

## ***Blends of Sulphur Prevulcanised Natural Rubber Latex and 2-(Dimethylamino) ethyl methacrylate -grafted latex for Improved Static Dissipative Properties***

K. VIVAYGANATHAN<sup>\*#</sup>, M. ASRUL<sup>\*</sup> AND M.Y. AMIR-HASHIM<sup>\*</sup>

*Improvement in static dissipative properties of cast films prepared from blends of natural rubber latex and 2-(Dimethylamino) ethyl methacrylate (DMAEMA)-grafted NR latex was demonstrated. The relative changes in surface properties of the cast films prepared from latex blends were investigated using surface resistivity measurements, contact angle and Fourier Transform Infrared-Attenuated Total Reflectance (FTIR-ATR). The results indicated that static dissipative properties and surface related properties, such as surface energy and wettability could be enhanced provided that an appropriate blend ratio of the DMAEMA-grafted NR latex and an effective amount of monomer was used in the preparation of the grafted NR latex. Differences in the properties of film surfaces, the air-facing and former-facing surfaces are also described.*

**Key words:** blends; static dissipative properties; DMAEMA; resistivity; contact angle; FTIR-ATR; surface energy; wettability

Natural rubber (NR) latex is known to be one of the best materials for producing gloves with good tactility and the ability to provide comfort to users. Nevertheless, with all these commendable performance, NR latex derived products such as disposable NR gloves still do not find much use in static control application due to its inherent insulative nature. In some applications, a certain level of static dissipation is required to prevent the accumulation of electrostatic charge, which could be damaging to products. In an environment where such protection is required, gloves made from synthetic materials such as nitrile and

polyvinyl chlorides (PVC) are widely used as an alternative to NR gloves.

The seemingly undesirable insulative properties of NR could be overcome via several approaches<sup>1</sup>. Films derived from NR latex could be rendered antistatic (high level of static dissipative properties) by incorporating conductive fillers such as carbon black or silica. Another approach deemed suitable is to utilise an antistatic additive that is hydrophilic in nature, for instance, polypropylene glycol<sup>2</sup>. It is envisaged that the migration of this hydrophilic material to the NR latex

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<sup>\*</sup>Rubber Research Institute of Malaysia, Malaysian Rubber Board, P.O. Box 10150, 50908 Kuala Lumpur, Malaysia

<sup>#</sup> Corresponding author (e-mail: vivayganathan@lgm.gov.my)

film surface can increase the level of static dissipation. However, in both aforementioned methods, there exists increased chances of contamination with antistatic additives during product handling. An alternative approach that is believed to be similar to the mode of action of hydrophilic additive but without this drawback is *via* latex blending.

Blending of two or more polymer latices is quite a well-known technique for improving cost efficiency, imparting desirable properties and reducing volatile organic compounds. Numerous studies on NR latex blends had been reported<sup>3,4,5</sup>. Most of the work done was to investigate the preparation parameters such as blending ratios, film formation, effect of prevulcanisation and miscibility of the blends. Previous studies also demonstrated that improvement in film properties such as film hardness and modulus were attainable by blending the rigid self-reinforcing polymethylmethacrylate grafted NR latex (MG latex) and NR latex<sup>6,7</sup>.

This paper describes the effect of blending of polar DMAEMA-grafted NR latex and NR latex on static dissipative properties in cast films prepared from the latex blend. The

changes in surface properties of latex films that are pertinent to static dissipative properties were investigated *via* surface resistivity measurements, contact angle and FTIR-ATR. The aim of the present work is to develop a relatively inexpensive means for improving the static dissipative properties of NR latex films. It was anticipated that an increased level of static dissipation is attainable by blending NR latex with polar latex such as the DMAEMA-grafted NR latex.

## MATERIALS AND METHODS

### Latex and Blends Preparation

Blends of DMAEMA-grafted NR latex with different DMAEMA loading and 30% total solid content (TSC) sulphur prevulcanised NR latex were prepared in different ratios as shown in *Table 1*. The details of the preparation of the DMAEMA-grafted NR latex is described elsewhere<sup>8</sup>. The blending was conducted at room temperature using a mechanical stirrer. Films with thickness of *ca* 0.5 mm were then obtained by casting on glass plates and left to stand at room temperature to dry.

TABLE 1. FORMULATION FOR THE PREPARATION OF DMAEMA GRAFTED NR AND NR BLENDS

Ingredients	Control	Parts by weight Blends			
		A	B	C	D
Sulphur prevulcanised NR latex (30% TSC, Top Tex Latex, Malaysia.)	100	90	80	90	80
DMAEMAx grafted NR latex*	—	10	20	—	—
DMAEMAy grafted NR latex*	—	—	—	10	20
Non-ionic surfactant (10% w/w)	1.0	1.0	1.0	1.0	1.0
Potassium hydroxide (10% w/w)	1.0	1.0	1.0	1.0	1.0

\*DMAEMA-grafted latex (30% TSC) containing x = (7) % and y = (21) % DMAEMA by weight

### Surface Resistivity Measurements

Measurements were conducted using a Megohmmeter Ohm-Stat RT 1000 (Static Solutions Inc). The measurements were carried out on both surfaces of the samples.

### FTIR-ATR Spectroscopy

The spectra of the films surfaces were obtained using a Perkin-Elmer Spectrum 2000 FTIR spectrophotometer on a Benchmark series ATR flat top plate accessory with a 45° ZnSe crystal. A hundred twenty-eight scans were accumulated with a resolution of 4 cm<sup>-1</sup>.

### Contact Angle and Surface Energy Measurements

Contact angles at equilibrium in an enclosed thermo-regulated cell maintained at 25°C and relative humidity of 60% were determined using water and ethylene glycol on a KRÜSS G-10 Contact Angle Measurement System. The surface energy of the films was then derived from contact angles measured using ethylene glycol, employing the *Equation of State* method.

### Surface Resistivity Measurements

Surface resistance ( $R_s$ ) indicates the ratio of a DC voltage ( $V_d$ ) to a current flow ( $A_s$ ) between two electrodes of a particular material, whilst surface resistivity is a measurement of the surface resistance of a material that is determined by the ratio of DC voltage drop ( $V_d$ ) per unit length ( $L$ ) to the surface current per unit width<sup>9</sup>. The latter could be correlated to surface resistance by *Equation 2*, whereby,  $R_a$  is the outer radius of the centre electrode

and  $R_b$  is the inner radius of the outer ring electrode of a concentric ring probe<sup>10</sup>. Surface resistivity is expressed in ohms per square (ohms/sq), independent of the physical dimension of the material; hence the term square could be related to any unit of surface area. By measuring the surface resistivity, static dissipation effect of a material could be determined, in which higher level of static dissipation is indicated by lower values of surface resistivity.

$$\text{Surface resistance } (R_s) = \frac{V_d}{A_s} \quad \dots 1$$

$$\text{Surface resistivity} = R_s \times \frac{2\pi}{\ln R_b/R_a} \quad \dots 2$$

Measurements were conducted using a Megohmmeter Ohm-Stat RT 1000 (Static Solutions Inc.). The measurements were carried out on both surfaces of the samples after conditioning at 25°C and 50% relative humidity.

## RESULTS AND DISCUSSION

It is generally believed that the electrostatic dissipating ability of amphiphilic polymer containing polar groups could be attributed to the hygroscopicity of its hydrophilic segments<sup>11</sup>. The results of surface resistivity measurements (*Table 2*) indicated that the incorporation of DMAEMA-grafted NR latex reduced the films resistivity, which could possibly be contributed by the presence of hydrophilic segments or moiety of the DMAEMA-grafted latex. A significant decrease was observed in the blend that contained the highest concentration of the grafted latex. In general, the results suggested that certain NR/grafted NR ratio and monomer loading of the grafted NR latex is required to achieve a desired level of

static dissipation. The possible explanation is that both higher ratio level and monomer loading contributed to a higher amount of the hydrophilic segments in the films and consequently to increase the level of static dissipative properties.

The measurements of contact angle are widely used in the evaluation of material surface characteristics for instance wettability, hydrophilicity and surface energy. The contact angle values could be related to surface energy based on the Young's equation,  $\gamma_s = \gamma_{sl} + \gamma_l \cos \Theta$ , and its derivation,  $\cos \Theta = -1 + 2(\gamma_s/\gamma_l)^{-1/2} e^{-\beta(\gamma_l - \gamma_s)}$ , where,  $\gamma_s$  denotes the surface tension of solid-vapour interface,  $\gamma_l$  corresponds to surface tension of liquid-vapour interface and  $\beta$  is a constant with a value of 0.00001247<sup>12</sup>. The validity of the *Equation of State* approach in the determination of surface energy has been argued<sup>13</sup> and it is shown not to agree with other methods of determination such as the Surface Component Theory<sup>14</sup>. Nonetheless, surface energy determination in this work was conducted on similar conditions and hence, the values obtained indicate comparative changes in surface energy.

Further changes in the film surface properties are clearly demonstrated by contact angles and surface energy values (*Table 3*). The lower the contact angle values, the higher the surface wettability and hydrophilicity. It is shown that better wettability and hydrophilicity are achieved in the films that contained higher ratio of the DMAEMA-grafted latex at the air-facing surface; consequently, an increased level of surface energy is exhibited. The results also indicated that there are differences between the air-facing and former-facing surface in the surface energy and wettability. The lower surface resistivity related to antistatic properties however is not at the air-facing surface and therefore could be indicative of a bulk property.

## FTIR-ATR Spectroscopy

The spectroscopy technique is used to determine relative changes in the surface chemical composition of the latex films. The changes in the surface could be attributed to the emergence of oxygenated groups in the regions of 1030 to 1100  $\text{cm}^{-1}$  or 1600 – 1800  $\text{cm}^{-1}$  (*Figure 1*). The oxygenated compounds in the control NR latex film may be due to latex stabiliser or surfactant present in the latex<sup>15,16</sup>.

The IR spectroscopy revealed the differences in the selective migration of the functional group that is observed in the film obtained. In graft polymerisation of NR latex, the surfaces of latex particles usually act as the loci of polymerisation, as such, it is believed that the grafted polymer particles are free to rearrange during film formation.

During latex film formation, the selective accumulation of a functional group is dependent on polymer mobility and the conformational difference as observed in poly (methyl methacrylate) solvent cast film<sup>17</sup>. Wu *et al.*<sup>18</sup> reported the preferential migration to surface regions of hydrophilic polyurethane segments in composite latex film. However, the reported occurrence<sup>17,18</sup> whereby hydrophilicity is more pronounced in former-facing surface was not observed. It is found that the air-facing surface of the latex blends displayed enhanced surface properties (better wettability and a higher level of surface energy) that may suggest the air-facing surface is more hydrophilic than the former-facing surface. The observed differences from the previous work could be attributed to the differences in the type of latex and the modification that took place. It is postulated that the preferential migration of grafted polymer on the surface of individual particles occurred after adsorption to the air surface followed by rearrangement and

TABLE 2. SURFACE RESISTIVITY MEASUREMENTS

Type of latex	DMAEMA in grafted NR latex wt (%)	NR/Grafted NR (weight ratio)	Surface resistivity of film* $\Omega/\text{square}$	
			Air-facing	Former-facing
Control	0.0	100/0	$2.6 \times 10^9$	$2.5 \times 10^9$
Blend A	0.7	90/10	$2.4 \times 10^9$	$2.8 \times 10^9$
Blend B	1.4	80/20	$7.0 \times 10^8$	$6.9 \times 10^8$
Blend C	2.1	90/10	$4.0 \times 10^8$	$1.3 \times 10^8$
Blend D	4.2	80/20	$9.8 \times 10^7$	$6.8 \times 10^7$

\* Means of three replications

TABLE 3. ETHYLENE GLYCOL CONTACT ANGLE AND SURFACE ENERGY OF NR/GRAFTED-NR BLENDS CAST FILMS

Type of latex	NR/Grafted NR (Weight ratio)	Contact Angle/ $\theta^*$		Total Surface Energy (mN/m)	
		Air-facing	Former-facing	Air-facing	Former-facing
Control	100/0	$65.2 \pm 0.5$	$64.7 \pm 1.2$	27.0	26.8
Blend A	90/10	$64.3 \pm 0.5$	$67.3 \pm 0.4$	25.9	27.2
Blend B	80/20	$63.1 \pm 1.9$	$69.1 \pm 0.5$	27.8	25.0
Blend C	90/10	$55.1 \pm 1.3$	$76.4 \pm 0.2$	32.2	21.6
Blend D	80/20	$41.3 \pm 0.8$	$62.5 \pm 2.0$	37.5	28.0

\*Means of three replications, all values of contact angle are in degrees. Total surface energy is calculated from the contact angle values of ethylene glycol.

partitioning based on coverage of DMAEMA during evaporative drying and particle coalescence. Hence, more hydrophilic moiety of the graft polymer may be concentrated at the air-facing surface.

### CONCLUSIONS

Improvement in static dissipative properties and other surface related properties such as surface energy and contact angle of cast latex films could be obtained by blending

prevulcanised NR latex with DMAEMA-grafted NR latex. The results obtained suggested that the blend ratio and the amount of monomer loading of the grafted latex in the blends influenced the relative changes in surface properties. The enhancement in wettability was shown to be more pronounced at the air-facing surfaces of the latex films in comparison to the former-facing surfaces which indicated better antistatic properties.

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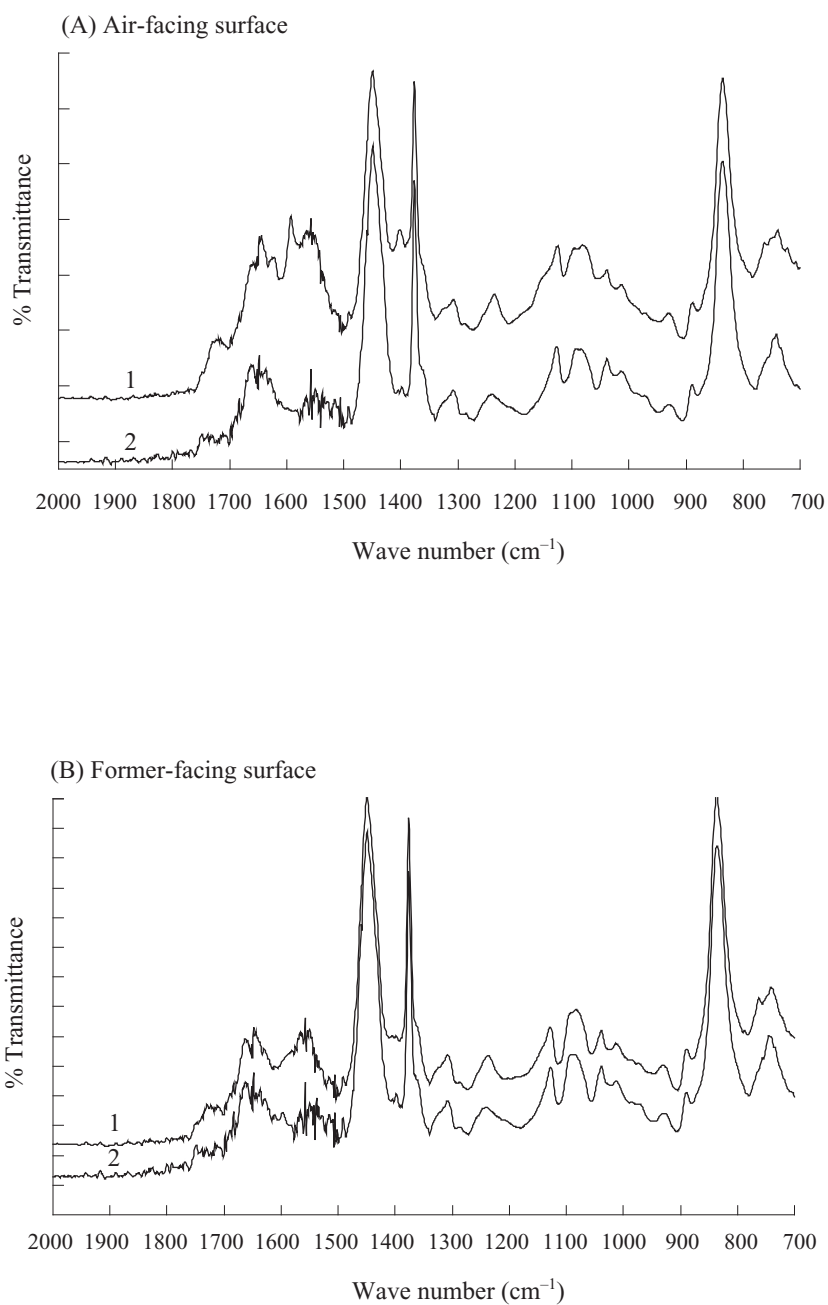


Figure 1. Typical FTIR-ATR spectra of air-facing surface and former-facing of the latex blends films.

1:  $\text{NRG}_{20}$  (D), 2: PVNR. Shown are the surface changes attributed to the IR region of  $1800 - 1600$  and  $1100 - 1000 \text{ cm}^{-1}$ .

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