

ICMIEE-PI-160202

Bond Strengths Analysis of Polyurethane and Polychloroprene Adhesives for Different Upper and Soling Materials

Muhammad Naimul Hasan*, Md. Imrul Kayes Limon, Md. Samsul Arefin, Md. Zahid Hasan

Department of Leather Engineering, Khulna University of Engineering & Technology, Khulna-9203, BANGLADESH

ABSTRACT

The modern footwear technology involves a widespread use of adhesives, major exceptions being the sewing of uppers and in some cases, the attachment of heels with nails. In this study, four different uppers, three types of soles and two solvent-borne adhesives are used for assembling twelve types of upper-sole combination and corresponding bond strengths were determined based on peel test following SATRA Adhesive Test Method AM2. The purpose of this work is to provide a clear guideline for selecting adherends, adhesives regarding application methodology, surface preparation for required bond strength in between upper-to-sole for footwear construction. Most of the obtained peel test results ≥ 3 N/mm which was quite noteworthy for everyday footwear. This paper also addresses the root causes of bond failure of upper-to-sole joint in footwear fabrication which was hardly ever attempted before.

Keywords: Adhesive, bond strength, footwear, peel test.

1. Introduction

Although outwardly, other than to meet the demands of fashion, footwear design does not appear to have changed completely over the last century, the techniques used in the fabrication of shoes have undergone revolutionary changes. These changes have resulted in a right choice of adherend-adhesive for durable footwear construction.

The introduction of adhesives in shoe making provides shoemakers with the opportunity to make a neat and continuous attachment of sole to upper without puncturing the materials being bonded. In sole bonding the adhesives used are almost solvent-borne type [1]. In the early 1950s, polychloroprene adhesive and synthetic rubber soles were developed. The next 15 years saw the introduction of isocyanate solutions to improve adhesion and the first SATRA primer, Lacsol to remove contaminants especially metallic soaps (e.g. zinc stearate) from the surface of the elastomers. At the same time, PVC also used as soling materials. By the 1970s, PU was firmly established as the preferred adhesive in the footwear industry. During the same time, nylon and ethylene-vinyl acetate (EVA) were introduced as soling materials [2]. Nowadays, the footwear industry has a close association to the adhesives industry, using bonding techniques to join the variety of materials employed in the fabrication of shoes [3]. At present, a wide range of materials used in shoe manufacturing including various types of natural and synthetic leathers, plastic materials, synthetic fabrics as uppers, different soling materials and various adhesives for joining upper and sole. Despite the advances made in adhesive bonded structure in footwear industry, problems are still encountered in bonding upper-sole joint due to large diversity of the materials. This paper addresses the factors which influence the bond-ability of different adhesives for different upper-to-sole combination. For the manufacture of an adhesive joint, one must take into account the materials which are

intended to be joined, using this to identify the most appropriate type of adhesive and surface treatments, enabling the maximization of joint resistance and durability through the adhesive joint design, as well as technical requirements for such joints [3-5]. In this work we used four different uppers- crust leather, denim, corrected grain leather, synthetic leather and three soles-polyurethane (PU), thermoplastic rubber (TPR) and leather soles. For upper-to-sole combination two types of solvent-borne adhesives-polyurethane (PU) and polychloroprene (PCP) are selected as joining materials. Here different upper-to-sole combination is joined with those adhesives and after conditioning bond strengths are determined.

Bond strengths are judged by peel test (SATRA adhesion test method AM2) to show a comparison and to analyze the different adhesion strength between upper and soling materials combination. The main objective of this study is to find out a suitable adhesive application method, proper surface treatment, adherend-adhesive specificity for the required bond strength of footwear fabrication.

2. Materials and Method

2.1 Materials

The samples (upper and sole) used in this investigation are very common in shoe-manufacturing and are varied in physical properties regarding various parameters as thickness, density, compressibility and absorbency. The materials are collected from a renowned footwear industry and brought back to the laboratory to carry out related test. Triplet test was done for each upper-to-sole combination. Adhesives category is also a fact indeed. The adhesives used in this work were solvent-based polyurethane and polychloroprene and these two adhesives were also collected from the industry. The adhesives met the international grade in case of quality and act. The materials used in this experiment are detailed in Table 1, 2, 3.

* Corresponding author. Tel.: +88-01721505564
E-mail address: namhasan@gmail.com

Table 1 Soling materials description.

Soling	Color	Thickness (mm)	Density (g/cm^3)
Leather	Brown	4.5	1.5
TPR	Black	3.3	1.3
PU	White	5.9	1.2

Table 2 Upper materials description.

Upper	Color	Thickness (mm)	Yarn count/cm Warp Weft	
Crust leather	Brown	1.5		
Synthetic (PVC coated)	Black	1.1		
Corrected grain leather	Black	1.5		
Denim	Blue	1.0	26	26

Table 3 Adhesives description.

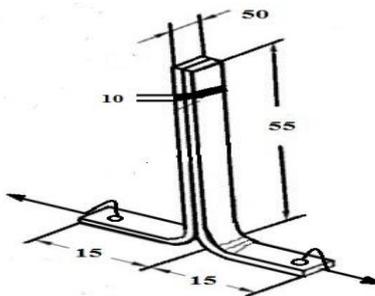
Physical/chemical properties	PU	PCP
Appearance	Creamy white liquid	light yellow liquid
Base	Polyurethane	Polychloro-prene
Diluents	Solvent	Solvent
Solid content (%)	40	60
Viscosity (mPa.s)	4000	750
Specific gravity	1.05	1.23
Flammability	Flammable	Flammable
Density (g/mL)	0.87	0.94

2.2 Test apparatus

The instrumentation used to measure the bond strengths was a tensile tester machine (model no: STM 172, SATRA, UK).

2.3 Methodology

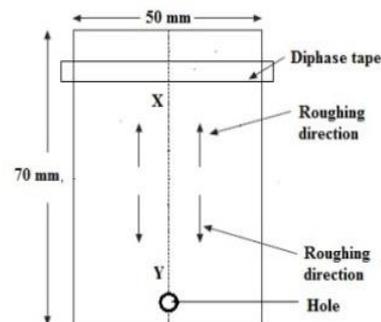
The bond strengths were determined followed by SATRA adhesion test method AM2. Tensile Testing machine (SATRA, UK) was used to measure the peel force. The sample clamping method is showed in Fig. 1.

**Fig. 1** Clamping of a test piece.

2.3.1 Specimen preparation for the peel test

A rectangle of 70 x 50 mm was cut from the tightness direction of upper material and a similar one was cut from soling material. A hole with a 2.5 mm diameter was done on upper and sole maintaining 15 mm distance from the edge at one end. The same procedure followed in preparing all the samples shown in Fig.2. Among the three soling materials – PU and Leather soles were sufficiently scoured and TPR sole was lightly scoured. In case of upper materials, corrected grain and crust leather were also scoured, PVC coated synthetic and denim were lightly scoured. An 80 grit emery paper was used for hand scouring from the centre line XY direction, shown in Fig.2. A dust- removing brush was used for removing all loose materials from the specimen surface. For PU sole, surface was wiped by MEK and in case of TPR, surface was halogenated. On the other hand, PVC synthetic and denim fabric were simply wiped by acetone for better adhesion. The samples were warmed near 2Kwt heater before applying the adhesives in order to speed up the drying time and to obtain better penetration of adhesives. The drying time considered for the solvent-borne PU and PCP adhesives were 20 seconds and 40 minutes respectively.

After drying, a strip of 10 mm diphasic tape was applied on the top of the upper-sole combination keeping 10 mm distance from the top edge in width direction as shown in Fig.2. For PU adhesive on soling, activation temperature was maintained as of 79 °C. Wax-crayon was used as an activation temperature indicator. After that the upper and sole was attached and given required pressured by rectangular wooden block and hammer as heavy to give vital pressure. Bond thickness was typically about 0.125 mm and was assumed to be the same for all specimens. The joints were left to dry in room temperature for about 72 h to reach full bond strength.

**Fig. 2** Preparation of sample for the peel test.

2.3.2 Determination of the peel strength

The adhesive bond strength or peel test is carried out to assess the strength of a bond by measuring how much force is required to peel apart the bonded materials. The bonded specimens were trimmed to 29 mm wide at an angle of 180° was measured on a tensile testing machine using a crosshead speed of 50 mm/min. The tested samples were judged against the standard set by

SATRA. Failure can occur at any one point of the possible sites, as shown in Fig. 3(a) and 3(b).

$$\text{Bond strength (N/mm)} = \frac{\text{Mean peel force (N)}}{\text{Sample width (mm)}}$$

The force range was measured from the dial of the tensile tester and the % extension was determined from the scale attached with the body of the machine for different upper-to-sole combination. Mean peel force was determined from force / % extension graph shown in Fig. 4(a) and 4(b). For each combination minimum three joints tested and average value was taken. The peel strengths, measured after allowing the adhesive to cure at 27⁰ C temperature.

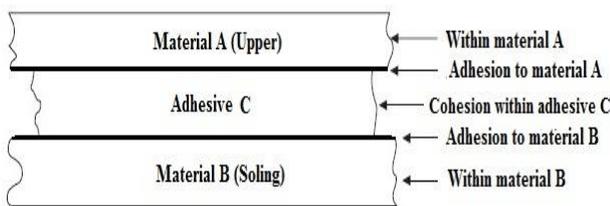


Fig. 3(a) Five possible sites of failure in a typical bonding chain. (From D. Roy, R. Chen & P. Callaghan; 2005).

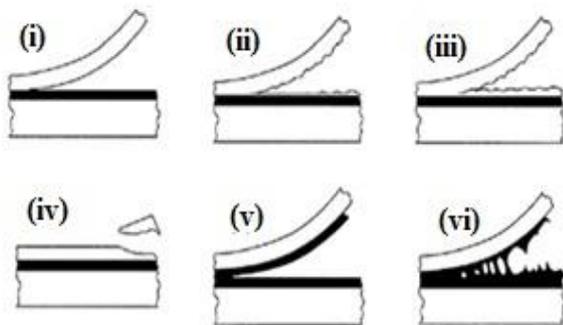


Fig. 3(b) Different types of failure of adherend. (i) Adhesion failure, (ii) Surface failure, (iii) Deep failure, (iv) Tearing upper, (v) No-coalescence of adhesive film, (vi) Cohesive failure

3. Results and discussion

3.1 Bond strengths

Bond strengths are determined from mean peel force which are attained from force/deformation graph shown in Fig. 4(a) and Fig. 4(b) respectively. Here, % of extension (cm) is fixed on a range and the corresponding peel forces are different for different samples. Bond strengths are judged against international standard. The obtained mean bond strengths for the twelve samples are shown in Table 4. Standard deviations also calculated from mean bond strength from which a range could be easily identified. These standard deviations are shown in Table 4 along with the value of bond strengths so that the maximum and minimum value might be observed, and the reference

values are given in a separate Table 5. The obtained values of bond strengths are examined based on European norms EN 15307.

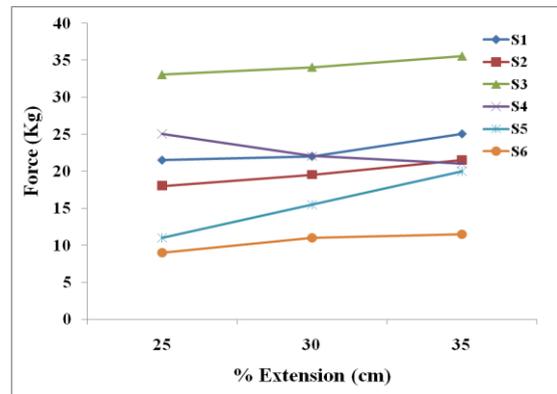


Fig. 4(a) Representation of a typical Force/ % extension graph for peel force determination of sample S1-S6.

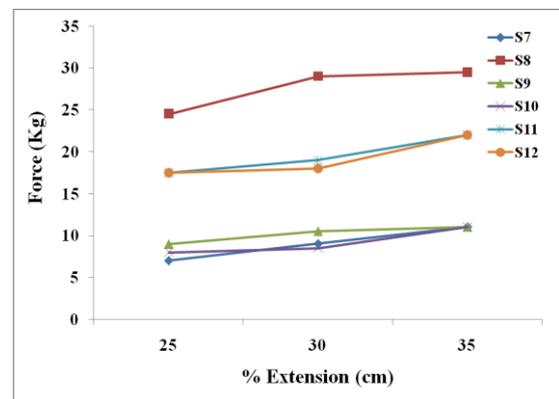


Fig. 4(b) Representation of a typical Force/ % extension graph for peel force determination of sample S7-S12.

Table 4 Bond strengths of adhesives joined samples

Sample ID	Materials	MPF (N)	BS (N/mm)
S1	CL - PCP - LS	223.56	4.47 ± 0.30
S2	CL - PU - LS	192.52	3.85 ± 0.28
S3	CGL - PCP - LS	334.83	6.70 ± 0.20
S4	CGL - PU - LS	225.4	4.50 ± 0.51
S5	D - PCP - LS	151.9	3.03 ± 0.72
S6	D - PCP - PUS	102.9	2.05 ± 0.21
S7	D - PU - TPRS	88.2	1.80 ± 0.32
S8	CL - PU - TPRS	271.13	5.42 ± 0.14
S9	CL - PCP - TPRS	99.63	1.99 ± 0.16
S10	PCS - PCP - PUS	89.83	1.79 ± 0.25
S11	PCS - PU - LS	191.1	3.82 ± 0.36
S12	PCS - PU - TPRS	187.8	3.76 ± 0.43

From Fig 4(a) and 4(b), it is clear that for sample (S3) the slope of the line is less inclined than that of the others samples and hence has the highest bond strength whereas for sample (S10) the phenomenon is totally

opposite and provided a lower value which is below standard shown in Table 5 and Fig. 4(b).

Table 5 Reference values of adhesion of upper-to-sole, according to European standard EN 15307.

Shoes (Upper-to-sole joint)	Peel strength per unit width (N/mm)
Infant	≥ 2.5 With material failure.
Men or Women (casual footwear)	≥ 3.0 or ≥ 2.5 with material failure.
Children	≥ 4.0 or ≥ 3.0 with material failure.
Mountain	≥ 5.0 or ≥ 3.5 with material failure.

3.2 Comparison of bond strengths

The peel strengths for specimen of twelve different upper-to-sole joints bonded with adhesives are presented in Table 4 and a comparison has shown in Fig. 5. From Table 4 and Fig. 5 it is evident that different joints have different bond strengths, these different performances indicated that the method of soles and uppers preparations also different. For TPR, the halogenation was done by iodine solution whereas PU was wiped with MEK.

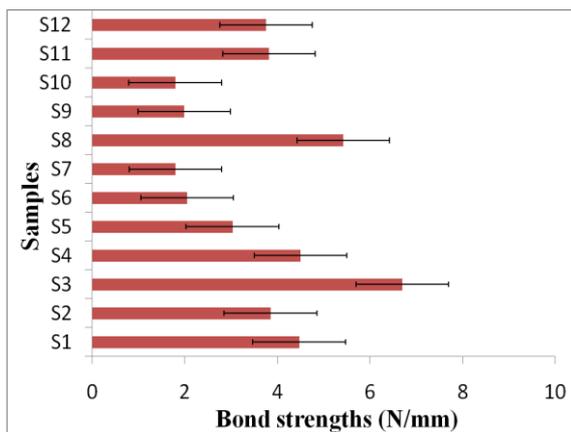


Fig. 5 Comparison of bond strengths of different upper-to-sole joints.

The obtained peel test results for sample S1 to S5, S8, S11 and S12 quite significant but samples S6, S7, S9 and S10 gave very poor or inconsistent results shown in Fig.5. In the case of corrected grain leather - PCL adhesive - leather sole (S3), partly tear surface of upper attached with the sole was noticed and gave a appreciably higher value 6.7 N/mm and that was an indication of material failure of adherend and represented extensively a strong bond. This joint is highly recommended for mountain footwear. This is also factual for sample S1, S5 and S8 shown in Fig. 3 (b) & Fig. 5. However, test results for samples S6, S7, S9 and S10 show poor adhesion of upper-to-sole combination and here, separation or breakdown of adhesive film at the surface was noticed shown in Fig. 3(b). Again, poor performances are notified in case of

TPR, PU soles. This may for inadequate roughing, poor surface preparation and inappropriate drying time.

It is concluded that a few bond strengths were limited due to materials incompatibility and overall bond strengths obtained in this work are adequate for everyday footwear.

4. Conclusion

In this paper, the adhesion test of solvent-borne polyurethane and polychloroprene adhesive for different uppers and soles joining are examined. Here, it is clear that most of the upper-to-sole joints gained sufficient bond strengths for footwear bonding but a few provided with poor performances which may have influenced by any of the reasons like incompatibility of adhesive with the materials, improper halogenations, cohesively weak layers of the materials or inadequate roughing. Therefore, results of this study can only be used as an instruction in choosing the right adhesive for various uppers against different soles for manufacturing footwear but these preliminary findings require further research and tests with a wide range of uppers, soling materials as well as adhesives considering different parameters like drying time, quantity of adhesive, environmental factors in order to reach more precise results.

Nomenclature

- MPF : Mean Peel Force
- BS : Bond Strength
- CL : Crust Leather
- CGL : Corrected Grain Leather
- D : Denim
- LS : Leather Sole
- TPR : Thermoplastic rubber
- PU : Polyurethane
- PCP : Polychloroprene
- PVC : Polyvinylchloride
- TPRS : Thermoplastics rubber Sole
- PUS : Polyurethane Sole
- PCS : PVC Coated Synthetics

References

- [1] D. Roy, R. Chen, P. Callaghan, Study of bond strengths of a water-borne polyurethane (PU) adhesive for shoe-soling materials, *The Journal of The Textile Institute*, Vol. 96, pp 17-20 (2010).
- [2] S. G. Abbott, D. M. Brewis, NE. Manley, I. Mathieson, N. E. Oliver, Solvent-free bonding of shoe-soling materials, *International Journal of Adhesion & Adhesives*, Vol. 23, pp 225-230 (2003).
- [3] R. M. M. Paiva, E. A. S. Marques, L. F. M. da Silva, C. A. C. Antonio, F. Aran-Ais, *Journal of Materials: Design and Applications*, Vol. 0(0), pp 1-18 (2015).
- [4] E. M. Petrie, The role of adhesives in the shoe industry, www.specialchem.com, 2007, (accessed 2016).
- [5] M. M. Pastor-Blas, J. M. Martin-Martinez, F. J. Boerio, Influence of chlorinating solution

concentration on the interactions produced between chlorinated thermoplastic rubber and polyurethane adhesive at the interface, *The Journal of Adhesion*, Vol. 78, pp 39-77 (2001).

- [6] E. Markovic, B. Glisic, I. Scepan, D. Markovic, V. Jokanovic, Bond Strength of Orthodontic Adhesives, *Journal of Metallurgy*, Vol. (14), pp 79-88 (2011).
- [7] D. Oldfield, TEF. Symes, Surface Modification of Elastomers for Bonding, *The Journal of Adhesion*, Vol. 16, pp 77-95 (2006).
- [8] D. Yang, L. Han, H. Zhang, Polyurethane solvent-based adhesives for footwear applications, *The Journal of Adhesion*, Vol. 68, pp 21-29, (1998).
- [9] C. Saikumar, Adhesives in the leather industry, perspectives for changing needs, *Journal of Adhesion Science and Technology*, Vol. 16, pp 543-563, (2002).
- [10] SATRA Adhesion Test Method AM2.
- [11] M. M. Pastor-Bias, R. Torregrosa-Macia, J. M. Martin-Martinez, J. G. Dillard, Failure analysis of treated unvulcanized SBS rubber/polyurethane adhesive joints, *International Journal of Adhesion & Adhesives*, Vol. 17, pp 133-141, (1997).