NATURAL RUBBER LATEX-BASED ADHESIVES: EFFECT OF METHYL METHACRYLATE-GRAFTED LATEX ON ADHESIVE PROPERTIES

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The effect of blending natural rubber latex (NRL) with various proportions of methyl methacrylate-grafted natural rubber latex (MGL) on the adhesive properties of NRL is reported in the paper. Blends were prepared by mixing NRL and MGL at various proportions and the adhesive properties studied. The effect of blending MGL with NRL on the glass transition temperature (T_g) of NRL was followed using differential scanning calorimetry (DSC). The adhesion strength of blends was measured by performing peel test on leather to leather joints. Brookfield viscosity, thermogravimetric analysis (TGA) and Fourier-transform infrared (FTIR) analysis of the blends were also carried out. The wettability and hydrophilicity of the NRL/MGL blends were examined by means of contact angle measurement. The effect of compounding on the NRL/MGL adhesive properties was also studied.The incorporation of MGL improved the peel strength of NRL-based adhesives. NRL/MGL adhesive showed good thermal ageing resistance compared to that of the control. The blend containing 20 wt% of MGL registered the optimum peel strength and thermal ageing resistance.

Keywords: Adhesive, Blends, Methyl methacrylate-grafted latex, Natural rubber latex, Peel strength

INTRODUCTION

NRL-based adhesives have the advantages of lower toxicity and freedom from solvent hazards, provision for getting desired viscosity and high total solid content. Lower adhesion strength and poor solvent resistance are the main drawbacks associated with NRL-based adhesives (Wetzel, 1962; Blackley, 1997).

Methyl methacrylate (MMA)-grafted natural rubber (Heveaplus MG or MGL) is one of the chemically modified forms of natural rubber (NR). It is produced by the graft copolymerization of NRL with MMA monomer in the presence of an initiator. The rigid poly (methyl methacrylate) (PMMA) chains are grafted onto the flexible NR chains which leads to the formation of Heveaplus MG (Gazeley and Wake, 1990; Blackley, 1997 b; Nakason *et al.*, 2001). Heveaplus MG which contains 49 per cent MMA content is termed as MG 49. Self-reinforcing ability and environmental stability are the major advantages possessed by MGL. It has been reported that, the film forming properties of MGL is very poor because the grafting reaction mainly occurs on the surface of the

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rubber particles (Sundardi and Kadariah, 1984; Schneider *et al.*, 1996; Arayapranee *et al.*, 2002; Lee *et al.*, 2002; Arayapranee and Rempel, 2008). The major application of MGL is in the field of adhesives (Ho *et al.*, 2001; Thongnuanchan *et al.*, 2018; Radabutra *et al.*, 2020). NRL has excellent film forming properties, but the environment stability and the adhesive properties are very low.

Blending two or more polymer latices is an excellent cost-effective technique for improving the properties of polymers. Blends of sulphur prevulcanised NRL and 2-(dimethylamino) ethyl methacrylate-grafted latex for improved static dissipative properties were reported by several researchers (Vivayganathan *et al.*, 2008). The film forming and mechanical properties of NRL and PMMA-grafted NRL blends were also reported (Lu *et al.*, 2002).

However, only few reports are available on the adhesive performance of blends of NRL and MGL in the latex form. The adhesive performance of blends of NRL with different proportions of MGL is presented in this study.

MATERIALS AND METHODS

NRL with dry rubber content (DRC) of 45 per cent used in the study was prepared by blending concentrated latex with field latex (Shybi *et al.*, 2017). Concentrated latex and field latex were obtained from the experiment station of Rubber Research Institute of India, Kottayam. MGL (MG 49- total solids content 49%) was obtained from Associated Chemicals, Kochi, Kerala. The other compounding ingredients used were commercial products. Natural leather was used as the adherent material.

NRL was blended with MGL at various ratios (Table 1). In the designation of blends, N-stands for NRL and M-stands for MGL, and the subscripts indicate the weight per cent of each latice. These NRL/MGL blends were initially used for the evaluation of adhesive properties. Later, the effect of different ingredients on the adhesion strength was studied.

Table 1. **Formulation of the blends containing various proportions of NRL and MGL**

Sample	Ingredients (dry weight)	
	NRL	MGL
$N_{100}M_0$	100	0
$N_{90}M_{10}$	90	10
$N_{80}M_{20}$	80	20
$N_{70}M_{30}$	70	30
$N_{60}M_{40}$	60	40
$N_{50}M_{50}$	50	50
$N_{40}M_{60}$	40	60
$N_{30}M_{70}$	30	70
$N_{20}M_{80}$	20	80
$N_{10}M_{90}$	10	90
N_0M_{100}	0	100

The viscosity of the NRL/MGL blend was measured using a Brookfield viscometer (Brookfield Engineering Laboratories, USA-Model LVT) at 60 rpm using spindle number 3. The particle size distribution of the different NRL/MGL blend was analyzed using a Malvern particle size analyzer (Mastersizer 3000) as per ISO 13320: 2009. The FTIR spectrum of the NRL/MGL film was taken using a FTIR spectrometer (Bruker Tensor 27, Germany) in the range 4000 to 400 cm^{-1}. Thermal stability of the NRL/MGL adhesive blend was determined using a Thermogravimetric Analyser (TA Instruments-Q 500) at a heating rate of 10°C / min under nitrogen atmosphere (heating range 30-600°C). The glass transition temperature (T_g) of NRL/MGL blend was determined by DSC (TA Instruments; Q 2000) under nitrogen atmosphere at a heating rate of 10°C/min from -80 to 100°C. The contact angle of water on the NRL/MGL blend film was measured by the sessile drop method, using a contact angle analyzer (SEO Phoenix). The volume of water was maintained as 5μl in all cases.

The adhesion strength was studied by T- peel test on leather substrates according to IS 9827-1981 using a universal testing machine (UTM- Zwick/Roell Model Z005) at a cross-head speed of 250 mm/min. Natural leather specimens having dimensions 15 x 2.5 cm was used for testing leather to leather peel strength. Test portion measuring 7.5 x 2.5 cm was used as the test area for peel strength. Peel strength was measured as the peel force per width of substrate tested.

The thermal ageing study was conducted by measuring the peel strength of leather joints after ageing at 70°C for 100 h in an air oven.

Table 2. **Brookfield viscosity of NRL/MGL adhesives**

Sample	Viscosity (cPs)
$N_{100}M_{0}$	55
$N_{90}M_{10}$	65
$N_{80}M_{20}$	85
$N_{70}M_{30}$	172
$N_{60}M_{40}$	315
$N_{50}M_{50}$	455
$N_{40}M_{60}$	700
$N_{30}M_{70}$	810
$N_{20}M_{80}$	650
$N_{10}M_{90}$	320
$N_{0}M_{100}$	25

RESULTS AND DISCUSSION

Effect of MGL content on the viscosity of adhesives

Table 2 shows the viscosity of NRL/MGL adhesives. The viscosity of NRL/MGL blends increased with increasing concentration of MGL. This observation is attributed to the interactions between dissimilar particles (NRL and MGL), which are stronger than those between particles of similar type. These interactions help to maintain the stability of the homogeneous dispersions (Ochigbo *et al.*, 2009). The viscosity showed marginal decrease at higher MGL concentrations. It has been reported that latex viscosity decreased with increased MMA content in the grafted latex (Satraphan *et al.*, 2009). Viscosity has a great influence on the performance of an adhesive. When the viscosity of the adhesive becomes high, it cannot wet the adherent surface properly. For better performance, an adhesive should wet the adherent surface properly so that it can penetrate into the voids and pores in the adherent surface efficiently.

Particle size distribution of NRL/MGL adhesives

Figure 1 represents the particle size distribution of NRL (control) and MGL. The data obtained from the particle size analysis of NRL/MGL blends at various blend ratios is shown in Figure 2. Compared to NRL, MGL contains high number of large particles. It is well known that the grafting of MMA onto NR particles occurs mainly at the surface and the particle size of NRL increases after grafting (Satraphan *et al.*, 2009). Volume of small particles (particle size <500 nm) remained almost constant up to NRL/MGL blend ratio of 50:50 and thereafter a reduction in the number of small particles was observed. Field latex contains more volume of small particles than the concentrated latex. Since the latex was prepared by blending

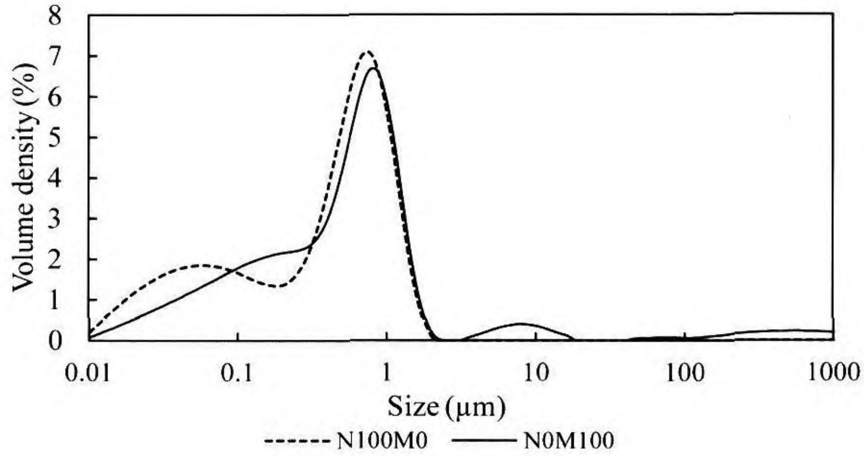

Fig. 1. Comparison of particle size distribution of NRL and MGL

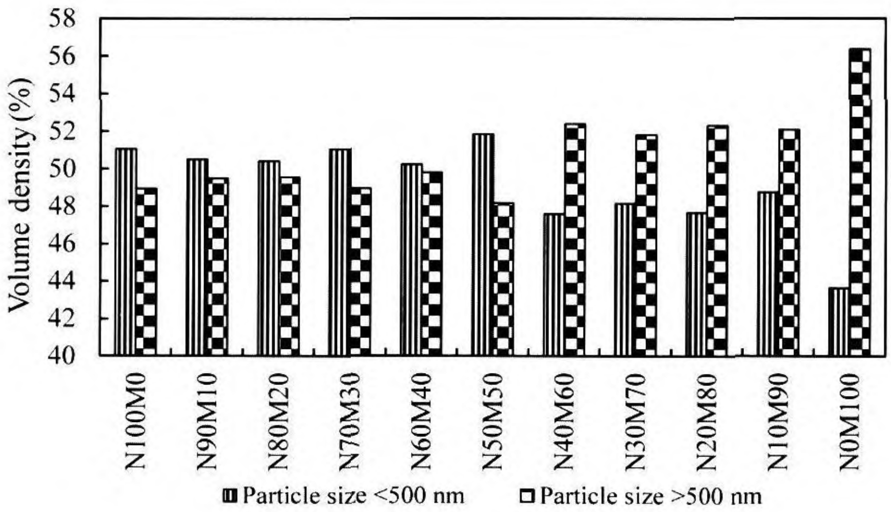

Fig. 2. Particle size distribution data of NRL/MGL blends

concentrated latex with field latex, volume of small particles will be high with blends having high NRL content. As a result, an increase in MGL content resulted in an increase in volume of large particles (particle size >500 nm) in NRL/MGL blends. Thus, particle size analysis revealed that lower concentration of MGL addition has only a nominal effect on the particle size distribution of NRL/MGL blends, but higher

Table 3. **Degradation temperature of NRL/MGL blends**

Sample	Degradation temperature (°C) and weight loss					
	$T_{5\%}$	$T_{25\%}$	$T_{50\%}$	$T_{75\%}$	$T_{90\%}$	T_{max}
$N_{100}M_{0}$	228	343	359	374	398	361
$N_{90}M_{10}$	231	345	362	375	404	363
$N_{80}M_{20}$	242	346	362	378	404	363
$N_{70}M_{30}$	248	348	363	378	405	363
$N_{60}M_{40}$	255	349	364	379	409	364
$N_{50}M_{50}$	253	348	364	379	404	364
$N_{40}M_{60}$	255	349	364	379	401	365
$N_{30}M_{70}$	282	349	364	379	395	365
$N_{20}M_{80}$	259	350	365	380	402	365
$N_{10}M_{90}$	291	351	366	381	395	365
$N_{0}M_{100}$	295	352	367	383	395	365

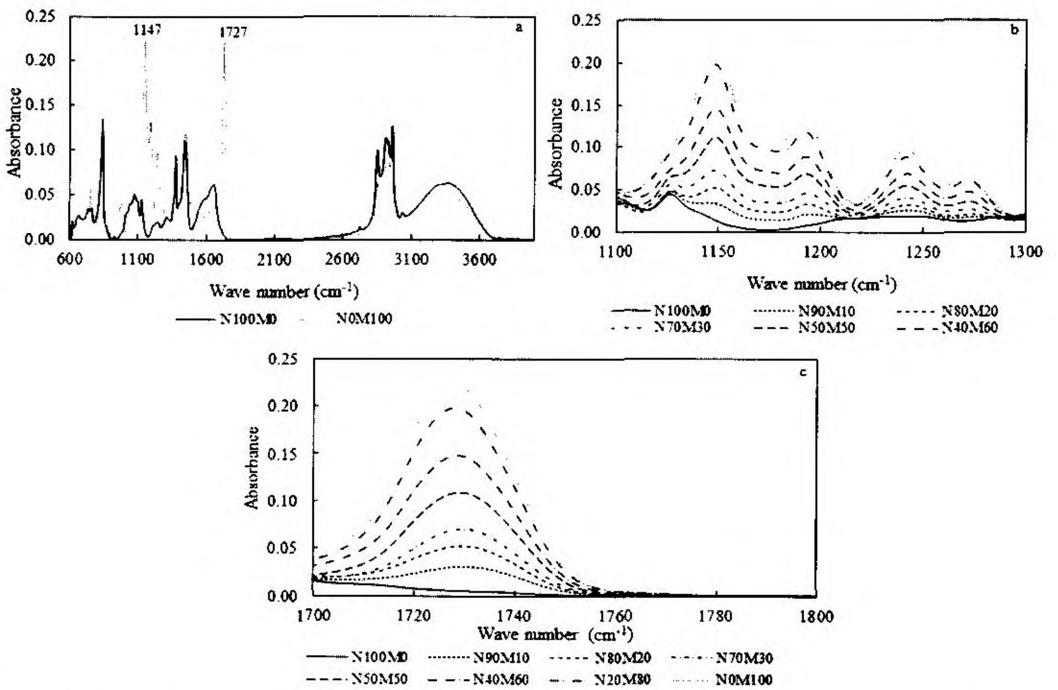

Fig. 3. FTIR spectra of (a) NRL and MGL films, (b) NRL/MGL blend films between 1000-1300 cm^{-1} and (c) Between 1700-1800 cm^{-1}

Table 4. **Contact angle of NRL/MGL adhesives**

Sample	Contact angle (°)
$N_{100}M_{0}$	65.2
$N_{90}M_{10}$	64.2
$N_{80}M_{20}$	61.7
$N_{70}M_{30}$	55.8

MGL concentration leads to an increase in the volume of large particles in NRL/MGL blends.

FTIR spectra of NRL/MGL blends

The FTIR spectra of NRL, MGL and NRL/MGL blends are given in Figures 3a-c. FTIR spectrum of NRL displayed the characteristic peaks at 840 cm^{-1} (=CH bending), 2920 cm^{-1} (asymmetric – CH_2 stretching) and 2850 cm^{-1} (symmetric – CH_2 stretching). The spectrum of MGL shows the same major peaks as obtained from NRL and additional intense peaks at 1727 cm^{-1} (-C=O stretching vibration of PMMA), 1147 cm^{-1} (-C-O stretching vibration of PMMA), 1193 cm^{-1} (skeletal vibrations coupled to C-H deformations) and 1242 cm^{-1} and 1272 cm^{-1} (the coupled C-O and C-C-O antisymmetric stretching (Ho *et al.*, 2001; Arayapranee *et al.*, 2002; Satraphana *et al.*, 2009; Sain *et al.*, 2012; Wang *et al.*, 2016; Moolsin *et al.*, 2017; Thongnuanchan *et al.*, 2018; Radabutra *et al.*, 2020). It was found that as the concentration of MGL in the blend increases, the intensity of peaks at 1727, 1147, 1193, 1242 and 1272 cm^{-1} also increased.

Role of MGL on the thermal stability of NRL/MGL adhesives

The thermal stability of NRL/MGL adhesive was studied using TGA. Figure 4 and Table 3 show the thermal properties of NRL, MGL and NRL/MGL blends. The table demonstrates that, the degradation temperature at the initial weight loss ($T_{5\%}$) was high for MGL compared to NRL. NRL/

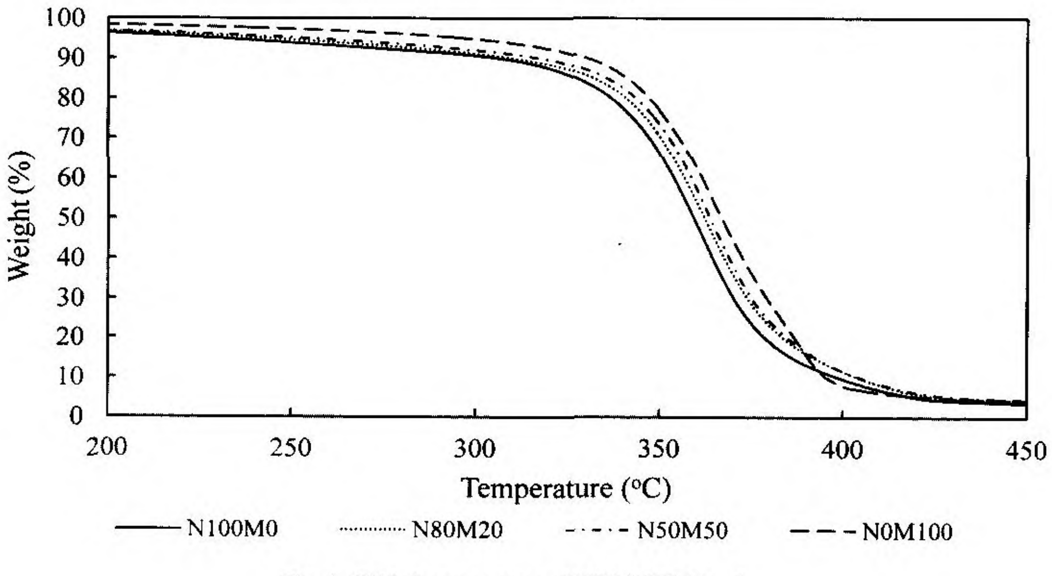

Fig. 4. TGA thermograms of NRL/MGL blends

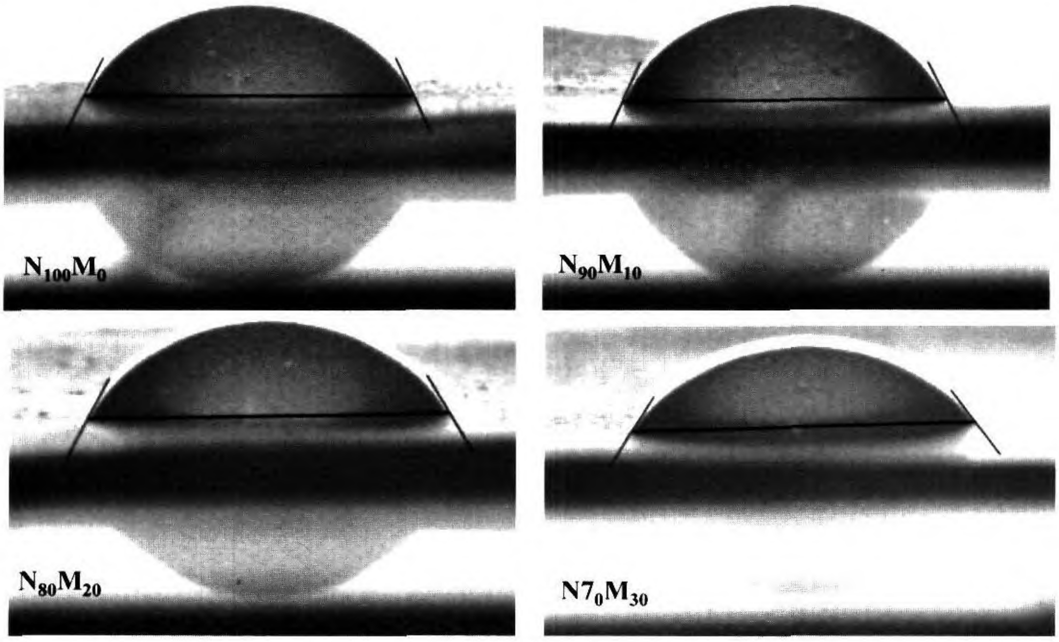

Fig. 5. Contact angle measurements on (a) $N_{100}M_{0,}$ (b) $N_{90}M_{10}$ (c) $N_{80}M_{20}$ and (d) $N_{70}M_{30}$

MGL adhesives also have high initial decomposition temperature, indicating that the thermal resistance was improved by the addition of MGL. Due to the presence of unsaturated double bonds, NRL is susceptible to thermal degradation. It has been reported that grafting improves the thermal stability of the NRL, as the grafted latex contains less unsaturated sites compared to NRL. The improved thermal resistance offered by MGL is the reason behind the improved thermal resistance of NRL/MGL adhesives compared to NRL-based adhesive. It was also found that the maximum degradation temperature (T_{max}) of NRL adhesive was slightly increased by the incorporation of MGL. This observation is attributed to the improved thermal stability provided by MGL in the NRL/MGL adhesives.

Contact angle measurements of NRL/MGL adhesives

The contact angle is defined as the angle formed between a solid surface and a tangent line drawn from the contact point along the liquid-vapor interface of the liquid droplet (Zisman, 1964). Contact angle measurements are mainly used for the evaluation of surface characteristics such as wettability and surface energy of materials. A lower contact angle indicates higher surface wettability of the material. In the present work, the contact angle of NRL/MGL films was assessed to measure their wettability. The contact angle for NRL was about 65.2° (Table 4 and Fig. 5). The results indicated that addition of MGL improved the wettability and hydrophilicity of NRL adhesives. Hydrophilicity and wettability

Table 5. **Tg values of NRL/MGL blends**

Sample	T_g (°C)
$N_{100}M_0$	-60.9
$N_{90}M_{10}$	-60.8
$N_{80}M_{20}$	-58.6
$N_{70}M_{30}$	-61.4
N_0M_{100}	-61.1

of NRL usually improved by grafting with MMA (Vivayganathan *et al.*, 2008; Thongnuanchan *et al.*, 2018; Radabutra *et al.*, 2020) and accordingly MGL has higher wettability than NRL. So, blending MGL into NRL improved the wettability of NRL-based adhesives. As the film forming ability of the NRL adhesives was reduced at higher MGL loadings, the contact angle measurements were carried only for NRL/MGL blends containing 30 wt% MGL.

Role of MGL on the glass transition temperature of NRL/MGL blends

Knowledge about the glass transition temperature (Tg) is an important parameter for evaluating performance of adhesives. Figure 6 shows the differential scanning calorimetry (DSC) curves of NRL, MGL and NRL/MGL blends. The Tg observed for NRL and MGL were -60.9 and -61.1, respectively (Table 5). The NRL/MGL blends showed a single Tg, which indicated the homogeneity of the blends (Schneider *et al.*, 1996; Kangwansupamonkon *et al.*, 2005; Satraphan *et al.*, 2009). The adhesive blend having NRL: MGL ratio 80:20 ($N_{80}M_{20}$) showed the maximum shift in the Tg of NRL compared to all other blends which indicated better compatibility of $N_{80}M_{20}$ blend adhesive.

Role of MGL on the peel strength

Figure 7 represents the results of peel strength measured on leather substrates.

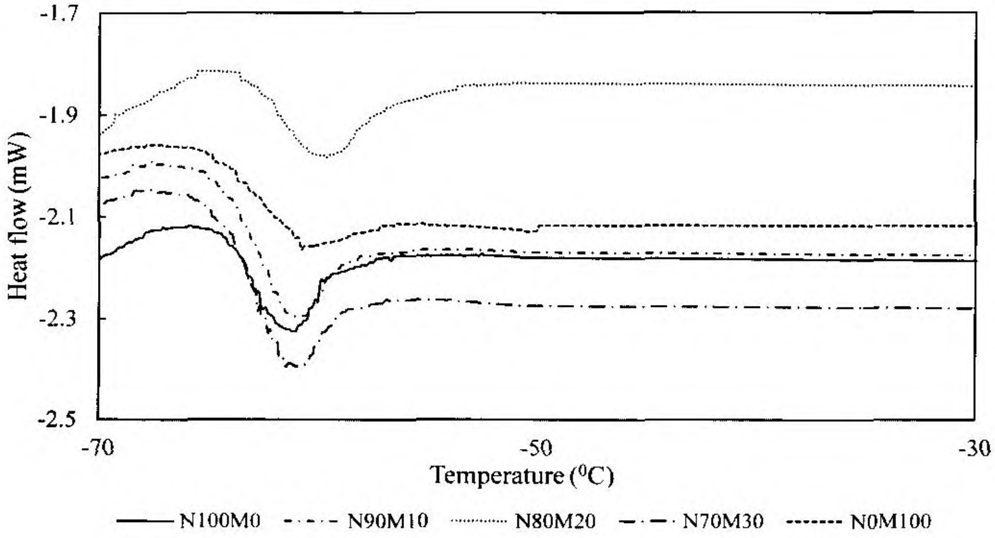

Fig. 6. DSC curves of NRL/MGL blends

Blending MGL with NRL improved the adhesion strength of NRL-based adhesives. The addition of MGL increased the peel strength up to an optimum level, and thereafter decreased. Grafting enhanced the hardness and modulus of NRL films, leading to an increase in the cohesive strength, which further improved the adhesion strength on various substrates (Thongnuanchan *et al.*, 2018). The improved adhesion strength observed with low concentrations of MGL addition was attributed to the self-reinforcing capacity of the MGL films. Another reason for the enhanced peel strength is the increased ability to wet or spread onto leather surface due to the increased hydrophilicity of NRL/MGL adhesives (Radabutra *et al.*, 2020) compared to NRL (control). At lower MGL content, a strong interfacial adhesion exists between NRL and MGL phases which may explain the enhanced peel strength of NRL. It has been reported that at higher MMA concentration, the film forming ability of MGL got greatly reduced, and cracks were developed in the film while drying. At higher MGL loading, the NRL/MGL films became more brittle and the adhesive may not able to wet the adherend substrate properly. For an adhesive to perform better, it should properly wet the adherend surface and spreads evenly on it. The maximum peel strength with 61 per cent increase was obtained for $N_{80}M_{20}$ blend in comparison with control NRL.

Figure 8 shows the results of peel strength after thermal ageing for 100 h at 70°C in an air oven. It can be seen that, the thermal ageing resistance of the blend adhesive increased significantly with the MGL content. It was also observed that, blends with MGL content less than 40 wt% had improved thermal resistance. The sample having a MGL content of 20 wt%

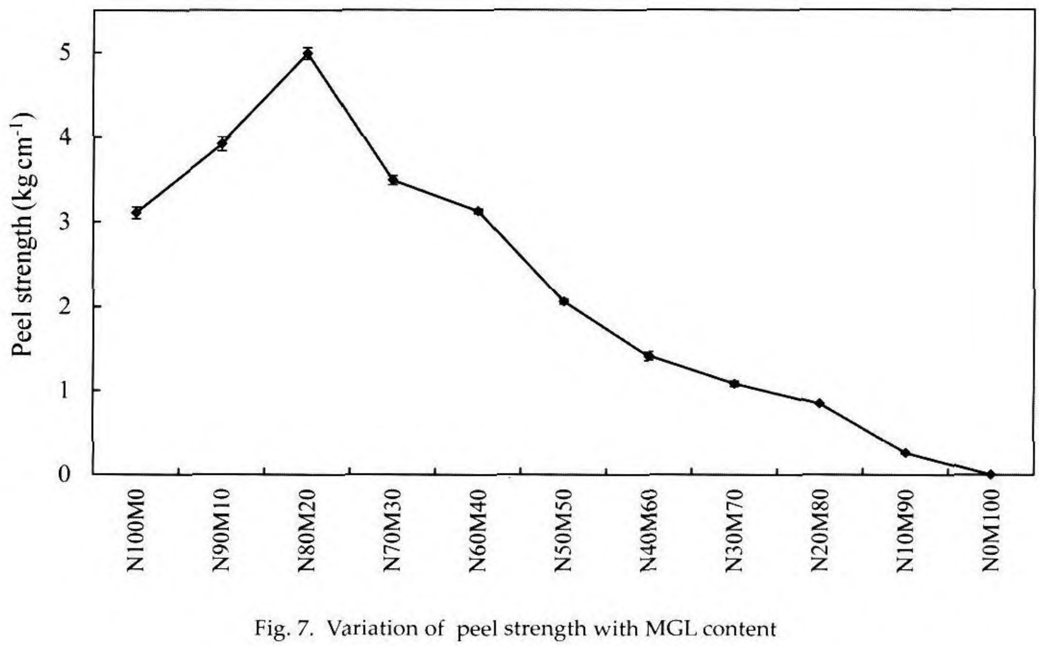

Fig. 7. Variation of peel strength with MGL content

Table 6. **Formulation of $N_{80}M_{20}$ adhesive**

Ingredients	Dry weight (g)	
	Mix 1	Mix 2
NRL	80	80
MGL	20	20
10% Potassium hydroxide (KOH) solution	-	0.05
10% Ethylenediaminetetraacetic acid (EDTA) solution	-	0.05
50% 2,2,4-trimethyl-1,2-dihydroquinoline (TDQ) dispersion	-	1

($N_{80}M_{20}$) showed the best thermal ageing resistance. When the MGL content was below 40 wt%, the decrease in peel strength was only to a small extent. Due to the presence of unsaturated backbone chain in NR, the polymer is prone to thermal oxidation. MGL has better thermal ageing resistance due to low unsaturation due to grafting with PMMA. In unaged samples, the peel strength decreased after an optimum concentration of MGL. This observation is in accordance with the lower film forming ability of the adhesive at higher MGL concentration.

Effect of compounding

From peel strength measurements, it was clear that the optimum gain in peel strength (61%) was registered for $N_{80}M_{20}$ blend. As mentioned earlier, NR chains are prone to attack by various degrading agents such as heat, oxidation, water and solvents. The thermal ageing resistance of NRL-based contact adhesives is an important parameter while rating the same for end-use application. For this reason, different compounding ingredients such as stabilizers, antioxidants, chelating agents, *etc.* are to be incorporated in

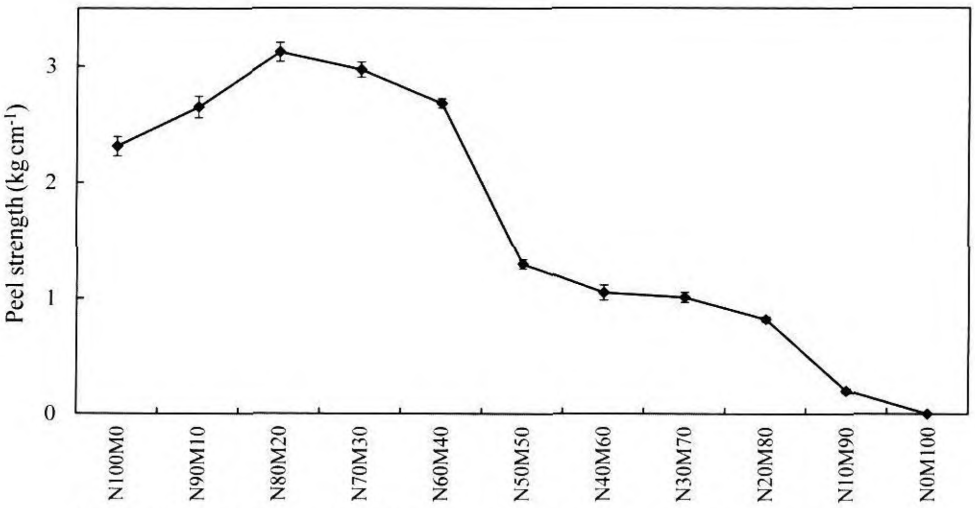

Fig. 8. Role of MGL on the peel strength after thermal ageing at 70°C for 100 h

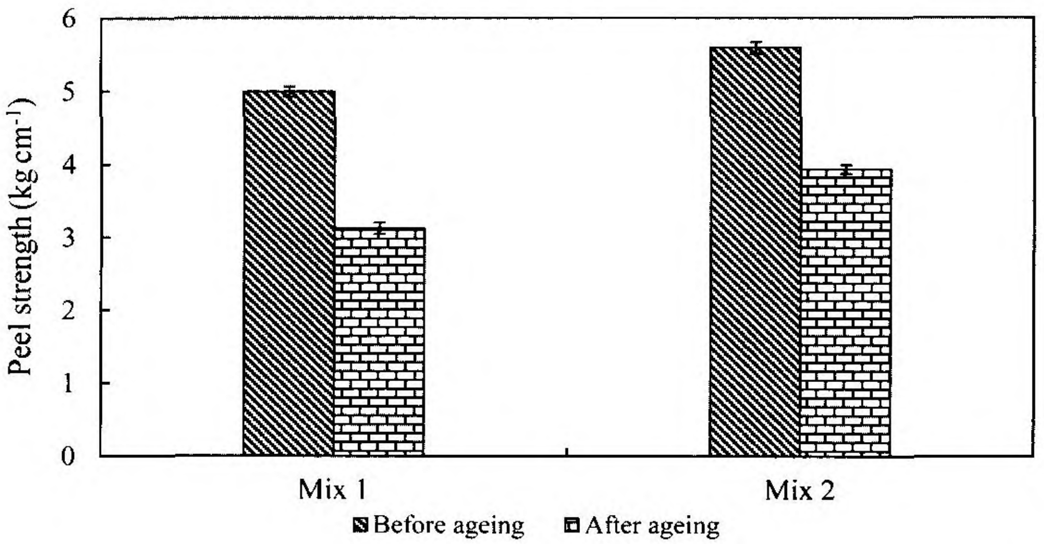

Fig. 9. Effect of compounding on the peel strength of NRL/MGL adhesive (before and after thermal ageing at 70°C for 100 h)

the adhesive formulation. In order to understand the role of compounding potassium hydroxide (KOH), ethylene diaminetetraacetic acid (EDTA) and 2,2,4-trimethyl-1,2-dihydroquinoline (TDQ) on adhesion strength, further experiments were conducted with $N_{80}M_{20}$ blend (Table 6). The purpose of adding EDTA to NRL-based adhesives is to protect it against the catalytic oxidation produced by heavy metals such as chromium present in leather adherends (Wake, 1974).

Figure 9 shows the effect of compounding (KOH, EDTA and TDQ) on the peel strength of NRL/MGL adhesives. Addition of these ingredients improved the peel strength of both unaged and aged samples.

CONCLUSION

The incorporation of MGL into NRL improved the peel strength of latex-based adhesives. NRL/MGL adhesive showed good thermal ageing resistance compared to that of the control. Optimum adhesive properties were obtained for the adhesive containing 20 wt% of MGL. Particle size analysis indicated that higher MGL concentration resulted in an increase in the volume of large sized particles. Contact angle measurements proved improved wettability of NRL-adhesives on addition of MGL. The presence of a single Tg in the DSC curves supported the homogeneity of the components of the adhesives. Compounding improved the peel strength of NRL/MGL adhesives.

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