VERSATILE NEW CLASS OF POLYMER FOR NATURAL AND SYNTHETIC RUBER GLOVES COATING

Dr. Shashidhar V. Govindaraju, Mr. Chetan Kulkarni Apcotex Industries Limited India And Mr. Khoo Siong Hui, Le Inoova Sdn Bhd, Malaysia

ABSTRACT

Powder coating and chlorination are the widely used processes for achieving good donning properties although polymer coating is also in practice with limited reach. With many restrictions being imposed on powder coated gloves, chlorination process is expected to assume bigger role although it poses many challenges like plant corrosion and health hazard. Taking the environmental restrictions in to consideration the future seems to be with only polymer coating (Polyacrylic or Polyurethane), which is very compatible with both glove and environment.

This study introduces a new class of polymer, namely <u>specialty carboxylated Styrene-Butadiene latex</u>, which is widely used in various coating applications, for its long-lasting donning performance. It outperforms Acrylic emulsion for its higher binding strength and elasticity that makes it more suitable for coating both Natural rubber gloves and Synthetic rubber gloves. While matching Polyurethane coating properties it possesses higher versatility in formulation tweaking for vast application conditions, yet providing better cost effectiveness. Relevant research data is presented for the excellent donning performance by the new class of polymer for both Natural rubber gloves (NR) and Nitrile rubber gloves.

BACKGROUND

It is known that rubber gloves are extensively used in various fields which include housekeeping, medical, food and the like for seeking protection against infection, contagious disease, chemicals, solvents, chemotherapy drugs, cuts, bruises and static electricity. Natural rubber gloves and nitrile rubber gloves find predominant share in the above applications due to their versatility and affordable cost. Various synthetic materials used for manufacturing gloves include carboxylated nitrile latex, and polychloroprene latex.

Though intended protection for the user is the key criterion for the success of any glove, its ease of wearing or donning and comfort while wearing also plays a pivotal role. One of the conventional methods for improving donning properties of gloves includes use of powder based lubricants. However, it suffers from many drawbacks. Powder gets easily dislodged during use, it increases the chances of contamination and it may cause allergies. The trend has predominantly shifted to powder-free gloves. Another known technique to improve donning properties of gloves, by reducing tackiness and decreasing the coefficient of friction of rubber, is chlorination of rubber surfaces. However, chlorination is associated with several disadvantages. It adversely affects the mechanical properties of the gloves material, may render the material brittle, unpleasant odor and also poses discoloration issues. Coating glove surfaces with various types of materials to introduce a layer with different surface characteristics to reduce surface friction of rubber in order to improve donning properties is known. A wide variety of materials have been used for coating glove surfaces. For example, U.S. Patents 4,499,154¹ and U.S. 4,575,476² teach coating hydrophilic hydrogel materials on the inner surface of a glove. U.S. Patent No. 5,088,125³ discloses coating the hand contacting surface of a glove with a blend of ionic polyurethane and other polymeric material. US 2003/0175500⁴ discloses an aqueous coating material with high Tg that employs a (meth) acrylic emulsion polymer for manufacturing powder free gloves. There is also disclosed in EP 2 581 100⁵ a method of coating gloves with polyisoprene latex based coating composition.

Presently acrylic polymer is widely used for polymer coating application on both NBR and NR gloves. However, the present study concludes that Styrene-Butadiene based specialty modified polymer can serve as a versatile polymer coating material for NBR and NR gloves due to its special features like higher hydrophobicity, rubber character, and binding strength.

TECHNICAL THEORY

Dispersion, emulsion and latex are the generally used terms for polymers that are used in glove industries. The dispersion indicates the presence of two phases where finely dispersed solid particles are present in a continuous liquid phase. In the case of latex, polymer particles are distributed in water phase. Naturally occurring polymer emulsion is natural rubber latex, where the polymer particles are stabilized by proteins. In case of synthetic emulsion, polymer particles are stabilized by various types of emulsifiers. Generally synthetic polymer emulsion is very stable to mechanical shear and chemical shock on account of suitably designed particle size, anionic charges and emulsifier levels.

There are various components required in formulating latexes: synthetic ingredients such as monomer(s), surfactants, and initiator and post-synthesis ingredients such as biocides added to serve a specific purpose. Ingredients affect both the rate at which latex particles are synthesized and the composition and characteristics of the final product.

In styrene acrylic emulsion, which is predominantly used in polymer coating application, styrene and acrylate repeating units form the backbone, in which acrylates are hydrophilic in nature. Carboxylation of the polymer increases hydrophilicity further and also imparts stability. Styrene-Acrylic polymers are generally with less elastic properties, thus their elongation is comparatively low to that of natural rubber. This difference in property during stretching may cause the acrylic coating to crack and possibly delaminate or separate from the natural or synthetic rubber surfaces.

In Carboxylated Styrene Butadiene emulsion Styrene and Butadiene repeating units form the backbone, in which both the units are hydrophobic in nature. This hydrophobic nature makes Styrene Butadiene polymer more compatible and suitable for polymer coating on natural rubber gloves which is hydrophobic in nature. However, carboxylation of Styrene Butadiene latex introduces optimal level of hydrophilicity that makes Carboxylated Styrene Butadiene latex a versatile polymer for polymer coating application on both NR and NBR rubber gloves. Specialty of Styrene Butadiene polymer includes its adhesion to rubber substrates and hydrophobicity.

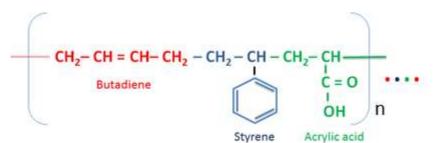


Fig. 1 Carboxylated Styrene-Butadiene copolymer

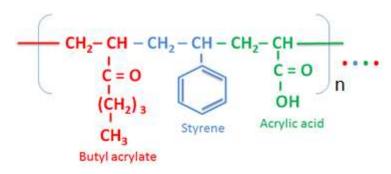


Fig. 2 Styrene Acrylic copolymer

Specialty Carboxylated Styrene Butadiene latex (XSB) used in the study was produced with state of the art emulsion technology followed by effective steam stripping to reduce VOC to standard limits. Base polymer emulsion was suitably modified with required additives to achieve lubrication, anti-blocking, wetting and spreading. Final formulation was characterized by total solid content, pH, viscosity and particle size as given below. Diluted version is also tabulated below.

Properties	Specification		
Appearance	Milky white viscous emulsion		
Total Solids (%)	20.0 <u>+</u> 1.0		
pH at 25°C	9.0 <u>+</u> 0.5		

Surface Tension (dynes/cm)	32 ± 5		
Viscosity (cps)	2000±500		

Table 1 Carboxylated Styrene Butadiene (XSB) based formulated latex properties

Generally, polymer coating application of glove surfaces is carried out at 1.5% to 2.0% dilution level of original emulsion formulation. The specification of diluted Carboxylated Styrene-Butadiene emulsion that is ready for coating application is given below:

Properties	Specification		
Appearance	Milky white emulsion		
Total Solids (%)	2.0 <u>+</u> 0.2		
pH at 25°C	9.0 <u>+</u> 0.5		
Surface Tension (dynes/cm)	32 ± 5		
Viscosity (cps)	20 MAX		

Table 2 Properties of diluted Carboxylated Styrene Butadiene based formulation latex

EXPERIMENTATION

Polymer coating experiments are carried out for both natural rubber gloves and nitrile rubber gloves as under:

- 1. Pre-heating ceramic former at about 80⁰C for 5-10 min;
- 2. Dipping the ceramic former in a coagulant solution (20% aqueous solution of calcium nitrate) for 5 sec;
- 3. Drying the ceramic former at about 80⁰C for 5 min;
- 4. Dipping the ceramic former in natural latex compound or Synthetic latex compound for 10 sec;
- 5. Drying the ceramic former at about 80⁰C for 5 min;
- Leaching the glove surface deposited on ceramic former at 60-70⁰C hot water for 2-3 min followed by imparting beading on the glove for easy release;
- 7. Dipping the glove surface deposited on ceramic former in polymer coating solution for 5 sec, dripping out the excess coating solution from the glove surface to form a uniform polymer coating;
- 8. Subjecting the polymer coated glove deposited on the ceramic former to vulcanization at about 100[°]C for 25 min to obtain a cured glove;
- 9. Subjecting the cured glove to leaching the cured glove formed on ceramic former at about $60-70^{\circ}$ C hot water for 2-3 min;
- 10. Stripping the polymer coated glove from ceramic former after cooling.

COATING PERFORMANCE EVALUATION

Coefficient Of Friction (COF) testing

Provided herein below is comparative test data from measurement of coefficient of friction for uncoated rubber gloves and gloves coated with Carboxylated Styrene Butadiene based formulation and Styrene Acrylic based formulation (market sample).

Name of test: Coefficient of friction test

Standards as reference: ASTM D1894

Name of equipment: Universal testing machine Gotech AI-3000 and COF text fixture

Setting parameter: Testing speed = 150 mm/min.

Properties		Natural rubber			Nitrile rubber		
		Uncoated Natural rubber	2% XSB	2% Polyacrylics	Uncoated Nitrile rubber	2% XSB	2% Polyacrylics 120
	Cuff	1.263	0.245	0.189	TBD	0.220	0.223
Static COF	Palm	1.263	0.154	0.156	1.163	0.158	0.259
	Finger	1.415	0.200	0.241	TBD	0.158	0.308
	Cuff	1.222	0.183	0.177	TBD	0.156	0.188
Kinetic COF	Palm	1.222	0.128	0.143	1.129	0.136	0.232
	Finger	1.348	0.168	0.202	TBD	0.141	0.288

Table 3 Comparative data of COF for uncoated and Carboxylated Styrene Butadiene based composition and Styrene Acrylic based composition coated natural rubber gloves and nitrile rubber gloves

Mechanical properties

Provided herein below is comparative test data form measurement of mechanical properties for uncoated rubber gloves and gloves coated Carboxylated Styrene Butadiene based composition and Styrene Acrylic based composition

Name of test: Mechanical properties of Dumbbell shaped rubber films

Standards as reference: ASTM D6319 standard

Name of equipment: Dak system Inc Make model no. UTM9052, Serial no. 353/11-12

Sample specification: Uncoated and polymer coated natural and nitrile rubber gloves

Shape: Dumbbell shaped film

Length: 150 mm

Width: 06 mm

Thickness: 0.12 mm

	Natural rubber gloves			Nitrile rubber gloves		
Properties	Uncoated natural rubber	2% XSB	2% polyacrylic s (market sample)	Uncoated nitrile rubber	2% XSB	2% polyacrylics (market sample)
Tensile Strength (MPa)	20-23	20-22	19-21	24-26	25-27	24-26
Elongation (%)	750-1000	730-900	690-850	510-540	490-540	450-510
Modulus at 500% (MPa)	3-4.5	3.3-5.6	3.5-5.5	17-20	18-20	19-21

Table 4 Comparative data of uncoated rubber gloves and gloves coated Carboxylated Styrene Butadiene based composition and Styrene Acrylic based composition

Scanning Electron Microscopy (SEM) images of uncoated and polymer coated natural and nitrile gloves:

Below provided is the surface view using Scanning Electron Microscopy (SEM) of uncoated NR and NBR gloves and gloves coated Carboxylated Styrene Butadiene (XSB) based composition and Styrene Acrylic based composition.

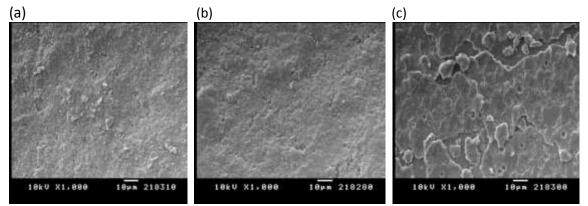


Fig.3 SEM images (a) surface view of uncoated natural rubber glove (b) surface view of 2% XSB coated natural rubber glove (c) 2% Styrene Acrylic based coated natural rubber glove

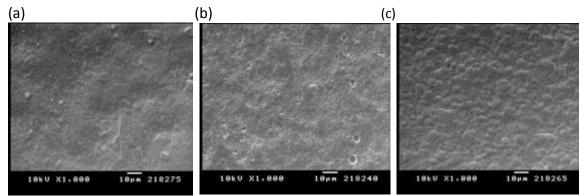


Fig.4 SEM images (a) surface view of uncoated nitrile glove (b) surface view of 2% XSB coated nitrile glove and (c) 2% Styrene Acrylic coated nitrile glove

Prufbau Verity images of uncoated and polymer coated natural and nitrile gloves

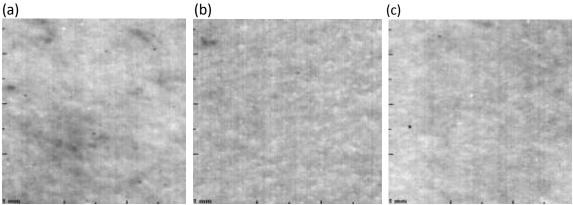


Fig.5 Prufbau images (a) surface view of uncoated natural rubber glove, (b) surface view of 2% XSB coated natural rubber glove and (c) 2% Styrene Acrylic coated natural rubber glove

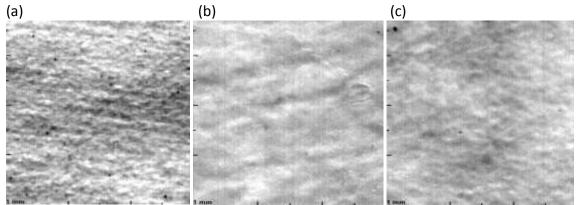


Fig.6 Prufbau images (a) surface view of uncoated nitrile glove (b) surface view of 2% XSB coated nitrile glove (c) 2% Styrene Acrylic coated nitrile glove

RESULTS AND DISCUSSION

Performance of the polymer coating with the experimental versatile carboxylated SB latex and the market acrylic latex were compared in terms of coefficient of friction (COF) of various points of the glove. Cuff, palm and finger parts were chosen to measure the COF to infer the ease of donning. Performance of the polymer coating latexes were tested on both nitrile gloves and natural rubber gloves. Table 3 gives values COF at three different points of the glove for both types of the gloves. Measurements of COF were taken both in static and kinetic condition for better understanding of the intended performance. As expected uncoated surfaces of natural rubber gloves and nitrile rubber gloves have rougher surface that resist easy donning. Polymer coating reduced the COF about by 8 to 10 times. For both static and kinetic COF carboxylated SB latex gave lower values that indicate the better donning properties. These lower values sufficiently prove the versatility of carboxylated SB latex based polymer coating for ease of donning.

Mechanical properties of the polymer coated natural rubber gloves and nitrile rubber gloves are tabulated in Table 4. Tensile strength, percentage elongation and modulus at 500% elongation are compiled for all uncoated and polymer coated gloves. Results indicate that polymer coating does affect the mechanical properties to some extent. In natural rubber gloves elongation dropped to less extent in case of carboxylated SB polymer coating compared to that of acrylic polymer coating on account of its better compatibility and flexibility. Similar trend was also observed in nitrile gloves. Lower drop in the values are due to flexibility of carboxylated SB latex. Rise in the modulus after polymer coating signifies the stiffening of glove films in both natural rubber gloves and nitrile rubber gloves.

Scanning electron microscopy (SEM) images gave actual visualization of polymer coating on the gloves surfaces. a, b and c images of Fig. 4 offer the visualization of carboxylated SB coating and Acrylic latex coating on nitrile gloves. At 1000X magnification Carboxylated SB coatings are observed to be uniform and properly

deposited. These visual observations are already converted to better COF values. SEM images in Fig. 3 give the visualization of polymer coating for natural rubber gloves, which are more hydrophobic in nature. Because of higher hydrophobic nature, carboxylated SB polymer coatings gave very good compatibility with glove surface, whereas Acrylic coatings are observed to be non-uniform on account of more hydrophilic nature. This visualization is already quantified in terms of COF values.

Prufbau verity images in Fig. 5 and Fig. 6 for natural rubber glove surface and nitrile rubber glove surface respectively, with and without polymer coating, also gave good visualization of surface at 3000 ppi resolution images. Both natural rubber glove surfaces and nitrile rubber glove surfaces images found to be more uniform with carboxylated SB polymer coating. Acrylic coating gave relatively rougher and non-uniform film deposition.

SUMMARY

Carboxylated Styrene Butadiene based polymer coating for both natural rubber gloves and nitrile rubber gloves, proves to be imparting the most efficient donning property compared to that of Acrylic polymer coating. Coefficient of friction values and surface image analysis prove fact beyond any doubt. Higher hydrophobicity, high elongation and good bonding combinedly appear to be making Carboxylated Styrene Butadiene polymer coating a very good choice for polymer coating to produce powder free gloves with long lasting donning properties.

Acknowledgment:

The authors express their sincere gratitude to the management of Apcotex Industries Limited, India for allowing to present the paper at 9thInternational Rubber Glove Conference & Exhibition 2018.

REFERENCES

- 1. Michael H. James, David M. Bratby Roger Duck, Howard I. Podell, Albert Goldstein, David C. Blackley U.S. patent no. 4499154
- 2. Howard I. Podell, Albert Goldstein, David C. Blackley, Michael H. James, David M. Bratby, Roger Duck (London) U. S. patent no. 4575476
- 3. Christopher W. Ansell, Nicholas Medcalf, Peter W. Williams U.S. patent no. 5088125
- 4. Apala Mukherjee, Chaodong Xiao U.S. patent no. 2003/0175500
- 5. Wei Cheong Wong, Shiping Wamg, Seong Fong Chen, Chaung Sim Chong EP no. 2 581 100
- 6. H. Warson and C.A. Finch, Application of Synthetic Resin Lattices, Lattices in Surface Coatings
- 7. Developments in Polymer Coatings for Dipped Goods by Bill Howe President, PolyTech Synergies LLC Canal Fulton, Ohio USA
- 8. Fung Bor Chen, *"Overview of Powder-Free Technology and Materials"*, 2004 International Latex Conference Akron, Ohio
- 9. Y.S.T. Yeh, "Powder-free gloves with a silicone impregnated cross-linked polyurethane inner coating and method of making same", US Patent Application No. 20020029402, March 14, 2002