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NATURAL RUBBER LATEX BASED CONTACT ADHESIVES

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Renewability and environmental friendliness impart natural rubber latex-based adhesives a greener outlook. The main objective of this study was to investigate the role of dry rubber content and the size of rubber particles in the latex on the adhesive properties of ammonia preserved natural rubber field latex as contact adhesives for bonding leather specimens. Both peel strength and shear strength of field latex adhesive were tested. It was found that adhesive strength of field latex was increased with dry rubber content (drc) and maximum strength obtained was for 45 per cent drc latex. The effect of particle size and proteins on the adhesive properties of natural rubber latex was confirmed by comparing the adhesive peel strength of centrifuged latex and its combinations with skim latex, field latex *etc.* Role of various compounding ingredients and tackifier resins on the peel strength of natural rubber latex at various ageing conditions was also studied.

Key words: Adhesive, Dry rubber content, Natural rubber latex, Non-rubber constituents, Peel strength

INTRODUCTION

Natural rubber (NR) latex based adhesives have great potential due to their renewability and environment-friendliness. NR is used in adhesive industry either as its naturally occurring form as latex or as its dry solid form dissolved in a suitable solvent (Palinchak and Yurgen *et al.,* 1962; SBP, 1979; Wake, 1974). Natural rubber latex based adhesives are superior to their rubber solution adhesives mainly because of low toxicity and inflammability, higher water and solvent resistance, reduced cost, provision for varying viscosity and total solid content (Blackley, 1997 a; Simon, 1962). Natural rubber latex based adhesives are mainly used for bonding flexible and porous materials like leather, paper, textiles, and has a large contribution in pressure sensitive adhesives (Puddefoot, 1948; Shields, 1970; Adams *et al.,* 1998; Shalub *et al.*, 1999). Both the adhesive and cohesive properties of NR latex help the adhesive to function as an excellent bonding agent for joining either similar or dissimilar adherends.

NR based adhesives are well known for their tackiness which involves the ability of two dried adhesive films to form a bond of measurable strength upon immediate contact with each other (Northeast, 1959; Palinchak and Yurgen 1962). This auto-

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adhesion property of natural rubber latex is widely explored in the area of contact adhesives. Solvent based synthetic adhesives are also used as contact adhesives, but they are toxic and have environmental issues. (Onyeagoro, 2012; Lehrle and Willis, 1997). Thus for contact adhesives which demand flexibility, freedom from toxicity and inflammability and good tack, adhesives derived from natural rubber latex are a great choice.

Most of the work related to NR contact adhesives used concentrated latex with high dry rubber content and low non-rubber constituents. For the production of contact adhesives, some compounding ingredients like tackifiers, stabilizers, viscosity modifiers and antioxidants are also required to mix with NR latex. The use of concentrated NR latex as a water based contact adhesive for bonding porous surfaces were reported (Adams *et al*., 1998; Shalub *et al*., 1999). The role of various compounding ingredients on the adhesive performance was also studied (John and Joseph, 1997). However there are very few reports on contact adhesives based on natural rubber field latex. The major constituents of natural rubber field latex are rubber (30-45%), proteins (1-1.5 %), resins (1-2.5 %), ash (1%), sugars (1%) and water (55-60%) and the composition of NR field latex depends on various parameters since it is a natural product (Blackley, 1997b).

The main objective of this study is to understand the role of dry rubber content on the adhesive properties of contact adhesives made of NR field latex at various ageing conditions including thermal, UV and water ageing. Another objective of the study is to explore the role of various compounding ingredients and non-rubber constituents on the adhesive properties of NR latex.

MATERIALS AND METHODS

Materials

Natural rubber field latex (45%), centrifuged latex (60 %) and skim latex (5 %) were obtained from the experimental station of Rubber Research Institute of India, Kottayam. Potassium hydroxide (stabilizer) and ethylene diamine tetraacetic acid (chelating agent) used for the study were of analytical reagent grade. Ammonia (preservative), toluene (solvent) and sodium alginate used were of laboratory reagent grade. Other compounding ingredients like antioxidant TDQ (2,2,4-trimethyl-1,2-dihydroquinoline), tackifier resins (wood rosin and terpene phenolic resin) were of commercial grade. Natural leather was selected as the adherend material.

Preparation of adhesive based on natural rubber field latex

In order to understand the role of particle size of rubber latex in adhesion, NR latex with 45 per cent was prepared by two different methods. In the first method latex having 45 per cent drc was collected and was preserved with ammonia (1 % by weight on latex) and kept for maturation for one month. During maturation, the *in-situ* soaps formed were supposed to increase the stability of the latex. This matured latex was used as a contact adhesive for bonding natural leather substrates. The optimization of the dry rubber content (drc) on the adhesive strength was carried out by diluting 45 per cent drc latex with water so as to obtain latices of varying dry rubber contents (30, 35 and 40 %). Another route used for the preparation of 45 per cent drc latex was by blending centrifuged latex (60 % drc) with water, field latex (30% drc) and skim latex. The skim latex used had 15 per cent drc which was produced by creaming.

The role of various latex ingredients such as stabilisers, antioxidant *etc.* on latex adhesive properties was also studied. Dispersion of antioxidant (TDQ) was prepared by conventional ball milling method. Tackifier resins (wood rosin and terpene phenolic resin) were added as emulsions. The resin emulsion was prepared by first dissolving the resin in toluene. To this, oleic acid was added with stirring which was then added to water containing ammonia with rapid stirring using a mechanical stirrer.

Measurement

A Brookfield viscometer (Brookfield Engineering Laboratories, USA- model LVT) was used to measure the viscosity of NR latex (at 60 rpm) as per IS: 9316 Part 2 - 1987.

Particle size analysis

The particle size and specific surface area of the NR latex with different dry rubber content were analyzed using a Malvern particle size analyzer (Mastersizer 3000, Malvern Instruments Ltd., UK) as per ISO 13320: 2009.

FTIR Analysis

The FTIR spectral analysis of NR latex was obtained from a Bruker FTIR ATR Spectrophotometer (Bruker Tensor 27, Bruker, Germany) using a Zn-Se crystal. The NR latex film prepared by casting method was used for FTIR analysis.

Peel strength and lap shear strength

Natural leather specimens having dimensions 15 cm x 2.5 cm were used for testing leather to leather T- peel strength and single lap shear strength. Test portions measuring 7.5 x 2.5 cm and 2.5 x 2.5 cm of leather specimens were the test area for peel strength and lap shear strength, respectively. Peel strength was measured as the peel force per width of substrate and lap shear strength was expressed as the shear force per unit area of the joint tested.

Test pieces were prepared and tested respectively as per IS: 9827-1981 and IS: 4663-1968 using a universal testing machine (UTM-Zwick/Roell model Z005) at 23 ^{o}C having a cross-head speed of 250 mm min^{-1}. Effect of different ageing conditions on the peel strength and lap shear strength of bonded specimens was also tested. The different ageing conditions selected are given below.

- Thermal ageing at 70^{0}C for 100h in an air circulated oven
- Immersion in water for 24h at room temperature
- Irradiation with UV-radiation for 100h in a UV Chamber (Philips TLD 30W-Holland)

The optical photographs of the adhesive deposited over leather specimen were recorded using a stereo microscope (Leica Wild M8, Switzerland).

RESULTS AND DISCUSSION

Variation of viscosity and specific surface area with dry rubber content

Table 1. **Effect of dry rubber content of natural rubber field latex on latex viscosity and surface area of rubber particles**

Dry rubber content (%)	Viscosity (cPs)	Specific surface area (m^2kg^{-1})
30	17.5	49140
35	20	51480
40	25	51980
45	40	52990

Viscosity plays an important role in the performance of adhesives based on NR latex. It can be seen that there is a gradual increase in viscosity of NR field latex as dry rubber content increased. As the dry rubber content of latex increases, friction due to particle – particle interaction also increases. Gel content in the rubber phase also increases which enhance latex viscosity. The specific surface area of rubber particles in NR latex also increases with dry rubber content. This can be attributed to the increase in small sized particles in the high drc latex (Figure 1). When the particle size of the latex is small, it can wet the adherend more efficiently. Accordingly, small sized rubber particles present in the NR field latex have a significant role in the adhesive properties.

Particle size analysis of latex

As the dry rubber content of latex increases, the volume of smaller sized particles also increases, and that of large particles decreases (Figure 2). Part of the proteins present in the latex is adsorbed on the surface of the rubber particles. The increase in smaller sized particles also cause an increase in surface adsorbed proteins as lower sized particles have large surface area. Protein also will enhance the adhesive properties of latex.

Peel strength and shear strength

Figures 2 and 3 show the effect of dry rubber content of NR field latex on the peel strength and shear strength of leather joints before and after exposure to various ageing conditions. It can be observed that both peel and shear strength of leather joints increases with increase in the dry rubber content (drc) and maximum strength was observed for 45 per cent drc latex. Evaluation beyond

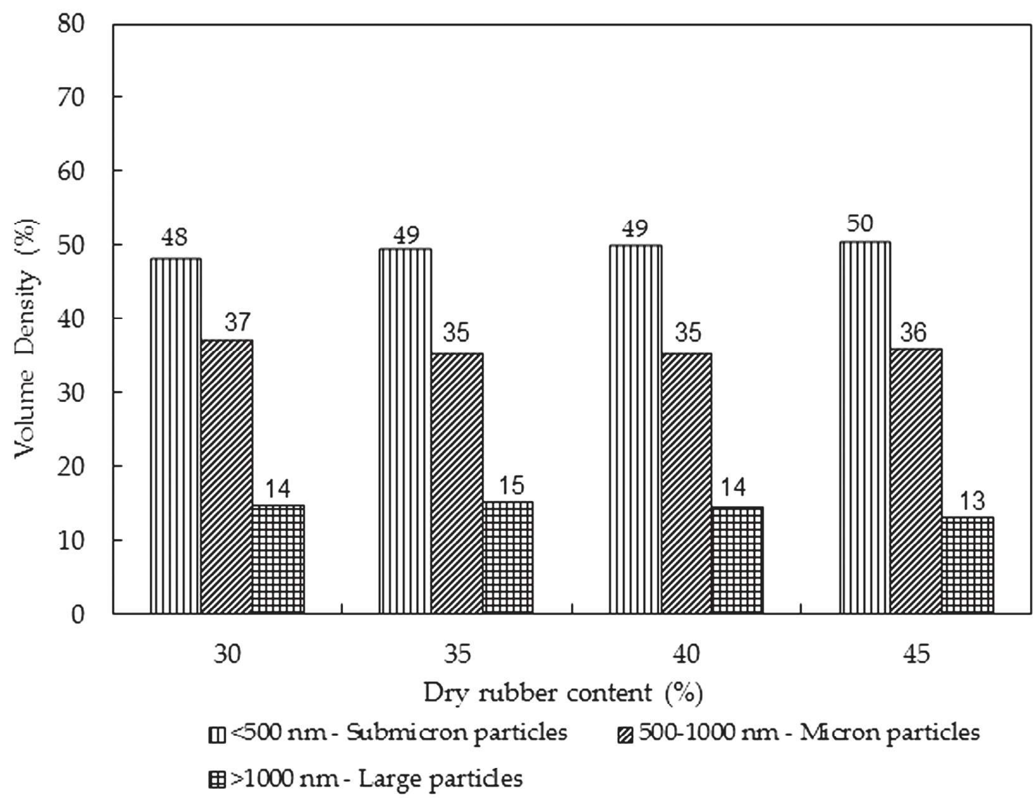

Fig. 1. Variation in particle size of NR field latex with varying dry rubber content.

45 per cent drc was not possible, since the maximum drc available for field latex was 45 per cent. This increase in adhesive strength of NR field latex with increase in dry rubber content can be attributed to the increased mechanical anchoring of rubber particles per unit area of the substrate. Another reason is the increased volume of small sized particles in higher drc latex and their increased surface area while forming the adhesive bond with the substrate. Adhesion is a combined effect of a number interfacial phenomena like mechanical interlocking, chemical bonding, diffusion, electrostatic attraction *etc* (McBain and Hopkins, 1925; Voyutskii, 1960; DeLollis 1970; Wake, 1978). Natural leather is a porous material and hence mechanical interlocking at the interface imparts better strength to joints. As the share of smaller sized rubber particles in the latex increases, the adhesive can strongly fill the gaps and voids on the adherend surface and thereby enhances the peel strength. When the adhesive film is formed in between the adherend the film integration will be facilitated due to the presence of small particles. When the proportion of small particles increases, the voids in between the large particles and the adherend are sealed effectively resulting in a strong adhesive interface as represented in Figures (a) and (b).

Ageing studies

Figures 2 and 3 reveal that both peel and shear strengths of NR field latex decreases after thermal ageing (100h at 70°C). This can be attributed to the degradation of rubber hydrocarbon chain. The thermal oxidative degradation of NR decreases with increasing dry rubber content. NR field latex contains natural antioxidants, mainly

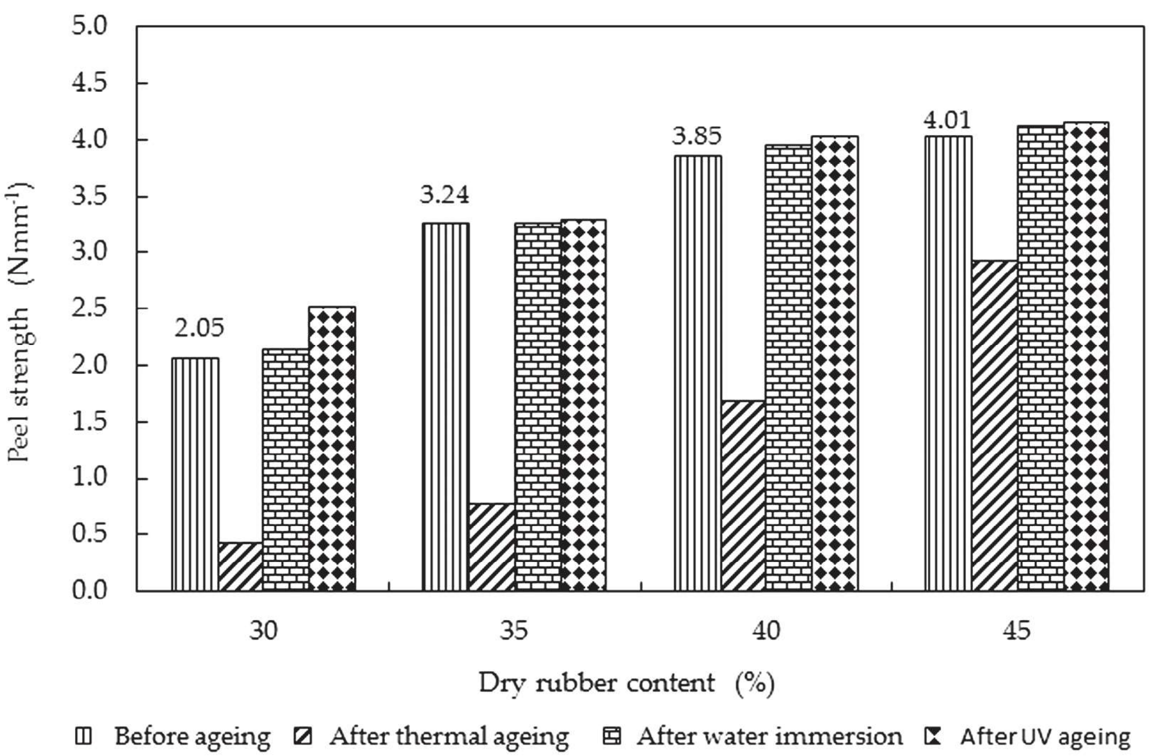

Fig. 2. Variation in peel strength of NR field latex with dry rubber content.

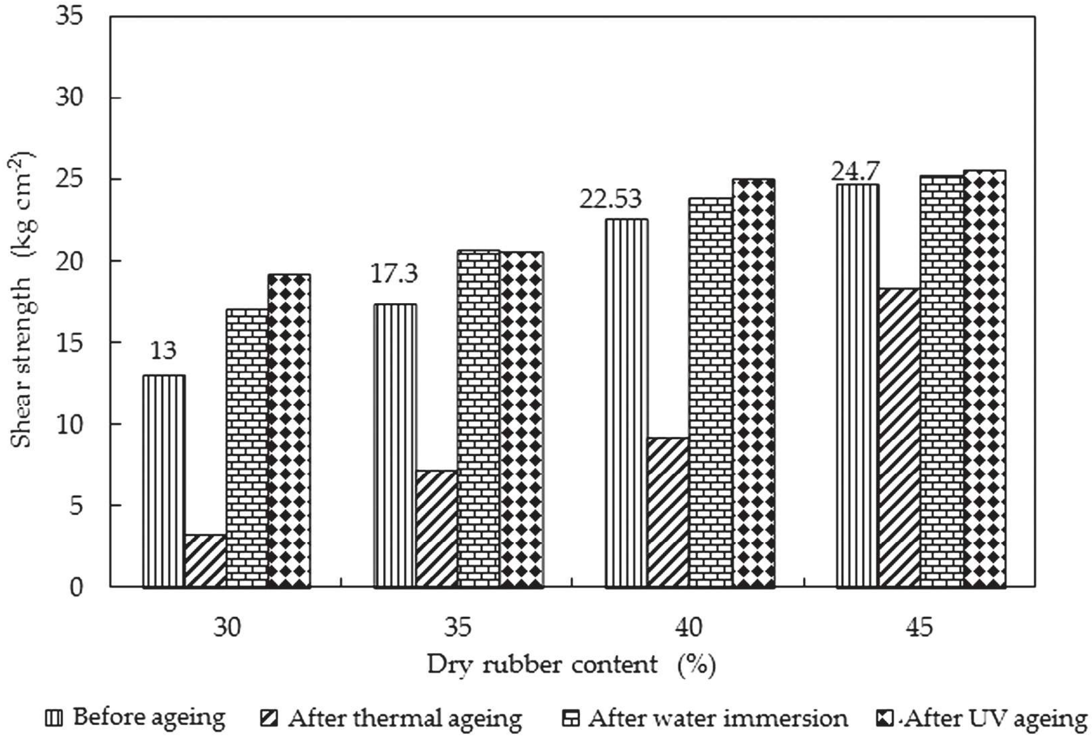

Fig. 3. Variation of shear strength of NR field latex with dry rubber content.

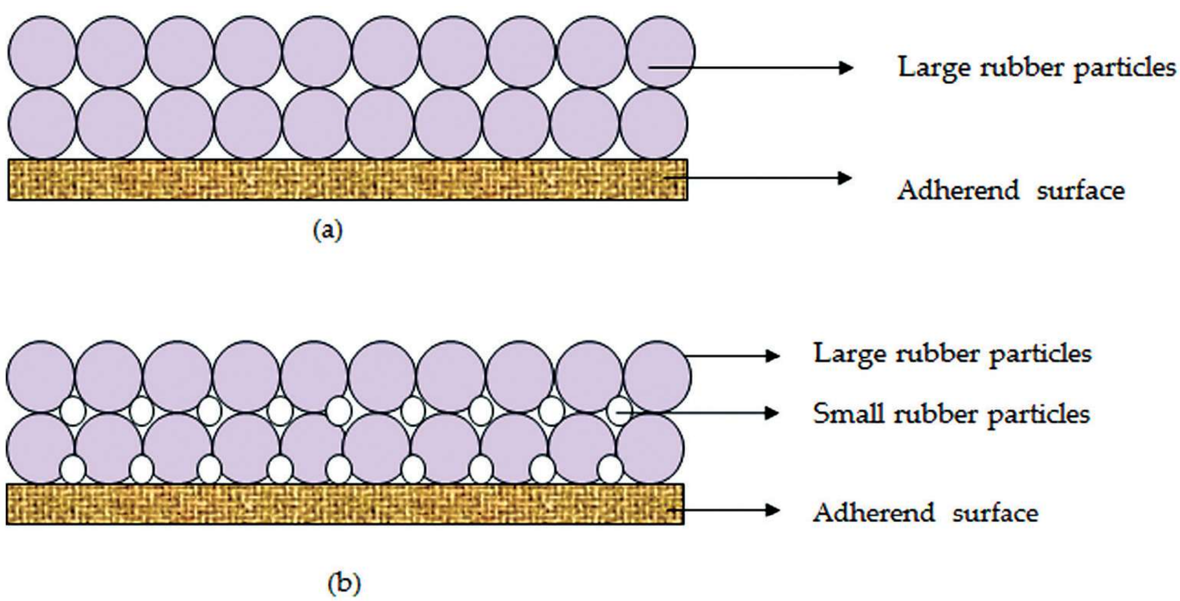

Fig. 4. Schematic representation of NR latex adhesive with a) large rubber particles and b) with large and small sized particles.

tocotrienols which are found to associate with the rubber membranes (Hasma and Othman, 1990). Thermal ageing resistance of NR latex with high dry rubber content may be due to the presence of more tocotrienols in the latex. The enhanced peel strength under UV exposure might be due to the cross-linking that happened in the rubber phase. Ageing in water has little effect on the peel strength and shear strength.

The optical photographs of the surface of leather specimen before and after the peel test are given in Figure 5. It is evident that the NR latex forms a thin film on the leather surface and it can wet and fill the voids and gaps present in the leather surface effectively. Hence when the top and bottom layers are bonded together, an interface of higher adhesive strength is obtained.

The variation in peel load against elongation is shown in Figure 6. The peel load was found to be highest for 45 per cent drc latex compared to others which also indicates the higher adhesive strength of high drc NR latex adhesive. As the interface of the leather joints is strong, more force is required to break the joints.

Effect of particle size

The role of small sized rubber particles and protein molecules was further confirmed by comparing the particle size distribution and adhesive peel strength of centrifuged latex (60% drc) and its various combinations with field latex, skim latex and water combinations. Different combinations examined are given in Table 2. The volume of small sized particles in centrifuged latex only 46 per cent whereas the same in skim latex was 96 per cent. Blending of centrifuged latex with skim latex and field latex increased the share of small sized rubber particles. However the population of small sized particles was low in centrifuged latex diluted with water. The peel strength of various combinations of centrifuged latex is also given Table 3. It was found that both field latex and skim latex combinations registered better peel strength compared to centrifuged latex diluted with water. The reason may be the sealing action of small sized rubber particles which can effectively penetrate into the voids and gaps of porous leather thereby increasing the adhesion strength. From the peel strength data, it can also be found that dilution of centrifuged

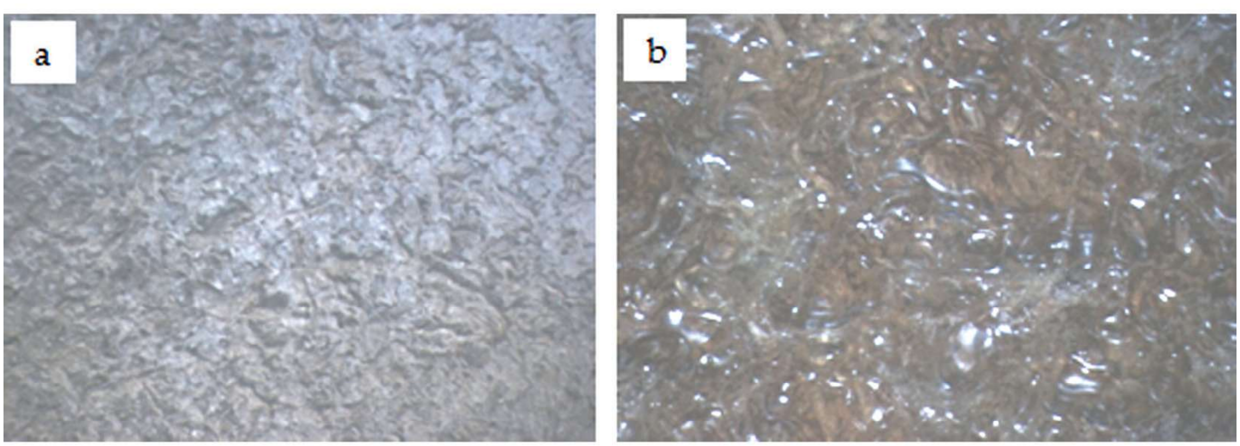

Fig. 5. Optical photographs of leather specimens: a) surface before adhesive application; b) surface after testing.

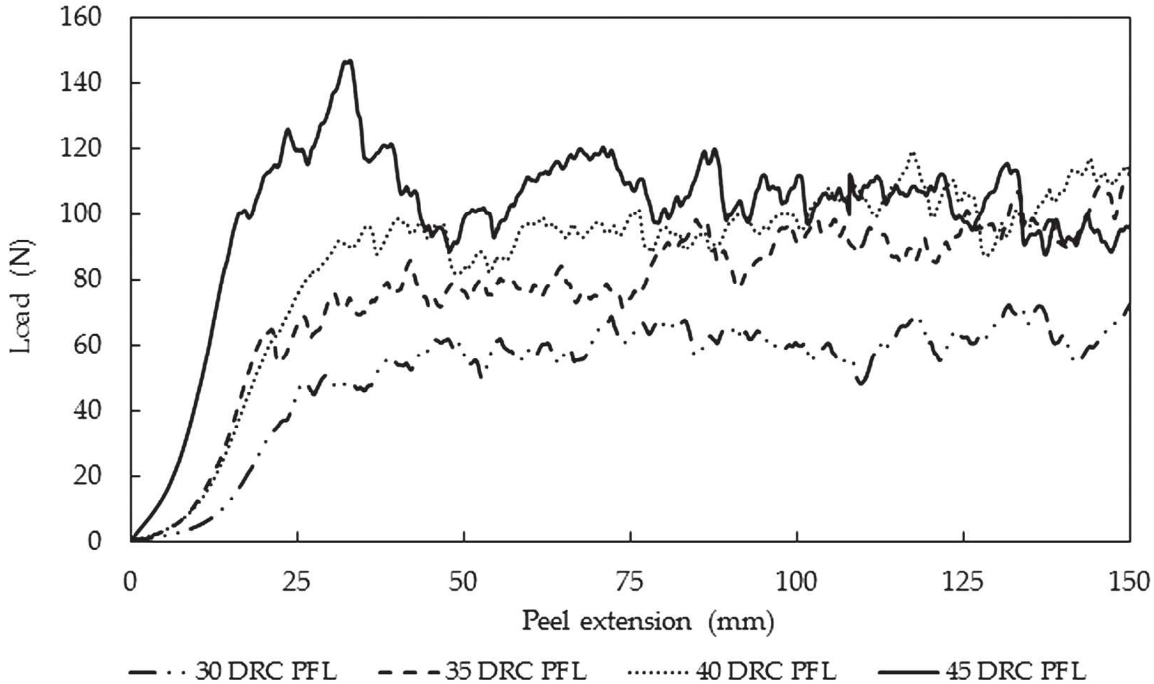

Fig. 6. Variation of peel load of NR adhesive with varying dry rubber content during peel testing.

latex with water could not impart any variation in adhesive strength. The low peel strength of skim latex compared to field latex may be due to the high amount of soaps present in the skim.

From the adhesive peel strength (Table 3), it was concluded that the adhesive developed using centrifuged latex-field latex blend (45% drc) showed better strength than all other combinations.

Table 2. **Comparison of particle size distribution of centrifuged latex and its various combinations**

Types of latex	Particle size (Volume density, %)		
	<500 nm	500-1000 nm	>1000 nm
Centrifuged latex (60% drc)	46.20	38.97	14.81
Creamed skim latex (15% drc)	95.98	0.73	3.17
Centrifuged latex -skim latex blend (45% drc)	50.03	38.77	11.20
Centrifuged latex -field latex blend (45% drc)	51.06	38.35	10.59
Centrifuged latex diluted with water (45% drc)	47.48	39.05	13.47

Table 3. **Comparison of peel strengths of centrifuged latex and its various combinations**

Types of latex	Peel strength (N mm^{-1})
Centrifuged latex (60% drc)	2.10
Centrifuged latex - field latex blend (45% drc)	3.11
Centrifuged latex - skim latex blend (45% drc)	2.76
Centrifuged latex - diluted with water (45% drc)	2.16

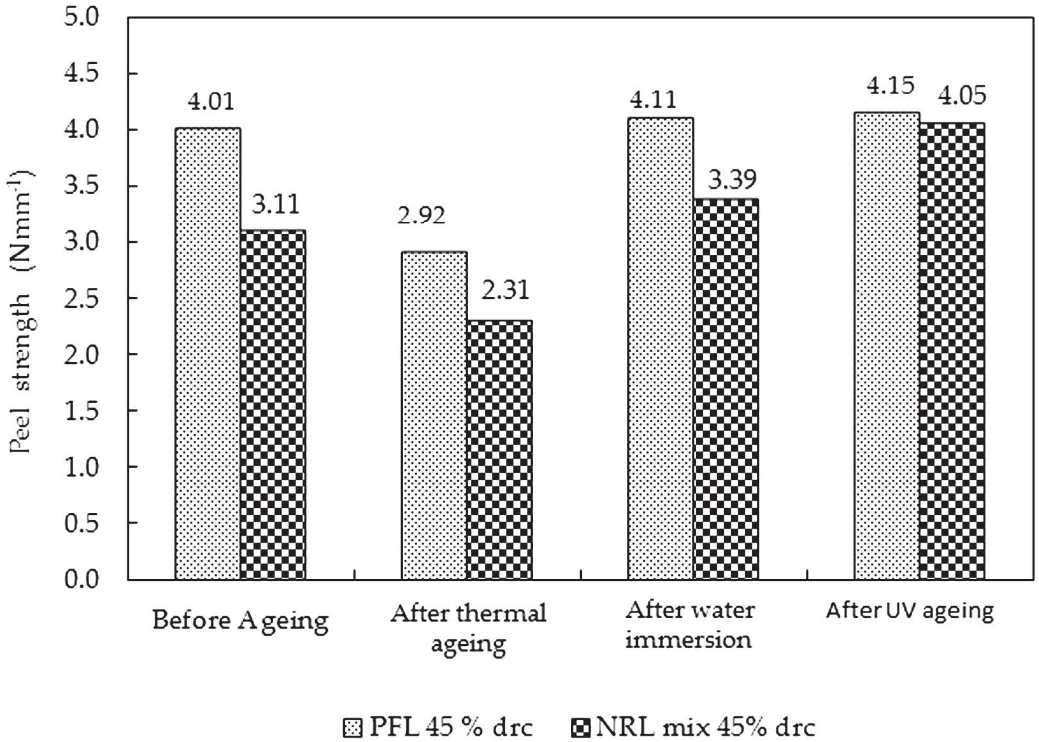

Fig. 7. Peel strength of NR field latex (PFL 45% drc) and field latex-centrifuged latex blend (NRL mix 45% drc)

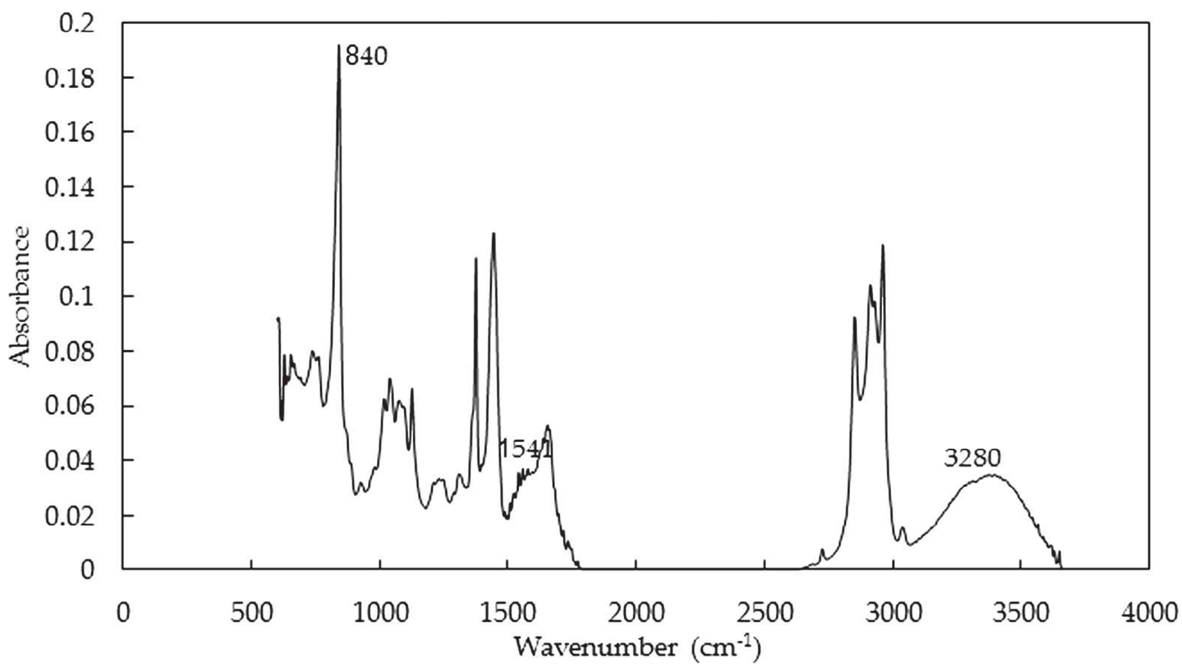

Fig. 8. FT-IR spectrum of NR field latex (45 % drc)

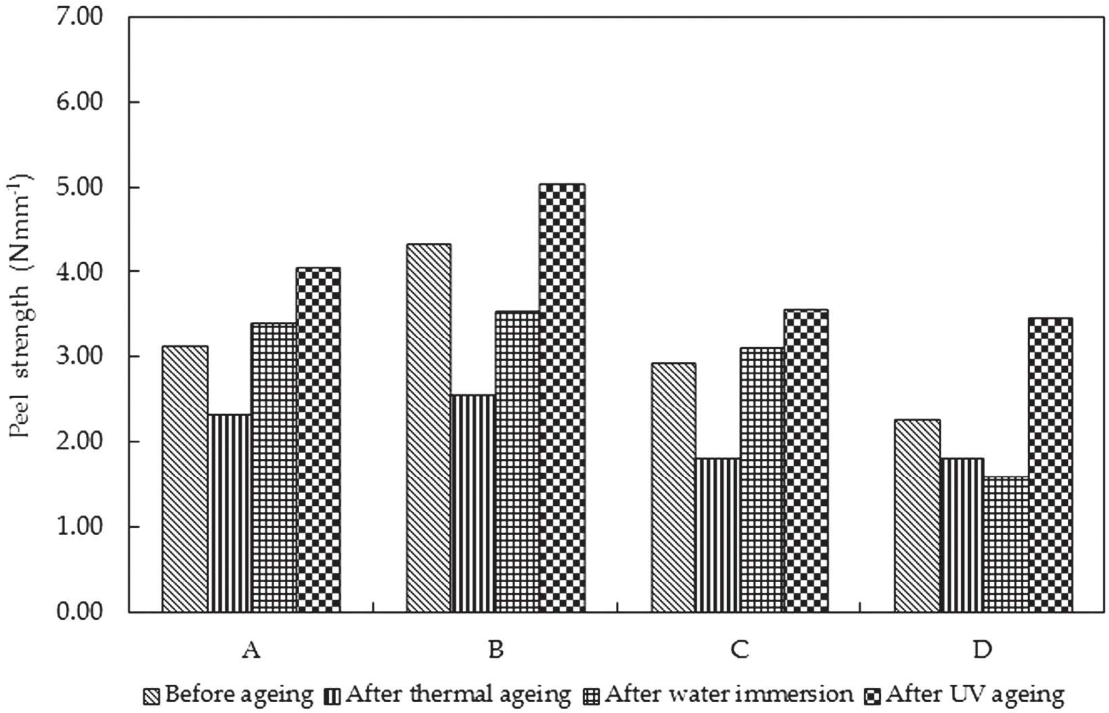

Fig. 9. Comparison of peel strength of NR latex adhesive mixes A, B, C and D at various ageing conditions.

Peel strength of blends of field latex with concentrated latex showed a reduction in strength compared to that of field latex having the same dry rubber content (45% drc) as given in Figure 7. This indicates that, not only the dry rubber content of NR latex but the non-rubber constituents like proteins and antioxidants present in the field latex also have some role on the adhesive properties of NR latex. While concentrating natural rubber field latex by centrifuging a good amount of the non - rubber constituents get removed (Blackley, 1997b).

The FTIR spectrum of dried NR field latex film (Figure 8) showed a major characteristic absorption peak at 840 cm^{-1} (=CH bending). The absorption bands at 1541 cm^{-1} (N-H bending) and 3280 cm^{-1} (N-H stretching) are mainly from the proteins present in natural rubber latex

Table 4. **Role of compounding ingredients on the peel strength (Centrifuged latex/field latex blend: 45 % drc)**

Formulation Ingredients	Mixes (Dry weight, phr) A	B	C	D
Preserved natural rubber latex (45% drc)	100	100	100	100
10% Potassium hydroxide solution	-	0.05	0.05	0.05
10% Ethylenediaminetetraacetic acid solution	-	0.05	0.05	0.05
50% 2,2,4-trimethyl-1,2-dihydroquinoline dispersion	-	1	1	1
30% Wood rosin emulsion	-	-	5	-
30% Terpene phendic resin emulsion	-	-	-	5

(Kalapat *et al*., 2009; Aik-Hee *et al*., 1992; Lim and Misran, 2013). Such peaks were weak in centrifuged latex (data not given).

The preserved NR latex (centrifuged latex/field latex blend: 45% drc) was compounded with, various ingredients as given in Table 4. The results obtained for peel strength on bonded leather specimens are shown in Figure 9. Maximum adhesive peel strength was shown by mix B and the strength was high for both unaged and aged samples. The results indicate that addition of small amount of stabilizer KOH, chelating agent EDTA (Wake, 1974) and antioxidant TDQ can improve both the ageing resistance and also the adhesive strength of natural rubber latex adhesives. These chemicals get physically adsorbed in to the natural rubber chains, and may increase the wettability and mechanical interlocking of the natural rubber latex adhesive. Addition of small amounts of tackifier resins like wood rosin and terpene phenolic resin could not improve the peel strength of latex adhesive which may be due to the incompatibility between rubber and the resins.

CONCLUSIONS

Preserved NR field latex was found to be an efficient contact adhesive for natural leather substrates. Both peel strength and single lap shear strength increased with increase in the dry rubber content of NR field latex adhesive. It was found that viscosity of ammonia preserved NR latex increased with dry rubber content. Both dry rubber content and small sized rubber particles in the latex play significant role in the adhesive properties of latex based adhesives. FTIR spectrum of ammonia preserved NR latex showed characteristic absorption band for non-rubber constituents. Presence of proteins and natural antioxidants in the latex improves the adhesive properties and also protects the rubber from oxidation. Adhesive properties were improved by the addition of stabilizers, chelating agent and antioxidant. Tackifier resins such as wood rosin and terpene phenolic resin did not improve the adhesive strength of NR latex which might be due to the incompatibility of resins with rubber.

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