

# Development and Aging Behaviour of Solvent-Based Polychloroprene Rubber Nano-Adhesive Using Multiwall Carbon Nanotubes

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## Abstract

Polychloroprene (PC) based contact adhesives are widely used in various applications; however, there is a possibility to improve the properties of PC adhesive. Modifications of polymers can enhance the properties of the material, e.g. increase in thermal stability, compatibility, rigidity, physical response, flexibility and improve the polymer process ability. In the current study, improved formulation of solvent-based adhesive was developed, and the properties were further enhanced by the addition of nano-reinforcement of multiwall carbon nanotubes (MWCNTs). The addition of nano-reinforcement was optimized to obtain improvement in the bond strength and also to enhance its resistance at a high temperature ( $\sim 100^{\circ}\text{C}$ ). This paper discusses the uniform dispersion of MWCNTs during the synthesis of polychloroprene solvent-based adhesive, thereby improving its structural properties. Incorporation of MWCNTs-solvent-based adhesives resulted in a 20% - 35% improvement in  $180^{\circ}$  peel strength determined on flexible substrates such as canvas, leather. The reinforced based adhesive also exhibited improved thermal stability and weather resistance compared with unreinforced adhesive. The MWCNTs-solvent-based contact adhesives is a potential candidate in an industrially relevant branch of adhesives commonly used in structural applications, e.g., footwear, plastic, leather, automobile, construction industries, etc.

## Keywords

Nanocomposite, Polychloroprene, Adhesive, Peel Strength, Carbon Nanotubes

## 1. Introduction

The phenomenon of transferring loads from adherend to adhesive joint is known as adhesion [1]. Mechanical properties of polymer control the interfacial forces necessary for good adhesion. Sustaining sufficient stresses at the interface is the basis for high adhesion [2]. There is always intermolecular diffusion taking place between the surfaces joined together by contact adhesives. In any interfusion process, the organic liquid evaporates, thus forming a strong bond between the layers; the bonding starts to take place when two properly layered bonding surfaces are brought closer. Several major parameters play a pivotal role in the auto adhesion to take place. The polymer or binding material must have diffusive properties. Diffusive property of binding material depends on solvent and the polymer used. There are only selective polymers which exhibit excellent auto adhesion properties. Intimate and close contact of the substrate is compulsory for the highest diffusion. Elastic stress and rheology of composition affect the quality of bond strength. When the adhesive is coated correctly on the material and dried in a lap of time under ambient conditions, this time is called open time. Adhesive layer alters all the physical properties in the open time due to evaporation of the solvent, interfacing of polymers, the base of polymer changes and crystallization of binding polymers [3]. When the open time has been passed, auto adhesion or good adhesive properties of the surfaces can't be achieved.

### 1.1. Properties of Contact Adhesive

Contact adhesives are used because of their excellent mechanical properties, high strength, fast setting time, easy applicability and durability [4]. It can be used as solvent-based as well as water-based depending upon the type of application. In solvent-based technology, the solvent evaporates very quickly from the surface, and very high bond strength is observed, which increases with time [5]. Some of the properties which affect the strength and its performance are viscosity [6], storage life [7] [8], working life, tack time [9] [10], acid acceptance [11], surface free energy and wettability [12] [13], etc. Resins are added in contact adhesives formulations to modify viscosity, tack time and strength of adhesive. Resins act as tackifying agent in adhesives. They are available in various colors ranging from transparent to brown. They are soluble in aliphatic, aromatic and organic compounds.

Phenolic resins are widely used in adhesive formulation; however, many alternatives are now being developed. Modified resins are also used in the adhesive formulation. Tack time is decreased when the resin amount is increased from 80 phr (parts per hundred) to 85 phr [9]. Solvent-based adhesives are commonly used in packing, automotive, construction, footwear and furniture industries. However, due to safety and environmental issues, chlorinated solvents are banned. Solvents are selected depending on the drying rate and retention time [14]. Contact adhesives have excellent thermal and electric insulation. They can

withstand the temperature of about 130°C. Uniform stress distribution and lightweight structures can be built by using contact adhesives [3] [15]. Water-based contact adhesives are gradually replacing solvent-based adhesives, however, they require excessive time to dry, which restrict their applicability [16] [17].

Adhesive bonding is a result of various physio-chemical interactions taking place between materials to be joined and the adhesive. So, adhesive bonding needs some understanding of these processes taking place on the surface of materials [17]. Various theories describing adhesion mechanisms are mechanical interlocking, electrostatic adhesion, diffusion, and surface reaction. However, it is challenging to associate adhesive bonding with a particular theory. Adhesive bonding is the result of the combination of these mechanisms, but the role of each mechanism changes for various adhesive systems [18]. An essential factor in adhesive bonding is the scale at which adhesive and adherend interaction takes place. **Table 1** shows a rough range of action of a particular mechanism [8]. Mechanisms of various theories have been explained at numerous references, e.g., a mechanical method [19], ways to improve mechanical bonding [20]; electrostatic theory [21]; weak boundary layer [22]; diffusion theory [23]; adsorption theory [24] etc.

## 1.2. Polychloroprene Rubber-Based Adhesives

One of the most critical applications in which Neoprene® adhesive finds its place is in shoe industry, for both permanent and temporary sole bonding. However, the early neoprene cement had two problems: 1) discoloration when stored in steel drums and 2) decrease in viscosity when stored for a more extended period [25]. The discoloration was due to the formation of hydrochloric acid formed by oxidation of Neoprene on ageing. Magnesium oxide and zinc oxide were added in small quantity to prevent the discoloration. However, their addition decreased the viscosity stability of adhesive. Addition of phenolic resin increases the threshold value of the cohesive strength of Neoprene while the former decreased its strength at high temperatures [26]. The essential requirement for the excellent bond is 1) Proper choice of adhesive; 2) Good joint design; 3) Surface preparation; 4) Wettability; 5) Proper bonding process. According to a few reports, surface treatment is directly proportional to life and service expectancy of any adhesive joint [17]. The surface treatment is required to remove any layer of containment

**Table 1.** Theories of adhesion [8].

Traditional	Recent	Scale of Action
Mechanical Interlocking	Mechanical Interlocking	Microscopic
Electrostatic	Electrostatic	Macroscopic
Diffusion	Diffusion	Molecular
Adsorption/surface reaction	Wettability	Molecular
	Chemical Bonding	Atomic
	Weak Boundary Layer	Molecular

like dirt, grease or oil, which appears to be the surface of substrates [27]. There are multiple ways to clean these surfaces for better wettability, some surface preparation methods: Solvent Cleaning [28]; Chemical treatment [29]; Mechanical treatment [5]; Chemical etching [30]; Plasma treatment [31]; Corona treatment [32]; Flame treatment [10] etc. A large-scale variety of rubber-based PCA (Polychloroprene adhesives) is available based on cost and end-use. Several components and the mixture of solvents are used to formulate PCA [33]. End-use of adhesive application having various rate of crystallization of neoprene rubber is also available, which includes neoprene AD, neoprene AC, neoprene blends of polychloroprene and its co-polymers are also used to attain desired properties of adhesive [34]. Polyphenols, hexamethylenetetramines and condensation products of amines with aldehydes, di-phenyl aniline and polyisocyanates can be used for self-curing of adhesives. Hexamethylenetetramine and paraformaldehyde are used as aldehydes. To increase the vulcanization, process promoters can be added [35]. Various functional groups are introduced to increase the strength of multilayer resin products of adhesives. Functional groups are in the form of additives to boost the adhesion strength to resins. Many researchers prefer phenol resins or resins based on cyclopentadiene to improve the gluing properties of the polychloroprene adhesives [34]. The ageing particularizations of contact adhesives can be affected using resins. The ageing can be increased and decreased using the resins. The resins must be blended with the antioxidants to get the best mechanical properties of the adhesives.

### 1.3. Nanoscale Reinforcement in Adhesives

The adhesion properties can be improved by introducing a minute amount of nanoparticles like multi-walled carbon nanotubes, Nano clay and graphene [36]. A successful dispersion of Nano-fillers (carbon nanotubes, nano-clay, nanofibers) into a matrix of a polymer (thermosetting or thermoplastic) plays an important role. A nanocomposite is a unique combination of improved properties like physical, chemical and mechanical properties. The Nano-fillers have exceptionality due to their size and large surface area over traditional fillers [37].

In this research, MWCNTs was added in solvent-based adhesives to increase the mechanical properties of adhesion in different ageing conditions from ambient to high temperature. Peel strength of unreinforced and reinforced based adhesives was investigated and compared it with commercially available adhesives.

## 2. Experimental Procedure

Materials used in the formulation of adhesive were: Polychloroprene rubber (Mw. 120,000); Phenolic Resin (Mw. 700); Solvents such as Toluene, Ethyl acetate, Naphtha, DMF (Dimethylformamide); Magnesium oxide (MgO)/Zinc Oxide (ZnO); Antioxidant; Nanofillers as Multi-walled carbon nanotubes (MWCNTs; diameter 10 - 30 nm). All materials were of commercial-grade expect DMF (role) (Sigma Aldrich, 99%). Commercial grade functionalized MWCNTs were

procured from Sun Nanotech<sup>®</sup> with a purity of 90%. **Table 2** displays the quantities of ingredients used for polychloroprene solvent-base adhesive; the amounts were optimized after multiple iterations.

Direct dissolving technique was used to carry out the experimentation in the laboratory. After successful tests at a smaller scale, the production was scaled up using an indigenously developed impeller mixing machine with controlled temperature and along with variable low rpm. All ingredients were added one-by-one in a mechanical mixer, and the temperature was gradually increased to 60°C. The optimized adhesive was given the name “PA-30”. Dispersion of MWCNTs in DMF was performed using ultrasonic bath [38]. The dispersed solution was added to already fabricate PCA (Polychloroprene adhesive) during a continuous mechanical mixing. Mixing of adhesive is done until the pale yellow colour of the adhesive changes into greenish colour and developing a nanocomposite adhesive. The whole process took 3 to 4 hours. Schematic diagram of mixing is shown in **Figure 1**.

### Preparation of Samples for Mechanical Testing

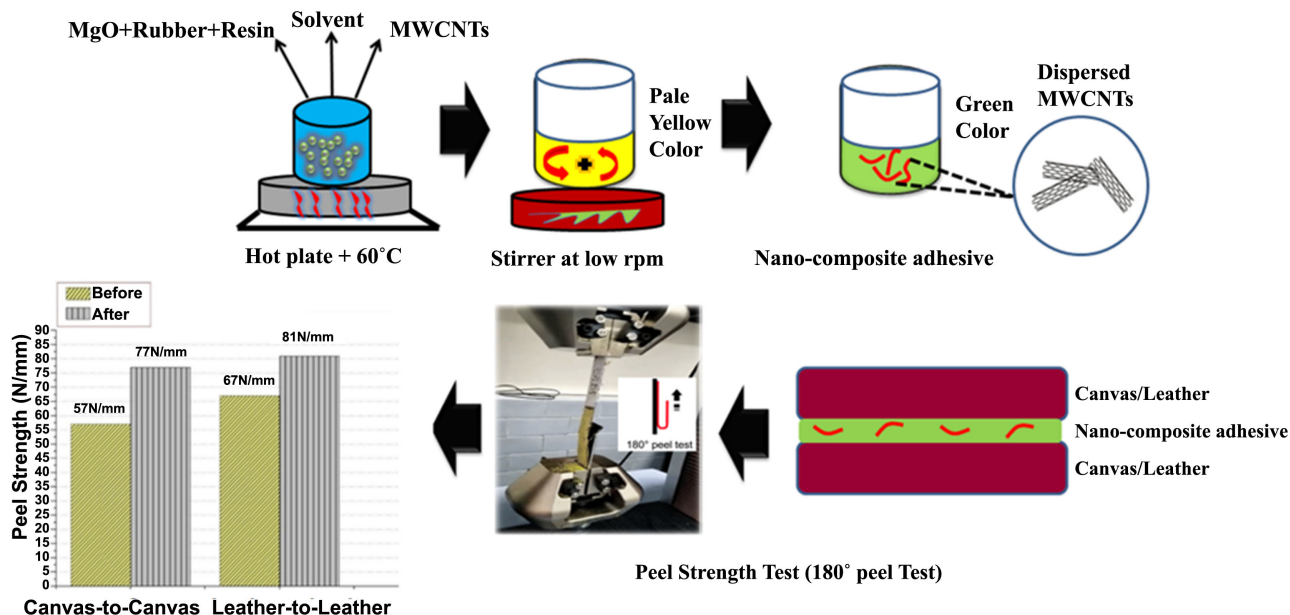
Two types of substrates 1) Canvas-to-Canvas and 2) Leather-to-Leather were used for peel testing as per ASTM standard D903 (2017). The adhesives were applied using a brush and a doctor blade and allowed to almost before joining together and gentle pressing using a roller. 180° angle peel testing was performed as per ASTM standard D3330, using a UTM.

### 3. Results and Discussion

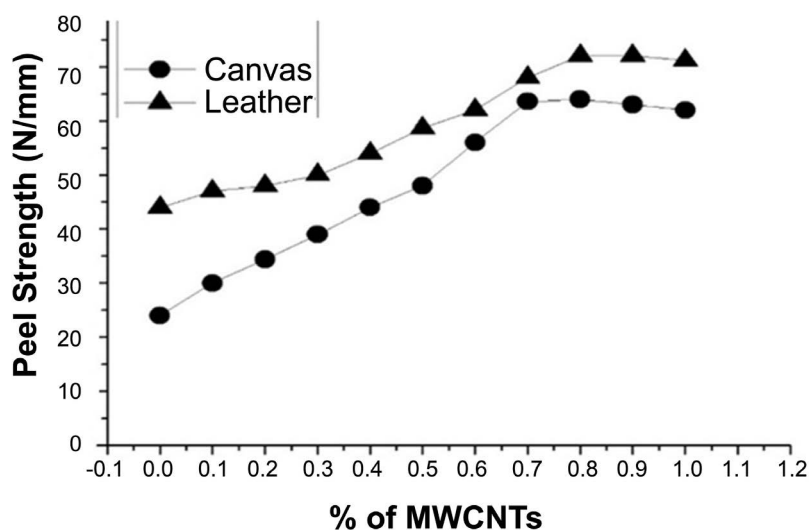
**Figure 2** displays the effect of MWCNTs' concentration on peel strength of the Nano composite adhesive. There was a gradual increase in peel strength up to a certain amount of MWCNTs (0-1%) followed by a stable rather a decreasing trend. The enhancement in strength was due to compatibility of the MWCNTs with the resin and the adhesive system. In both cases *i.e.* canvas-to-canvas and leather-to-leather substrates, maximum peel strength was obtained by incorporating  $\approx 0.8\%$  MWCNTs.

**Table 2.** The optimized formulation of solvent-based adhesive “PA-30”.

Sr. No	Chemicals	Parts per hundred
	CR	100
	Resin	55
	Antioxidant	4
	Ethyl Acetate	320
	Toluene	180
	MgO	3
	Naphtha	220
	ZnO	3



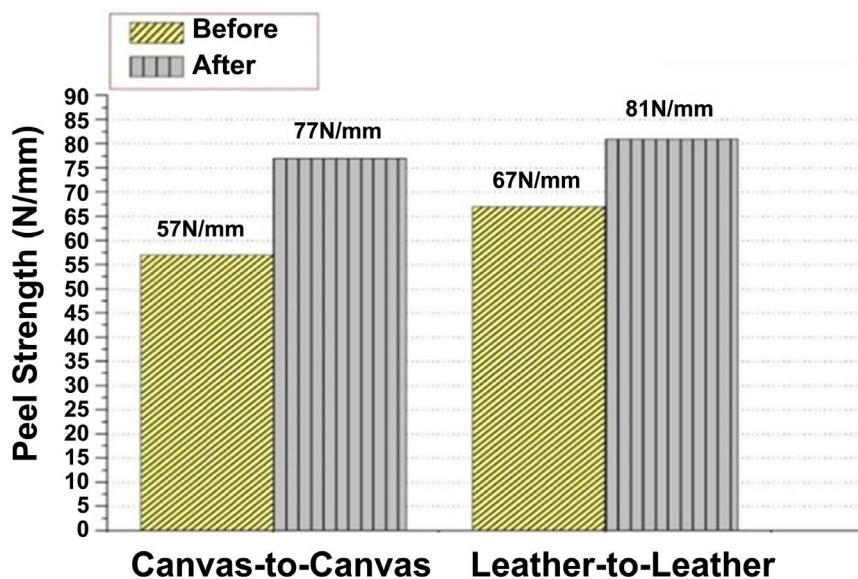
**Figure 1.** Schematic diagram of preparation of nanocomposite adhesive.



**Figure 2.** Effect of MWCNTs concentration on peel strength of the Nano composite adhesive.

In **Figure 2**, a decreasing trend in peel strength after a maximum value, was presumably due to diminution in cohesive forces between adhesive and substrate; it may also be an effect of poor wetting [6]. Another possible reason for the decrease in peel strength could be self-agglomeration of CNTs at higher contents [39].

**Figure 3** displays a comparison of the amount of improvement in peel strengths of the unreinforced and reinforced adhesive, indicating a significant enhancement in peel strength on canvas-to-canvas and leather-to-leather substrates. In canvas-to-canvas substrate, peel strength improved up to 35% while on leather-to-leather substrate the rise was 21%, under optimized conditions.



**Figure 3.** Improvement in peel strength by adding MWCNTs.

The graph demonstrates that the presence of MWCNTs significantly increased the bonding capability of the adhesive. Presumably, the nanotubes caused reinforcement within the adhesive by either possible crack bridging or by crack deflection mechanism which did not allow the crack to propagate at lower loading condition [39].

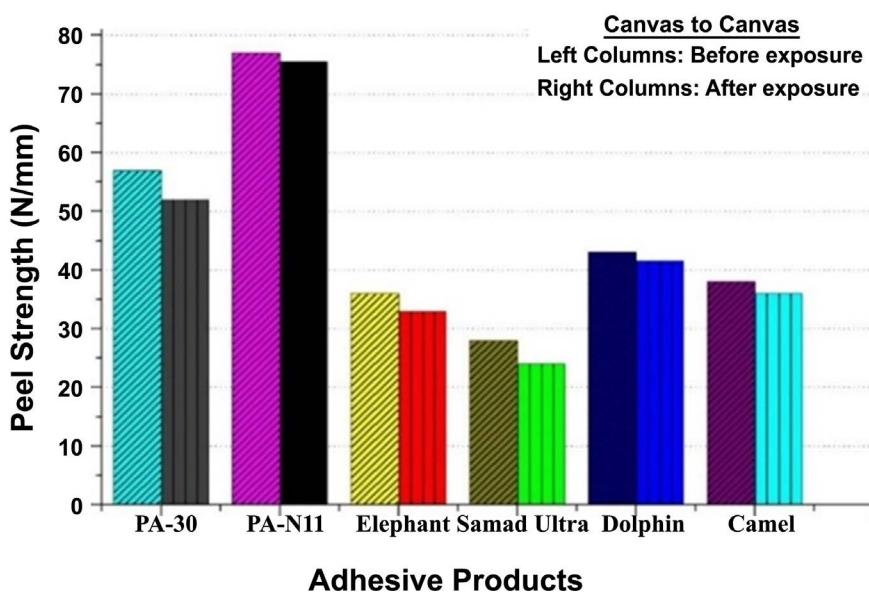
The (PA-30) unreinforced adhesive formulation showed satisfactory performance in normal environmental conditions; however, it exhibited degradation issues when exposed to humidity, temperature, chemicals, seawater and mechanical loading during service.

The role of MWCNTs was of significant consideration to overcome these ageing conditions, by increasing adhesive stiffness, thermal stability and fracture durability [9]. The reinforced Nano-adhesive (PA-N11) was formulated using MWCNTs to overcome these conditions. Due to the presence of MWCNTs, the adhesive performance was significantly higher in relatively aggressive environments. The bond strength, thermal stability and liquid barrier properties were improved due to incorporation of highly dispersed MWCNTs [40].

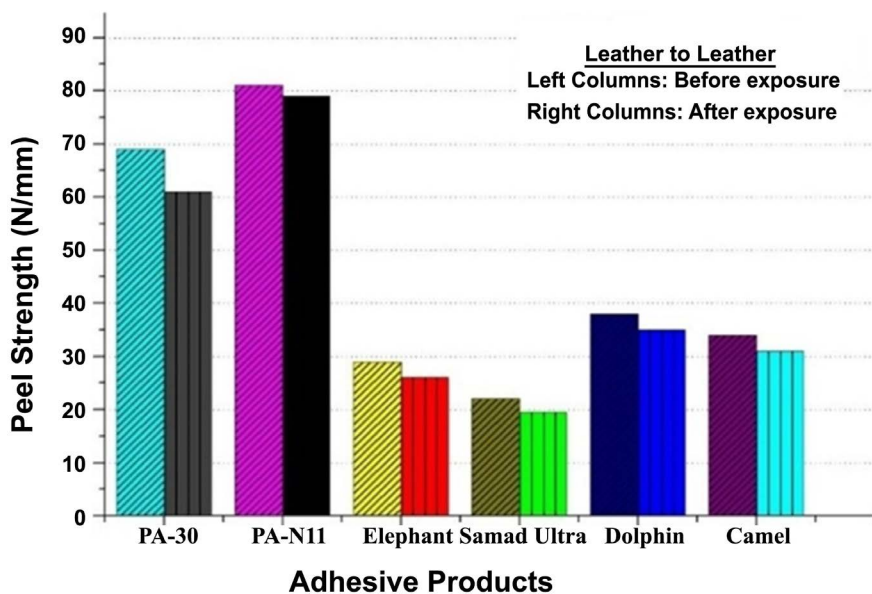
The shelf life of the adhesive was estimated by studying ageing under ambient environment. Peel strengths of the unreinforced and reinforced adhesives were determined after shelving at ambient condition for up to 4 months. The data were also compared with commercially available adhesives (Elephant<sup>®</sup>, Dolphin<sup>®</sup>, Samad ultra<sup>®</sup>, Camel<sup>®</sup>) of the same category, under similar conditions. **Figure 4** and **Figure 5** show a graphical comparison of the effect of ageing on peel strengths, tested on canvas-to-canvas and leather-to-leather substrates, respectively.

**Table 3** shows the peel strengths of unreinforced and reinforced nanocomposite adhesives, and commercially available adhesives of the same category. PA-30 and commercial adhesives lost their adhesion strength to a mentionable value;





**Figure 4.** Effect of ageing on peel strengths for various adhesives under the ambient condition on canvas substrate (except PA-30 and PA-N11, all are commercial adhesives of the same category acquired from the local market, indicated by their brand names).



**Figure 5.** Aging under ambient environment leather substrate.

however, PA-N11 (nanocomposite adhesive) displayed significantly higher performance; the mechanical properties were enhanced with a minimum decrease in peel strength after ageing.

**Table 4** shows peel strengths data of various adhesives after the bonds were exposed to of 100°C. It is believed that the network of crosslinked phenolic resin present in adhesives is usually affected by high temperature. Thermal stability of PA-N11 was enhanced due to the presence of nanotubes which helped to resist high-temperature environment [9]. The flexibility of the adhesive system was



**Table 3.** Characteristics of various adhesives under the ambient condition for four month.

Adhesive	Canvas-to-Canvas	Leather-to-Leather
-----	% Fall in peel strength	% Fall in peel strength
PA-30	8.77	11.59
PA-N11*	1.95	2.47
Elephant <sup>®</sup>	8.33	10.34
Samad ultra <sup>®</sup>	14.29	11.36
Dolphin <sup>®</sup>	3.26	7.89
Camel <sup>®</sup>	5.26	8.82

\*Addition of 1% MWCNTs with adhesive.

**Table 4.** Characteristics of various adhesives under ageing at 100°C for 24 hours.

Adhesive	Canvas-to-Canvas	Leather-to-Leather
-----	% Fall in peel strength	% Fall in peel strength
PA-30	5.26	8.7
PA-N11*	6.62	4.94
Elephant <sup>®</sup>	13.88	17.24
Samad ultra <sup>®</sup>	23.21	22.73
Dolphin <sup>®</sup>	8.37	13.89
Camel <sup>®</sup>	8.42	11.76

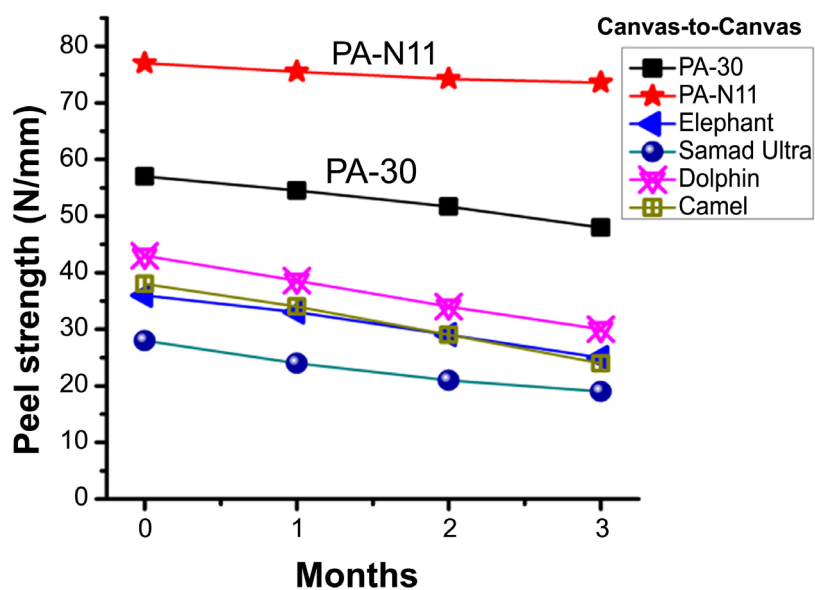
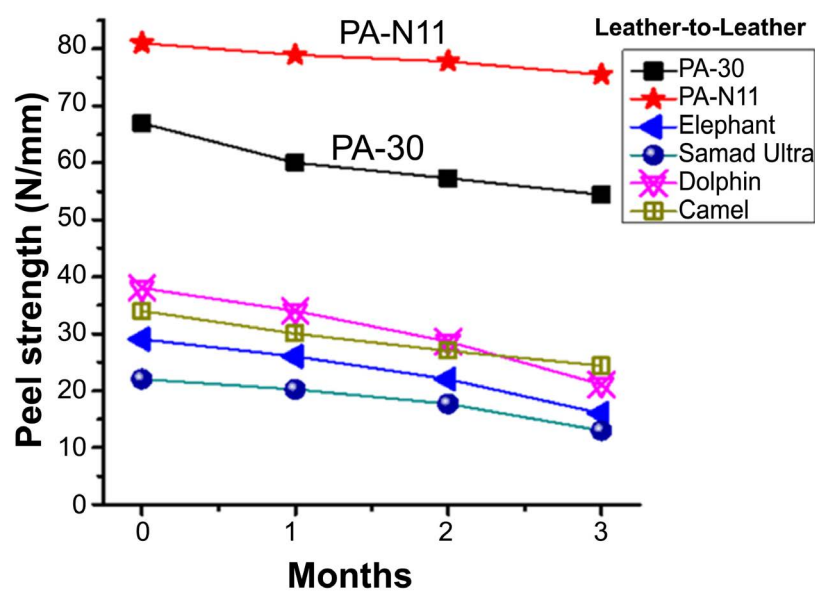
\*Addition of 1% MWCNTs with adhesive.

essential to operate at high-temperature environment. PA-N11 had better flexibility at high-temperature environment. PA-N11 had a minimal amount of MWCNTs, which provided a better crosslinking network to surfaces of the substrates [40]. Mismatch of properties leads to failure of adhesive bond strength even at low loads and temperature. PA-N11 showed excellent thermal stability in ageing conditions owing to the existence of the MWCNTs crosslinking network.

It is generally known that an adhesive joint is deteriorated when exposed to saltwater since the ability for the diffusion of water increases by the ingress of Cl<sup>-</sup> and Na<sup>+</sup> in the adhesive joints, resulting in poor durability of the joint [41] [42]. The various adhesive joints were exposed to 3.5% saltwater at ambient temperature for 24 hours, and the peel strengths were determined. The testing was repeated after every month for for a duration of three months to validate the performance of the adhesives after prolonged shelving. The data is displayed in **Figure 6** and **Figure 7**. Reinforced adhesive showed better resistance compared with unreinforced adhesives including commercial counterparts. The resistance against the corrosive nature of the solution was due to the crosslinking network of MWCNTs in the adhesive. **Table 5** summarizes fall in peel strengths as a result of immersion saltwater at ambient temperature for 24 hours.

**Table 5.** Characteristics of adhesives under ageing in 3.5% saltwater for 24 hours.

Adhesive	Canvas-to-Canvas			Leather-to-Leather		
	% Fall in peel strength			% Fall in peel strength		
PA-30	4.39	9.30	15.79	10.14	14.35	18.12
PA-N11	3.9	6.49	9.74	2.47	3.95	6.79
Elephant	8.33	19.44	30.55	10.34	24.14	44.83
Samad ultra	14.29	25	36.84	8.38	19.37	36.11
Dolphin	10.23	20.93	30.23	10.34	24.13	44.82
Camel	10.53	23.68	38.84	11.76	20.59	38.23

**Figure 6.** Three months ageing comparison in a brine solution (canvas substrate).**Figure 7.** Three months ageing comparison in a brine solution (leather substrate).

## 4. Conclusion

Incorporation of MWCNTs in the solvent-based adhesive successfully improves the bond strength of adhesive joint on flexible substrates. The formulations of PA-30 (unreinforced adhesive) exhibited improvement in 180° peel strengths on canvas and leather substrates, up to 57 N/mm and 67 N/mm, respectively. The formulation of PA-N11 (1% MWCNTs), demonstrated an enhancement in peel strength up to 77 N/mm on canvas and 81 N/mm on leather substrates respectively. The improvement in peel strength was 35% on canvas and 21% on leather substrates as compared to unreinforced adhesive. The optimized unreinforced adhesive displayed a 25% - 50% increase in peel strength compared with commercial adhesives used for investigation. The optimized reinforced adhesive showed 46% - 64% increase in peel strength compared with commercial adhesives investigated. Fall in peel strength of unreinforced adhesive after 4-month shelving at the ambient environment, was 8% - 10%, whereas the reinforced adhesives showed a decrease of 2% - 3%. Fall in peel strength of unreinforced adhesive after 24 hours' immersion in 3.5% sodium chloride solution was 12% - 17%, whereas the reinforced adhesives showed a decrease of 4% - 6%.

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## Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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