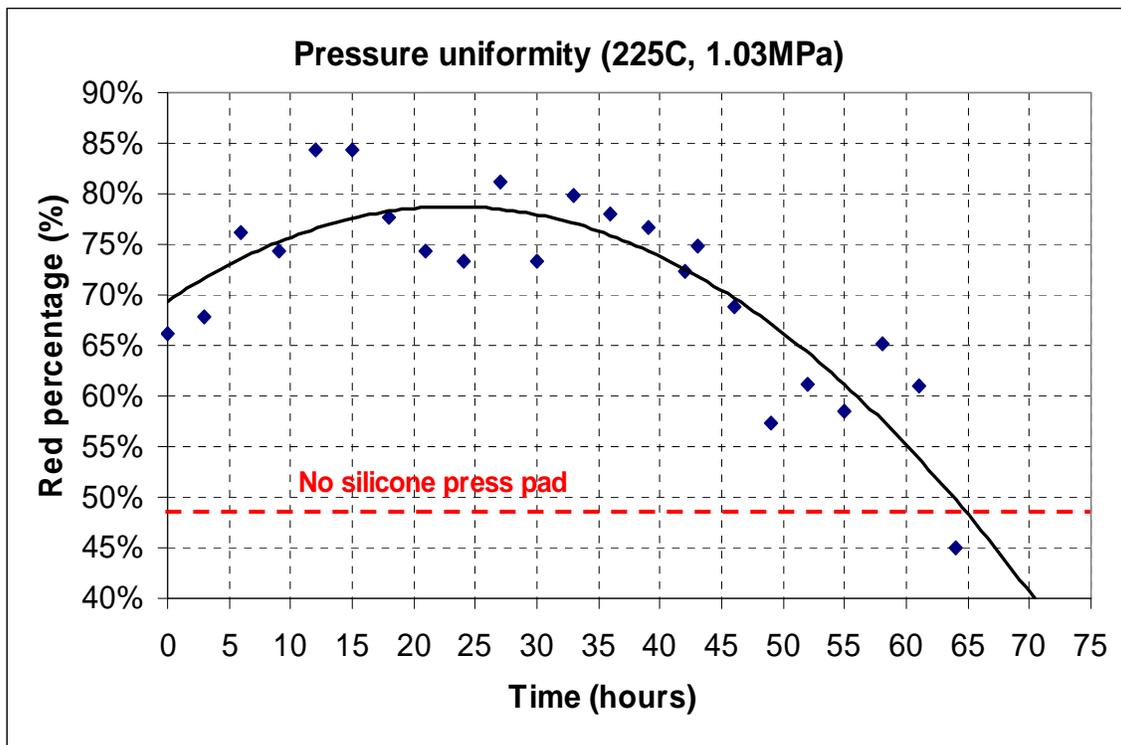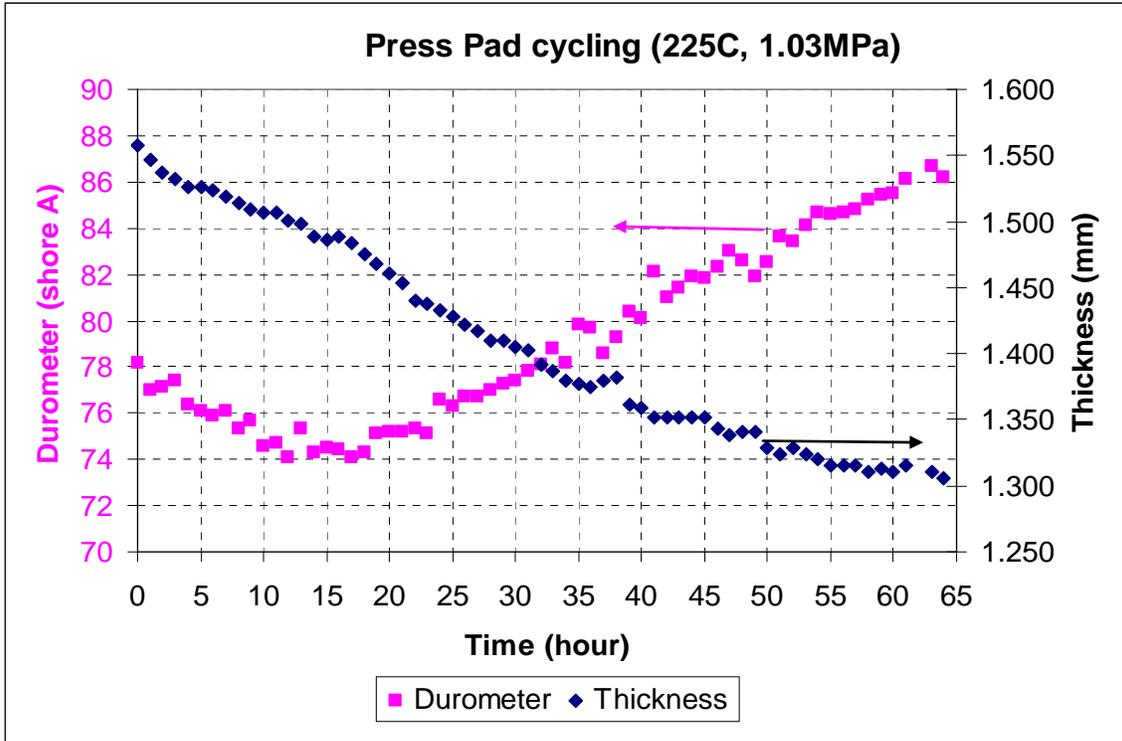**Figure 4 Pressure uniformity measured by pressure sensitive paper**

Figure 5 The durometer and thickness during cycling
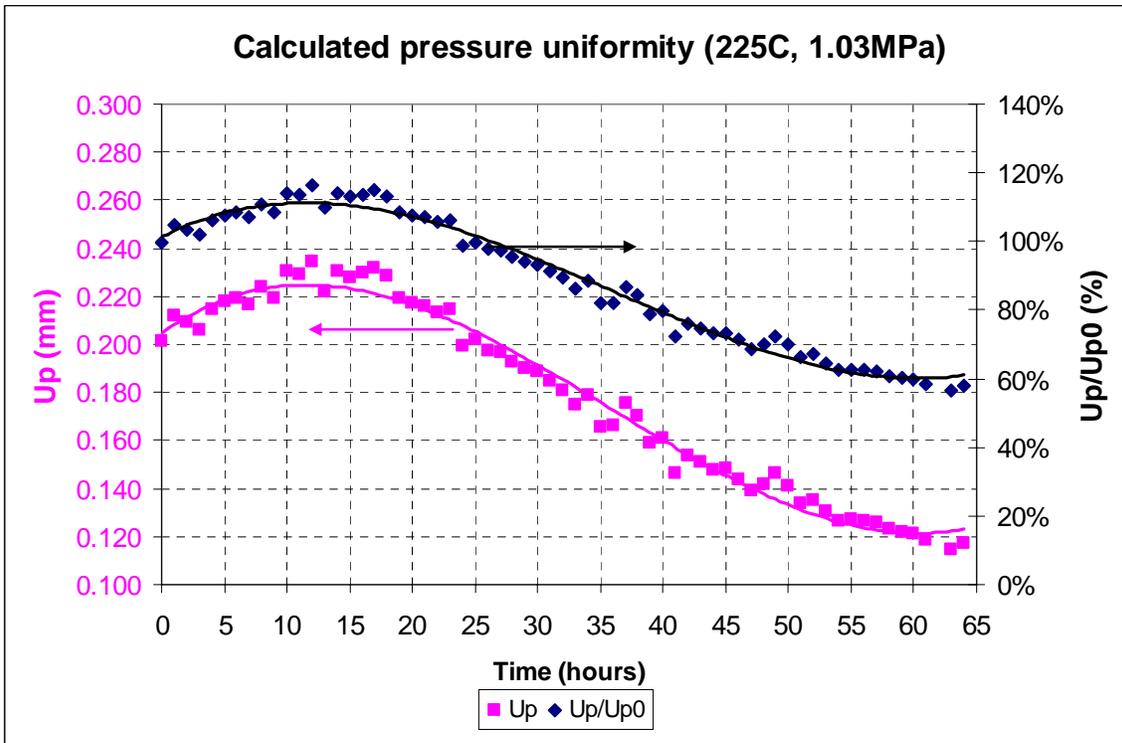

Figure 6 Calculated pressure uniformity measured by application pressure and silicone based press pad durometer & thickness

3.3 The applications of the pressure uniformity calculation

From **Equation (6)**, we know that pressure uniformity depends upon applied pressure and press pad durometer & thickness. The applications for this equation include press pad design, pressure uniformity evaluation, and service life prediction

• *Press pad design*

Equation (6) indicates that higher hydraulic press pressure improves press pad pressure uniformity. Since higher pressure may damage a laminate, application pressure may vary depending on laminate material robustness.

Press pad durometer significantly affects pressure uniformity. An elastomeric press pad with a lower durometer provides better application pressure uniformity than a higher durometer elastomeric press pad. In press pad design where pressure uniformity is critical, a low durometer silicone should be chosen. However, low durometer silicones usually have greater compression set. Therefore, the thickness of the silicone based press pad decreases more rapidly than a higher durometer silicone based press pad, resulting in a shorter service life. The type of flex or rigid-flex PCB to be laminated may determine the choice of silicone press pad hardness.

Press pad thickness is also a deterministic material characteristic. A press pad with greater thickness yields better application pressure uniformity. Fiberglass is usually used to reinforce silicone based press pads. If there is no fiberglass reinforcement, a silicone based press pad would yield too much deformation under high temperature and pressure and consequently dramatically compress. A fiberglass prime coating process is necessary to provide excellent adhesion between the silicone rubber and the fiberglass substrate.

• *Pressure uniformity calculation for users*

Silicone based press pads users can utilize **Equation (6)** to determine the pressure uniformity of any press pad. Equation (6) can also help identify which press pad is suitable for a particular PCB lamination application. After a silicone press pad has been used for a certain time period, a customer can use **Equation (6)** to calculate the pressure uniformity and determine service life. This method is less expensive and more precise than using pressure sensitive paper.

• *Silicone based press pad Service Life prediction*

The procedure is as follows, 1) measure durometer and thickness with time, 2) calculate pressure uniformity by **Equation (6)**. 3) plot pressure uniformity with time. 4) extrapolate pressure uniformity to predict service life.

4. Service Life Criteria

In this study, the following two criteria have been empirically chosen to determine the Service Life (E_f) of a silicone based press pad. Press pad E_f is reached if one of the criteria is reached during a press cycling application.

1) Durometer>85 SAP (Shore A Points)

First of all, pressure uniformity at D>85 SAP for a silicone based press pad is very low according to **Equation (6)**. The elasticity of a silicone based press pad at D>85 SAP is very low and therefore press pad fundamental functionality is lost. Secondly, the surface of a silicone based press pad may begin to fracture at D>85 SAP. The fractured areas may produce defects in the PCB during lamination.

2) Relative pressure uniformity (U_p/U_{p0})<50%

Pressure uniformity also depends on press pad thickness. For some press pads, the durometer may remain lower than 85 SAP during its life cycle, even when pressure uniformity reaches very low levels due to dramatic thickness reduction. **Equation (7)** can be used to calculate relative pressure uniformity, (U_p/U_{p0}). A silicone based press pad is considered to have reached E_f when pressure uniformity is 50% of the initial pressure uniformity.

$$U_p / U_{p0} = \frac{10^{0.02(D-D_0)}\, t}{t_0} \qquad \textbf{Equation (7)}$$

Where, U_p is the resulting application pressure uniformity after a given number of press cycles
U_{p0} is the initial resulting application pressure uniformity
D_0 is the initial press pad durometer
D is the press pad durometer after a given number of press cycles
t_0 is the initial press pad thickness
t is the press pad thickness after a given number of press cycles

5. The Effect of Temperature and Pressure on Service Life

The effect of pressure on E_f is shown in **Figure 7**. Higher press application pressure results in shorter E_f. The relationship between E_f and pressure is linear between 0.3-3 MPa for most silicone based press pads. Press pad E_f can be calculated by **Equation (8)**.

$$E_f = aP+b \qquad \textbf{Equation (8)}$$
Where a and b are constants at a certain temperature, but are functions of temperature.

The effect of temperature on E_f is shown in **Figure (8)**. Higher press application temperature results in a lower number of cycles until E_f. The relationship between E_f and temperature is exponential between a temperature range of 200-250°C for most silicone based press pads. E_f can be calculated from **Equation (9)**.

$$E_f = ce^{dT} \qquad \textbf{Equation (9)}$$
Where c and d are constants at a certain pressure, but are functions of pressure.

Utilizing regression analysis to determine c and d in **Equation (9)** versus pressure, **Equation (10)** can be used to calculate press pad E_f at any temperature and pressure.

$$E_f = a_0 e^{b_0 P} e^{(a_1 P + b_1) T}$$ **Equation (10)**

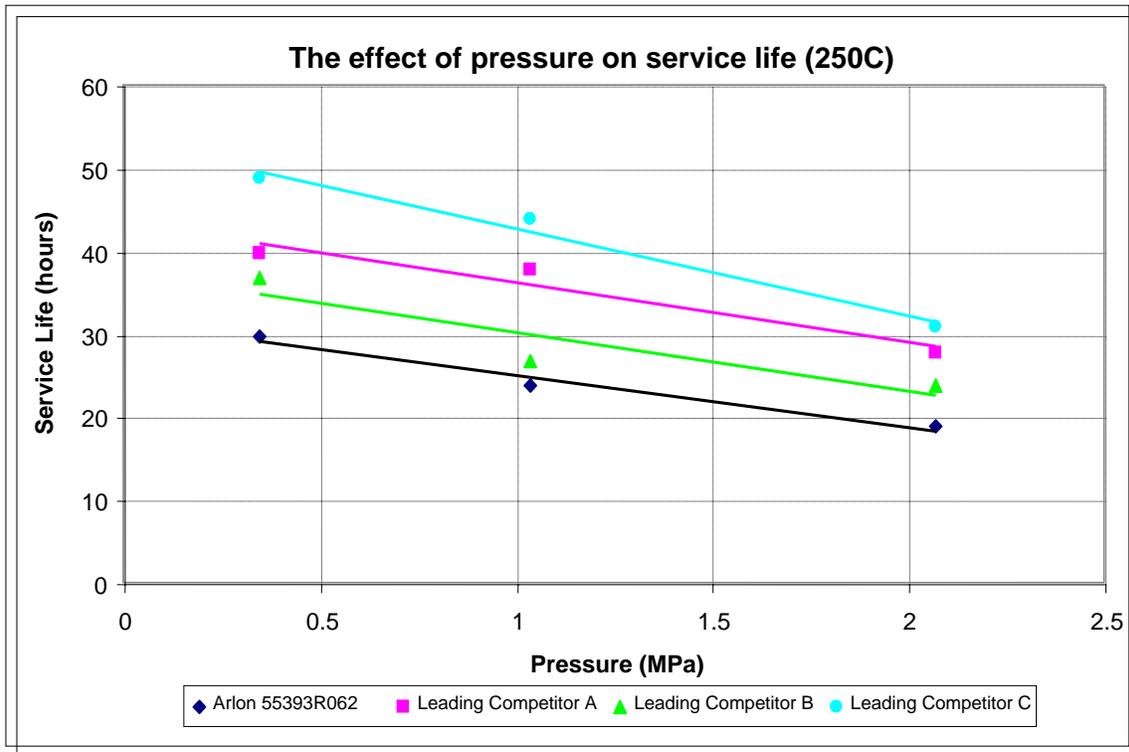Where, a_0, b_0 and a_1, b_1 are constants

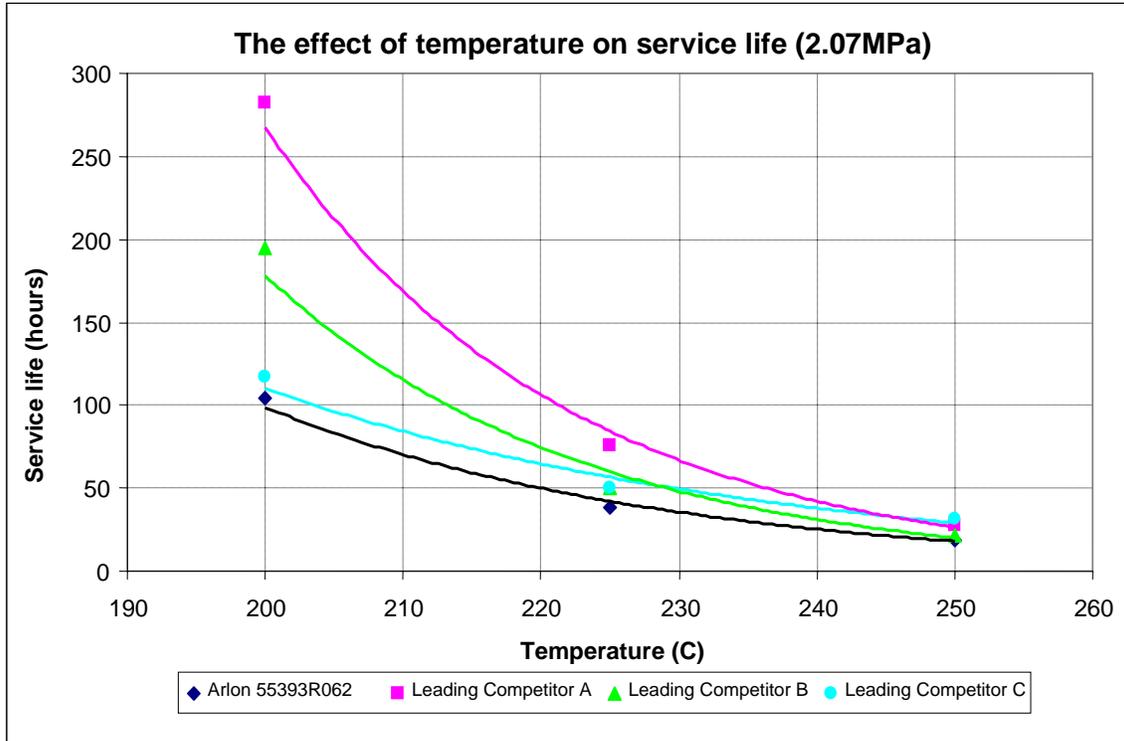**Figure 7 The effect of press pressure on service life**

Figure 8 The effect of temperature on service life

6. Comparison of Arlon's Current Press Pad and Leading Competitors

Press cycling experiments are chosen to compare Arlon's current silicone press pad (55393R062) with Leading Competitive silicone press pads (A, B, and C). Three temperature levels, (200°C, 225°C, 250°C), and three pressure levels (0.35MPa, 1.03MPa, and 2.07MPa) are chosen for this comparative study. Press pad durometer, thickness, and oil loss are measured during cycling.

5.1 Arlon's current product 55393R062

After regression analysis with data from **Table 1**, the E_f for Arlon's 55393R062 press pad is calculated from **Equation (11)** at any application pressure and temperature.

$$E_f = 886179e^{-1.11P}e^{(0.00338P-0.0411)T} \qquad \textbf{Equation (11)}$$

Table 1 Service Life for Arlon press pad 55393R062

Service Life (hours)		Temperature (°C)		
		200 °C	225 °C	250 °C
Pressure (MPa)	0.35MPa	219	71	30
	1.03MPa	158	57	24
	2.07MPa	104	38	19

5.2 Leading Competitor A

After regression analysis with data from **Table 2**, the E_f for Leading Competitor A can be calculated from **Equation (12)** at any application pressure and temperature.

$$E_f = 159319924e^{-2.04P}e^{(0.00716P-0.0605)T}$$

Equation (12)

Table 2 Service Life for Leading Competitor A

Service Life (hours)		Temperature (°C)		
		200 °C	225 °C	250 °C
Pressure (MPa)	0.35MPa	757	189	40
	1.03MPa	503	84	38
	2.07MPa	282	76	28

5.3 Leading Competitor B

After regression analysis with data from **Table 3**, the E_f for Leading Competitor B can be calculated from **Equation (13)** at any application pressure and temperature.

$$E_f = 16197546e^{-1.43P}e^{(0.00449P-0.0520)T}$$

Equation (13)

Table 3 Service Life for Leading Competitor B

Service Life (hours)		Temperature (°C)		
		200 °C	225 °C	250 °C
Pressure (MPa)	0.35MPa	494	108	37
	1.03MPa	256	70	27
	2.07MPa	195	50	22

5.4 Leading Competitor C

After regression analysis with data from **Table 4**, the E_f for Leading Competitor C can be calculated from **Equation (14)** at any application pressure and temperature.

$$E_f = 72997e^{-0.575P}e^{(0.00108P-0.0287)T}$$

Equation (14)

Table 4 Service Life of Leading Competitor C

Service Life (hours)		Temperature (°C)		
		200 °C	225 °C	250 °C
Pressure (MPa)	0.35MPa	204	95	49
	1.03MPa	173	78	44

	2.07MPa	117	50	31

While pressure has a similar effect on different silicone based press pads, different silicone based press pads respond quite differently to changes in application temperature. The E_f of certain silicone based press pads is less sensitive to temperature than others, such as Leading Competitor C. E_f is longer at 250°C than for Leading Competitor A or Leading Competitor B, but very similar to both at 200°C. To summarize:

1) E_f at 250°C: (Leading Competitor C)>(Leading Competitor A)>(Leading Competitor B)>(Arlon 55393R062)
2) E_f at 225°C: (Leading Competitor A)>(Leading Competitor C)>(Leading Competitor B)>(Arlon 55393R062)
3) E_f at 200°C: (Leading Competitor A)>(Leading Competitor B)>(Leading Competitor C)>(Arlon 55393R062)

6. Arlon's UltraPad™ Press Pad

Arlon has developed a family of next generation silicone based press pads. This family of UltraPad™ silicone based press pads are reinforced with a fiberglass fabric. The specific silicone rubber formulations have much improved thermal stability. A proprietary prime coat was designed to bond the newly developed silicone elastomers to the fiberglass with excellent adhesion strength. This excellent adhesion strength prevents silicone rubber from being squeezed out at high application pressure and temperature. Three new silicone elastomers (Durometer of 75, 70, and 65 SAP) have been developed to meet the requirements of a range of press lamination applications.

After regression analysis with data from **Table 5**, the E_f of UltraPad™ D75 can be calculated from **Equation (15)** at any pressure and temperature.

$$E_f = 51928586 \, e^{-0.788P} e^{(0.00217P - 0.0543)T}$$ **Equation (15)**

Table 5 Service Life for UltraPad™ D75

Service Life (hours)		Temperature (°C)		
		200 °C	225 °C	250 °C
Pressure (MPa)	0.35MPa	909	248	61
	1.03MPa	621	196	48
	2.07MPa	502	140	41

After regression analysis with data from **Table 6**, the service life for UltraPad™ D70 can be calculated from **Equation (16)** at any application pressure and temperature.

$$E_f = 59967323 e^{0.043P} e^{(-0.00206P - 0.0538)T}$$ **Equation (16)**

Table 6 Service Life for UltraPad™ D70

Service Life (hours)		Temperature (°C)		
		200 °C	225 °C	250 °C
Pressure (MPa)	0.35MPa	1094	303	71
	1.03MPa	792	251	49
	2.07MPa	568	155	31

After regression analysis with data from **Table 7**, the E_f for UltraPad™ D65 can be calculated from **Equation (17)** at any application pressure and temperature.

$$E_f = 53705920e^{-0.164P}e^{(-0.00151P-0.0531)T}$$ **Equation (17)**

Table 7 Service Life for UltraPad™ D65

Service Life (hours)		Temperature (°C)		
		200 °C	225 °C	250 °C
Pressure (MPa)	0.35MPa	1065	305	72
	1.03MPa	778	263	52
	2.07MPa	470	133	28

Compared to Arlon's current silicone based press pad and the Leading Competitor's commercially available press pads, the family of UltraPad™ press pads has the following key characteristics beneficial to many press lamination applications.

7.1 Greater number of press cycles or greater Service Life

Comparative E_f determination for Arlon 55393R062, Leading Competitor A, Leading Competitor B, Leading Competitor C, UltraPad™ D75, UltraPad™ D70, and UltraPad™ D65 silicone based press pads are shown in **Tables 1-7** respectively. **Figure 9** graphically depicts press pad E_f as a function of temperature at an application pressure of 2.01 MPa. Arlon UltraPad™ silicone press pads will not reach E_f until well after E_f is reached for the Leading Competitor's products and Arlon's current commercial product, 55393R062. At press parameters of 250°C and 2.07 MPa, E_f for Arlon's best UltraPad™, D75, is 32% longer than that of the best Leading Competitor's product (C). At press parameters of 225°C and 2.07 MPa, E_f for Arlon's best UltraPad™, D70, is 104% longer than that of the best Leading Competitor's product (A). At press parameters of 200°C and 2.07 MPa, E_f of Arlon's best UltraPad™, D70, is 101% longer than that of the best Leading Competitor's product (A). Greater press cycles to press pad E_f results in a potentially lower cost per press cycle of a specific press pad within a PCB application.

7.2 Lower cost per press cycle (hours)

A silicone based press pad with higher material price does not necessarily translate into higher cost. Cost per press cycle hour for a press pad in a PCB lamination application is a better method for determining the true cost of press pad utilization. Arlon UltraPad™ is likely to have lower cost per hour due to longer service life than Leading Competitive products.

7.3 Predictable Service Life, E_f

E_f for all UltraPad™ press pads in this study at any lamination application pressure and temperature can be calculated by **Equation (15)-(17)**. These results were determined empirically at Arlon and may not be completely consistent with all real world applications. In the real world of PCB manufacturing, process temperature ramp rates may not be consistent. So the best method to determine E_f is to measure press pad durometer and thickness after a predetermined number lamination cycles. Then the criteria for E_f in section 4 are utilized:

1) Durometer>85 SAP
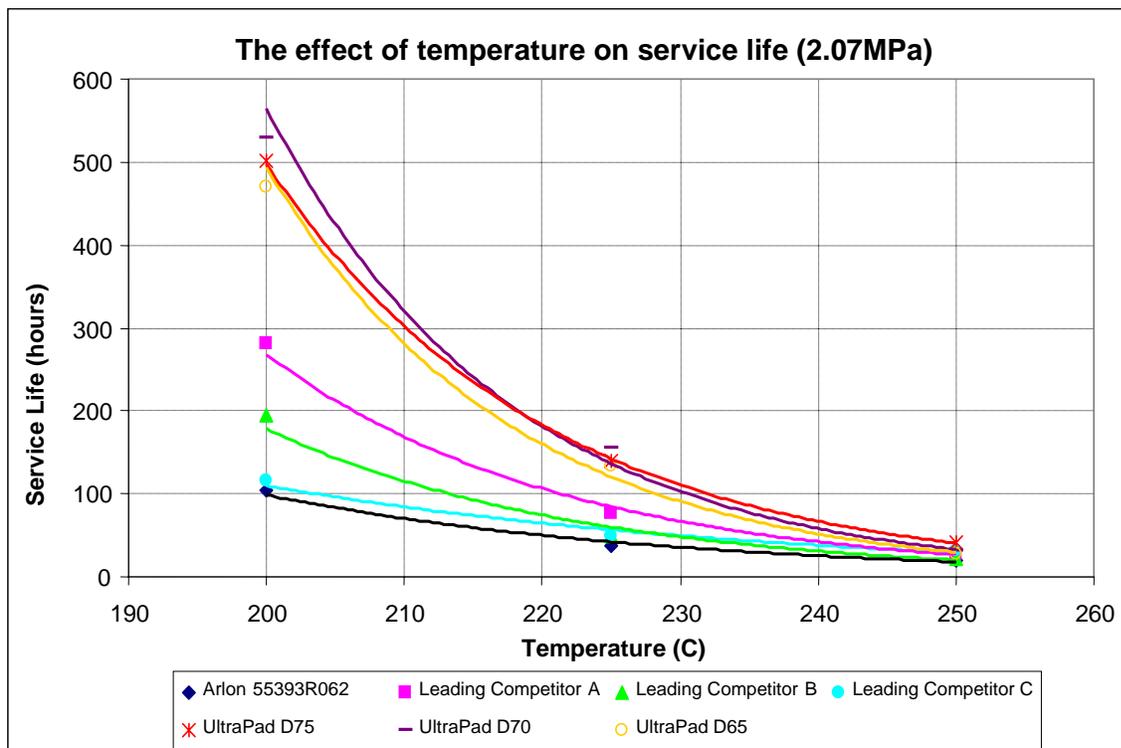2) Relative pressure uniformity (U_p/U_{p0})<50% from **Equation (7)**

Figure 9 The effect of temperature on service life at 2.07MPa

7.4 Better pressure uniformity

Better pressure uniformity ensures higher quality PCB lamination. Arlon's UltraPad™ press pads have lower durometer than both the Leading Competitor products and Arlon's current product, as shown in **Table 8**. Each press pad also has the same initial thickness. Assuming an application pressure of 2.07MPa, initial pressure uniformity is calculated by **Equation (6)**. Arlon UltraPad™ press pads have better (except when comparing D75 to A) pressure uniformity than Leading Competitor products and Arlon's current product.

Table 8 Initial pressure uniformity (2.07MPa)

Properties	UltraPad™ press pads			Current Press pads			
	D75	D70	D65	Arlon 55393R062	Leading Competitor A	Leading Competitor B	Leading Competitor C
Initial durometer	75	70	65	79	75	77	80
Initial thickness (mm)	1.58	1.58	1.58	1.58	1.58	1.58	1.58
U_p (mm)	0.47	0.60	0.75	0.39	0.47	0.43	0.38

7.5 More consistent pressure uniformity

Since silicone based press pads are used for many cycles and cycle durations, consistent pressure uniformity from cycle to cycle is important for consistent PCB lamination quality. Silicone based press pad durometer and thickness determine pressure uniformity. Arlon's UltraPad™ press pads have much slower thickness reduction during press cycling than Leading Competitor products and Arlon's current product, as shown in **Figure 10**. The durometer change of Arlon's UltraPad™ press pads also remain consistent during press cycling compared to Leading Competitor products and Arlon's current product, as shown in **Figure 11**. Consequently, the UltraPad™ press pad family has more consistent pressure uniformity from cycle to cycle than Leading Competitor products and Arlon's current product, as shown in **Figure 12**. The result at only 225°C*2.07MPa is shown in this paper, although the results at (200°C, 225°C, 250°C) and (0.345MPa, 1.03MPa, 2.07MPa) were determined. All results show that Arlon UltraPad™ press pads have more consistent pressure uniformity from cycle to cycle.
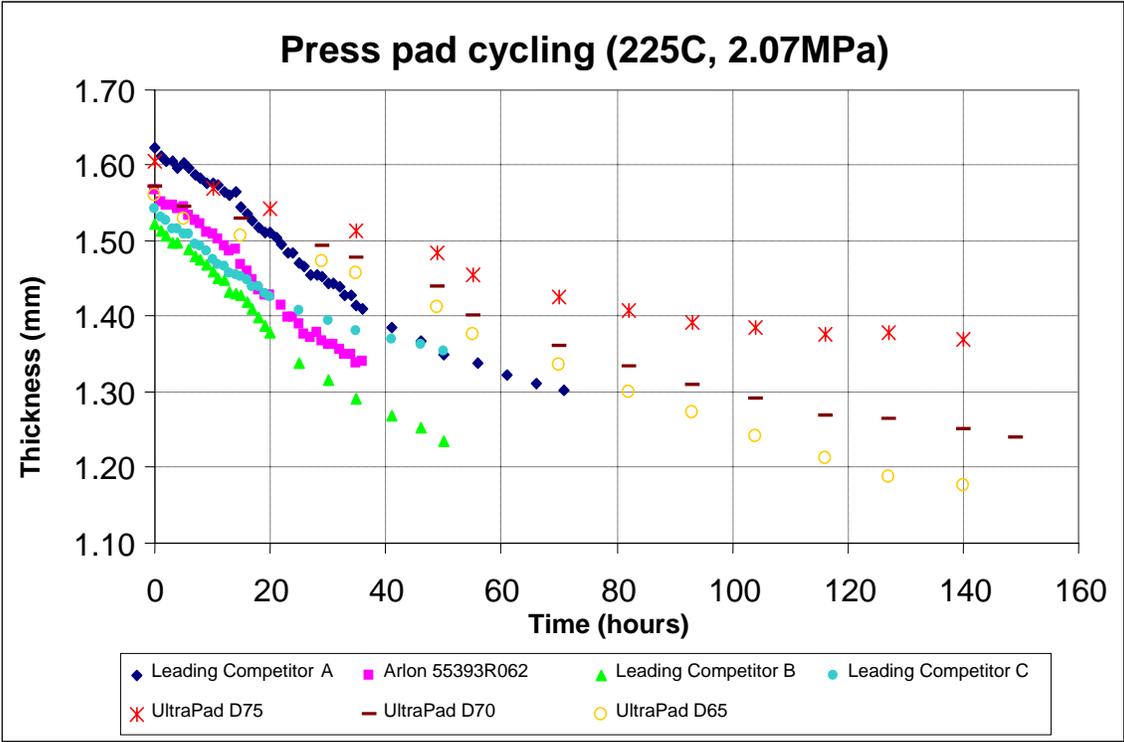

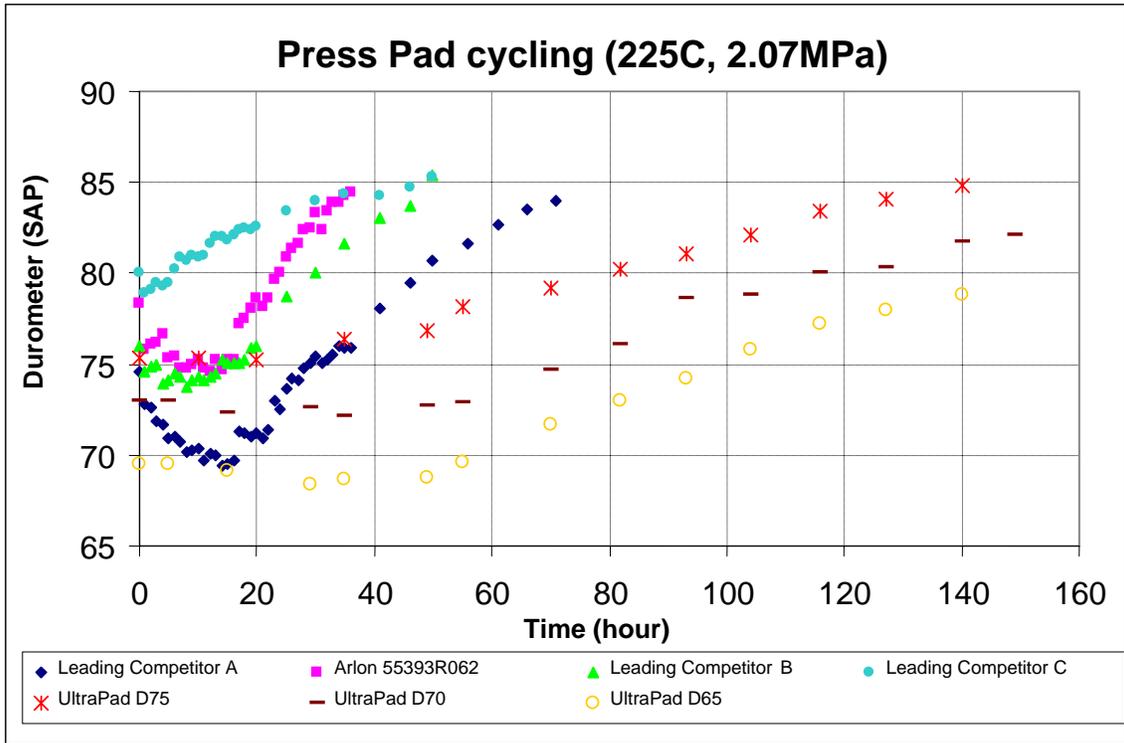**Figure 10 Thickness change during cycling for different press pads at 225°C*2.07MPa**

Figure 11 Durometer change during cycling for different press pads at 225°C*2.07MPa
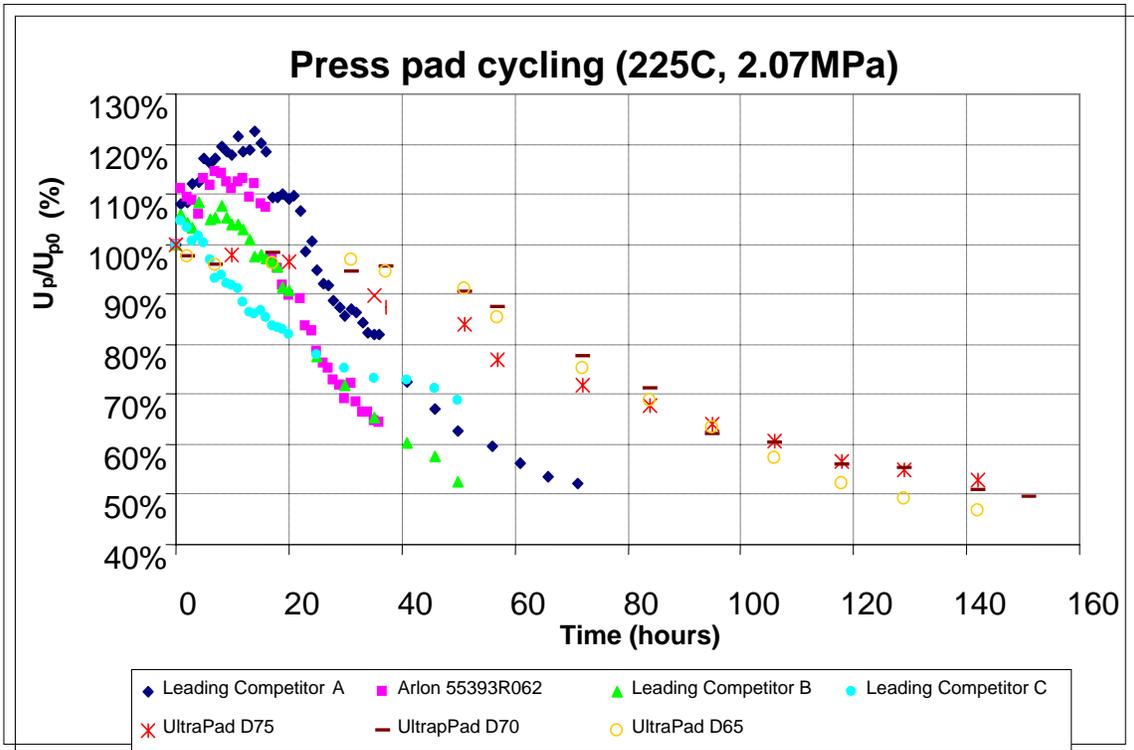

Figure 12 Relative pressure uniformity change during cycling for different press pads at 225°C*2.07MPa

8. Summary

Press pad durometer and thickness are used to calculate lamination application pressure uniformity. Pressure sensitive paper confirms the accuracy of the calculation. The pressure uniformity calculation is helpful for press pad design and service life determination. The calculation can replace expensive pressure sensitive paper to verify press pad effectiveness in an actual application. Arlon's UltraPad™ silicone based press pads have been developed to yield a longer service life, lower cost per press cycle, predictable service life, better application pressure uniformity, and more consistent pressure uniformity than Leading Competitor products and Arlon's current product.

9. References

1. E. L. Warrick, O.R. Pierce, K. E. Polmanteer, and J. C. Saam, <u>Rubber Chemistry and Technology</u>, **52**, 437(1979).
2. J.E. Mark; Ed., "Polymer Data Handbook", Oxford University Press, Oxford, 1999
3. P.R. Dvornic, "Thermal Properties of Polysiloxanes", in "Silicon-containing Polymers", Jones, R.G.; Ando, W.; Chojnoski, J., Eds., Kluwer Academic Publishers, Dordrecht, the Netherlands, 2000, pp. 185-212.
4. C. Woerner, R. Birneder, "Silicone Composition Having Improved Heat Stability", US Patent: 2003/0187131 A1 (2003)
5. F. Achenbach, W. Hechtl, N. Egerter, S. Schreyer,"Porphyrin-containing Silicones Having Increased Thermal Stability", US Patent: 5,847,034 (1998)
6. R. Zhang, A.R. Pinhas, J.E. Mark, "Synthesis of Poly (tetramethyl-m-silphenylenesiloxane), An Elastomer of Enhanced High Temperature Stability", Macromolecules, 30, 2513-2515 (1997)
7. S.P. Sun, S.P. Murarka, "Thermal Stability of Polyimidesiloxane (SIM-2000)", J.Vac. Sci. Technol., B6(6), 1763-1767 (1988)
8. P.R. Dvornic, R.W. Lenz, "Exactly Alternating Silarylene-siloxane Polymers. 6. Thermal Stability and Degradation Behavior", Polymer, 24, 763-768 (1983)
9. U. Lauter, S.W. Kantor, K. Schmidt-Rohr, W.J. MacKnight, "Vinyl-substituted Silphenylene Siloxane Copolymer: Novel High-temperature Elastomers", Macromolecules, 32, 3426-3431 (1999)
10. H.D. Zhu, S.W. Kantor, W.J. MacKnight, "Thermally Stable Silphenylene Vinyl Siloxane Elastomers and Their Blends", Macromolecules, 31, 850-856 (1998)
11. A.A. Berlin, R.M. Aseeva, S.M. Mezhikovsky, et. al., "Methods for Increasing the Thermostability of Organopolysiloxanes", US Patent: 3,928,489 (1975)
12. D.F. Merrill, "Silicone Resins Having Good Thermal Stability", US Patent: 4,085,084 (1978)
13. T.J. Swihart, J.E. Jones, "Polydimethylsiloxane Having Improved Thermal Stability", US Patent: 4,528, 313 (1985)
14. S.B. Lin, "Pressure Sensitive Adhesives", European Patent: 0 576 164 A2 (1993)
15. Y. Peng, Z. Su, J. Liu, et. al., "Effect of Fe_2O_3 on Thermal Stability of High Temperature Vulcanized (HTV) Silicone Rubber", Youjigui Cailai, 19, 14-16 (2005)

16. F. Achenbach, H. Barthel, "Crosslinked Silicone Rubber Composition with Enhanced Thermal Stability Containing Palladium-based Heat Stabilizers", European Patent: 668 325 A1 (1995)

17. J. Meyer, M. Scholz, D. Kerner, "Pyrogenic Titanium Dioxide as Additive for Improving the Thermal Stability of Silicone Rubber", German Patent: 10059002 A1 (2002)

18. G.B. Sohoni, J.E. Mark, "Thermal Stability of In Situ Filled Siloxane Elastomers", Journal of Applied Polymer Science, 45, 1763-1775 (1992)

19. M.J. Dams, M.C. Murray, "Silicone Rubber-Improvements in Heat Resistance", Kautschuk Gmmi Kunststoffe, 34, 15-18 (1981)

20. M.C. Murray, "Improved Heat-aging Stability for Silicone Rubber Wire and Cable Insulation", Elastomerics, 113, 58-62 (1981)

21. H.V. Newton, "Stabilized Heat Curable Silicone Elastomers", US Patent: 4265800 (1981)

22. M. Hamada, H. Koyanagi, Y. Adachi, "Poly(siloxane) of Improved Mechanical and Thermal Stability", Japan Kokai Tokkyo Koho: 48032200 (1973)

23. F. Kay, "The Thermal Stability of Phenyl Containing Silicone Rubbers", U.S. Govt, res. Develop. Rep., 69, 137 (1969)

24. L.G. Hanu, G.P. Simon, Y.B. Cheng, "Thermal Stability and Flammability of Silicone Polymer Composites", Polymer Degradation and Stability, 91, 1373-1379 (2006)

25. Y. Kubota, N. Fujisawa, "Heat Stabilizer for Silicone Rubber", Japan Kokai Tokkyo Koho: 49033950 (1974)

26. Y.A. Aleksandrova, J.S. Nikitina, A.N. Pravednikov, Vysokomol. Soedin., Ser. A. **10**, 1078 (1968)

27. V.V. Rode, V.A. Verkhotin, S.R. Rafikov, Vysokomol. Soedin., Ser. A. 11, 1529 (1969)

28. T.H. Thomas, T.C. Kendrick, J. Polym. Sci. Part A-2, 7, 537 (1969)

29. N. Grassie, I.G. Macfarlane, Euro. Polym. J., 14, 875 (1978)

30. K.A. Andrianov, Metalorganic Polymers, Interscience, New York, p. 50 (1965)

31. A.N. Gent, "On the Relation between Indentation Hardness and Youbg's Modulus", Transactions of the Institute of the Rubber Industry, 34, No.2 (1958)

32. D.L. Hertz, A.C. Fairnella, "Shore A Durometer and Engineering Properties", presented at the Fall Technical Meeting of The New York Rubber Group (1998)