



## Preparation and Characterisation of Poly(Dimethylaminoethyl Methacrylate) Grafted Natural Rubber (PDMAEMA-g-NR)/Poly(Vinyl Alcohol) Blend Membranes

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Received 1<sup>st</sup> April 2014; Accepted 20<sup>th</sup> April 2014.

Editor in Chief: Dr. K.S.V. Krishna Rao; Guest Editors: Dr. Siddaramaiah, Dr. G. M. Shashidhara.

Presented at the POLYCON-2014, 6<sup>th</sup> National Conferences on Advances in Polymeric Materials [Energy, Environment & Health] (NCAPM), Mysore, India, 25-26 April 2014.

### ABSTRACT

Natural rubber latex (NRL) technology has by now attained an unchallengeable status due to its unique features and industrial importance. In the present work, NR has been chemically modified by seeded emulsion polymerization using cumene hydroperoxide (CHP)/tetraethylene pentamine (TEPA) initiator system and dimethylamino ethylmethacrylate (DMAEMA) as the monomer. The modified latex showed a significant increase in the colloidal stability at low pH. After removing the homopolymers, monomers and initiators by dialysis, the treated latex was blended with PVA, a hydrophilic polymer and casted into membranes. The blend membranes were characterized in terms of mechanical properties, morphology (using SEM) and compatibility (using FTIR). The particle size was examined using dynamic light scattering (DLS).

**Keywords:** Natural rubber latex, redox initiation, grafting, PDMAEMA, PVA.

### 1. INTRODUCTION

Natural rubber latex is a biomacromolecule, having cis-polyisoprene particles dispersed in aqueous medium. The excellent elastomeric properties make NR a highly utilized bio material [1]. Its excellent physical properties make it a highly preferred material for a variety of applications [2]. Its applications in various fields often require reinforcing by fillers, physical blending with other polymers or chemical modification of the polymer particle morphology [3].

Polyvinyl alcohol is a water soluble synthetic polymer. It is a macromolecule of great interest because of its desirable characteristics such as hydrophilicity, good film forming ability, resistance to oxidation and excellent mechanical properties [4]. It has also been employed for different pharmaceutical and biomedical applications [5, 6].

In the present work NRL was chemically modified with DMAEMA by using redox initiator system CHP/TEPA. The modified systems were physically blended with PVA and casted into films. The characterization has been done in terms of mechanical properties, morphology and

compatibility.

### 2. EXPERIMENTAL

#### 2.1. Materials:

Natural rubber latex (NRL) used in this study was a commercial sample purchased from a rubber plantation at Thekkumkutti, Calicut, Kerala. Dimethyl aminoethylmethacrylate (DMAEMA) monomer and tetraethylene pentamine (TEPA) co-initiator were purchased from Aldrich, Germany. Sodium dodecyl sulfate (SDS) and cumene hydroperoxide (CHP) were procured from Alfa Aesar, Briton. PVA used for blending was purchased from Fischer Scientific, India with a molecular weight in the range 80,000 - 1, 20,000. All the chemicals were used as such without further purification.

#### 2.2. Fourier Transformation Infrared (FT-IR) spectroscopy

The grafted linkages and the compatibility of blended systems were examined by FTIR spectroscopy using the spectrometer (Thermo Nicolet 5700, USA) in the range of 4000 to 500  $\text{cm}^{-1}$ . Casted grafted and blended films were scanned as such in ATR mode.

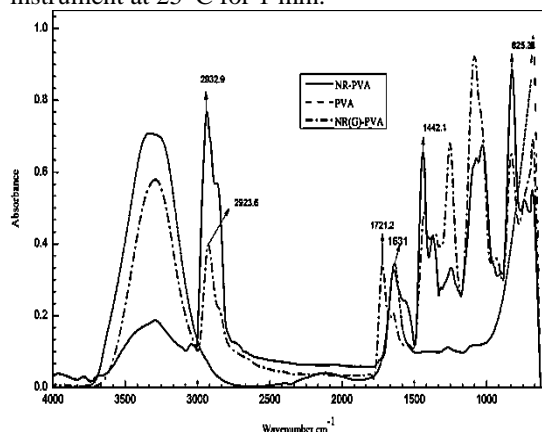
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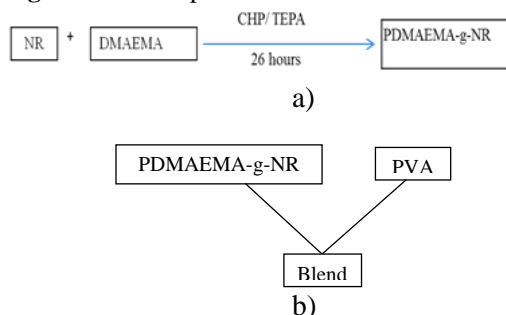
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### 2.3. Dynamic Light Scattering (DLS)

The change in NR particle size before and after grafting was examined using Malvern ZS nano instrument at 25 °C for 1 min.



**Figure 1:** FTIR spectrum of blends and PVA



**Scheme 1:** a) Grafting of hydrophilic monomer DMAEMA onto NRL b) Preparation of blend from the modified latex and PVA

### 2.4. Mechanical Properties

The patches were cut into rectangular shapes and their mechanical characteristics were monitored in terms of Young's modulus and ultimate tensile strength (UTS) using Tinius Olsen H10KS having a load range of 10 kN. The 10 mm × 30 mm patches

were examined with the gauge test length of 10 mm and the cross-head speed of 10 mm/min (slightly modified ASTM D412).

### 2.5. Scanning electron microscope (SEM)

Cross-section of the samples was scanned using a Hitachi Su 66000 SEM for studying the morphology of the blended systems.

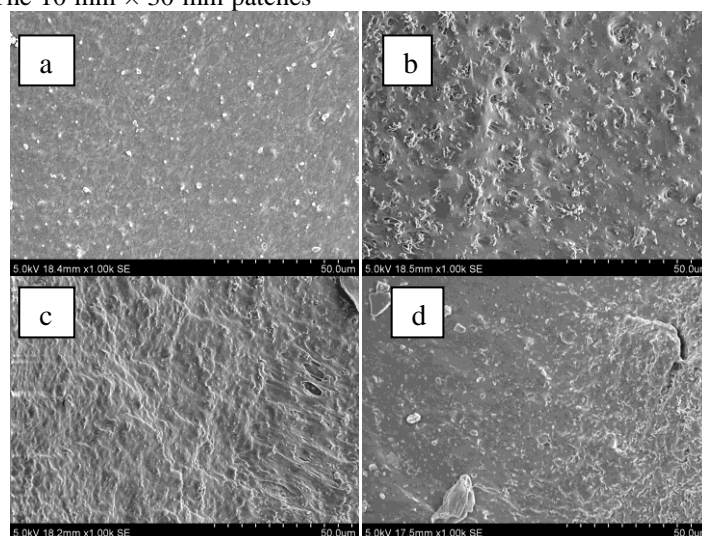
## 3. RESULTS AND DISCUSSION

### 3.1. Fourier Transformation Infrared (FT-IR) spectroscopy

Figure 1 shows the FTIR spectra of PVA, NR-PVA and NR (G)-PVA blends scanned in the range of 1000 to 4000  $\text{cm}^{-1}$ . The peak at 2932.9 and 2923.6  $\text{cm}^{-1}$  were due to C-H stretching in NR and the peak at 1631  $\text{cm}^{-1}$  corresponds to the C-O stretching in PVA. Also, PVA produced a peak at 3342.5  $\text{cm}^{-1}$  due to stretching vibration of OH group. There occurs a peak in the range 3059-3567.9  $\text{cm}^{-1}$  in NR (G)-PVA, which is due to the Hydroxyl group from PVA and the NH group from the PDMAEMA. The peak at 1721.2  $\text{cm}^{-1}$  corresponds to C=O stretching of the ester group derives from PDMAEMA grafted to NR. Thus the major peaks of NR, PVA and PDMAEMA were also found in the NR (G)-PVA blended patches. No additional peaks apart from those of the basic materials were found for the polymer blends. This shows the absence of any chemical interactions between NR and PVA.

### 3.2. DLS studies

The study was done with ungrafted latex and grafted latex. Table 1 shows the particle size and polydispersity index (PDI) of the latex. The study shows that the particle size increased as the grafting was executed.



**Figure 2:** SEM images of: a) NR-PVA, b) NR (G)10-PVA, c) NR(G)15-PVA and d) NR(G)20-PVA.

**Table 1.** The Particle sizes and PDI.

S.No	Sample	Average dia (nm)	PDI
1	NR latex	765.6	0.590
2	PDMAEMA-g-NR	805.6	0.515
3	PDMAEMA-g-NR	1221	0.615
4	PDMAEMA-g-NR	1644	1.000

### 3.3. Mechanical Properties

Mechanical properties of the systems were measured in terms of tensile strength and modulus. Both the properties show an increasing trend (Table 2) with an increase in grafting percentage and blending with PVA.

**Table2.** Mechanical Properties of the blends.

S.No	Sample	Tensile strength (MPa)	Modulus (MPa)
1	NR- PVA	2.837	3.4
2	NR (G) 10-PVA	3.618	4.1
3	NR (G) 15-PVA	4.067	6.1
4	NR (G) 20-PVA	4.375	8.1

### 3.4. Morphology

The morphology of the blended systems was analysed by using SEM. Noticeable changes have been observed in the morphology of the blended samples as shown in Figure 2. The surface became more homogeneous as the grafting enhanced.

## 4. CONCLUSION

Grafting DMAEMA onto NR has been done in the latex phase by using redox initiators. It was then blended with PVA. The FTIR spectra of the blended systems show the compatibility of the system. The morphology analysis of the samples also confirms the observation. DLS also highlighted the success in grafting process. Mechanical properties of the systems were also

enhanced as grafting and blending increased. The modified system is currently being examined for its biomedical applications.

## 5. REFERENCES

- [1]. W. Wongthep, S. Srituileong, S. Martwiset, S. Amnuaypanich, (2013) Grafting of poly(vinyl alcohol) on natural rubber latex particles, *Journal of Applied Polymer Science*, **127**: 104-110.
- [2]. P. C. Oliveira, A. Guimaraes, J. Y. Cavaille, L. Chazeau, R. G. Gilbert, A. M. Santos, (2005) Poly(dimethylaminoethyl methacrylate) grafted natural rubber from seeded emulsion polymerization, *Polymer*, **46**: 1105–1111.
- [3]. A. Bogner, A. Guimaraes, R. C. O. Guimaraes, A. M. Santos, G. Thollet, P. H. Jouneau, C. Gauthier, (2008) Grafting characterization of natural rubber latex particles: wet-STEM imaging contributions, *Colloid and Polymer Science*, **286**: 1049-1059.
- [4]. A.M. Mathur, S. K. Moorjani, A. B. Scranton, (1996) Methods for synthesis of hydrogel networks: a review, *Journal of Macromolecular Science-Reviews in Macromolecular Chemistry and Physics*, **36**: 405-430.
- [5]. C. C. DeMerlis, D. R. Schoneker, (2003) Review of the oral toxicity of polyvinyl alcohol (PVA) *Food and Chemical Toxicology*, **41**: 319-326.
- [6]. K. C. S. Figueiredo, T. L. M. Alves, C. P. Borges, (2009) Poly(vinyl alcohol) films crosslinked by glutaraldehyde under mild conditions, *Journal of Applied Polymer Science*, **111**: 3074-3080.