Palm-based Esterquats as an Active Ingredient in Fabric Softeners

Haliza Abdul Aziz*; Zainab Idris*; Parthiban Siwayanan* and Salmiah Ahmad*

INTRODUCTION

The search for renewable resources, specific requirements by certain ethnic communities and growing concern for the environment have increased interest in using plant-based raw materials in household consumer products. The fabric softeners market, which belongs to the luxury product category, is expanding proportionally with the Gross National Products (GNP) and living standards with an annual growth of 3%-8% globally. The Asian market has grown from 50 000 – 75 000 t in 2000 to 50 000 – 100 000 t in 2005 (Levinson, 1999) (*Figure 1*). The main ingredient in the formulation of fabric softeners is cationic surfactants, accounting for 23% of their global consumption (Dan Scheraga, 1998). With the development of new washing machines, having separate automatic dispensers for detergent and fabric softener, consumers are increasingly using softeners because they imparts softness, comfort and fragrance and sometimes, ease of ironing to their laundry. The general trends in fabric softeners is more concentrated products (15%), although the regular product (3%-8%) predominates in many markets in co-existence with the ultra-concentrate (25%-35%).

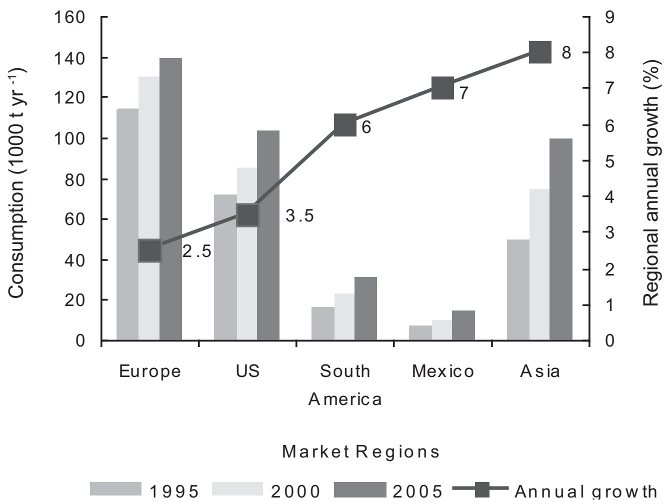
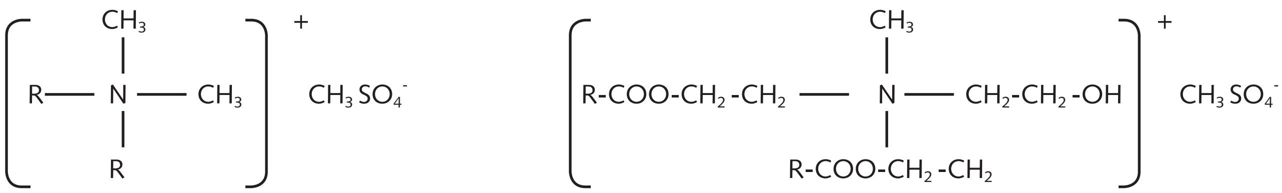


Figure 1. Consumption of fabric softeners worldwide.

* Malaysian Palm Oil Board,
P. O. Box 10620,
50720 Kuala Lumpur,
Malaysia.
E-mail: liza_azi@mpob.gov.my

Esterquats are cationic surfactants, which are increasingly used because of their softening effect and excellent biodegradability compared to the conventional quats. Although the conventional quats (distearyl dimethyl ammonium compounds) also posses excellent softening performance, their poor biodegradation limits their use with stringent environment regulations in developed countries today. Thus, esterquats are becoming the surfactant of choice. Unlike the conventional quats, esterquats has a structure, which consist of at least one ester group between the long alkyl chain and the hydroxyl group of triethanolamine as shown in *Figure 2*. This ester link provides a potential point for easy hydrolysis into fatty acids and small quat molecules (Puchta *et al.,* 1993).

Vegetable-based raw materials are also gaining acceptance over animal-based raw materials. The growing interest in vegetable-based raw materials has created new market niche for fabric softeners. The major market for esterquats is the textile industry, as the worldwide leading ingredient for fabric softener. Apart from fabric care, other applications of esterquats are in hair conditioner, as anti-static in polymers, in bacterial and sanitizer products and products as describe in *Figure 3*.



Distearyl dimethyl ammonium compound

Esterquats

Figure 2. Structures of distearyl dimethyl ammonium compound and esterquats.

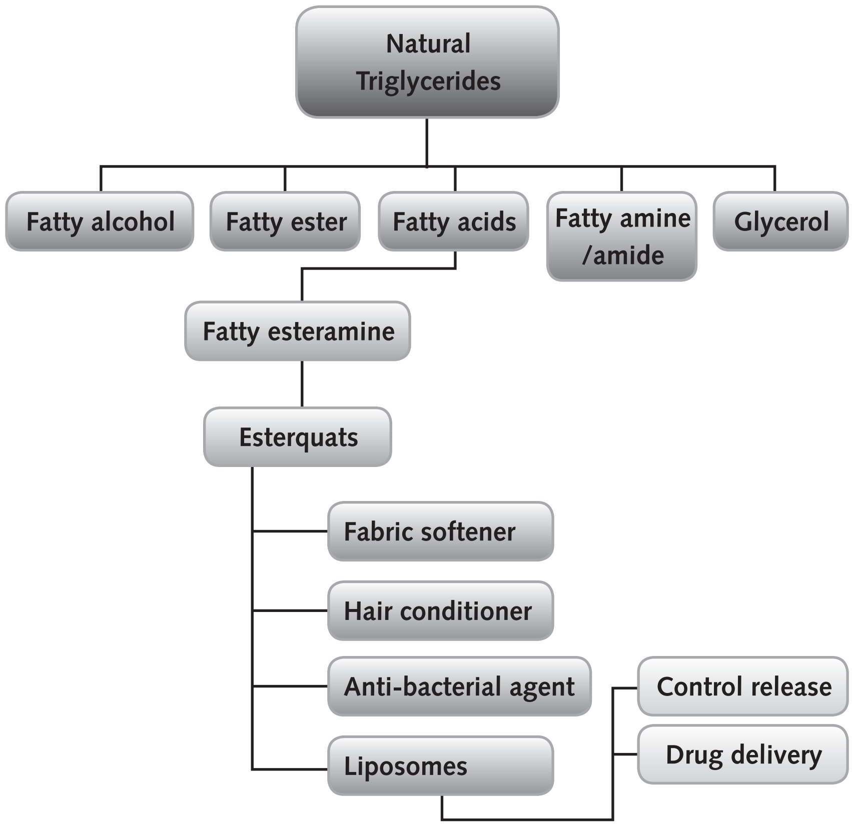


Figure 3. Product and application flow chart.

This article highlights the uses of palm-based esterquats as active ingredient in the production of fabric softeners. The performance of this surfactant is evaluated on the softening, rewetting and anti-static properties on the treated fabric.

PALM-BASED ESTERQUATS

Esterquats molecules contain a positively charged nitrogen atom linked to at least one hydrophobic chain by an ester. The positive charge enables them to be deposited on surface that are normally negatively charged. When the positively charged molecule is adsorbed on the negatively charged surface, the charges are neutralized to provide an anti-static effect for the treated surface. The long hydrophobic chain extends outward, away from the surface to provide a softening and lubrication effect (*Figure 4*).

Research started in MPOB to replace tallow-based esterquats with palm-based esterquats as the primary component in fabric softeners. Tallow-based esterquats dominate the surfactant market for fabric softeners because they have sufficient carbon chains to provide a good softening effect. Nevertheless, their demand is declining due to the fear of infection from mad cow disease (bovine spongiform encephalopathy or BSE). It is thus an appropriate time to develop suitable palm fraction as replacement.

Tallow and coconut oils are the traditional main feedstocks for oleochemicals production. Other oils and fats, competitive in price, can also be used including soyabean oil, fish oil, rapeseed oil, fish oil and sunflower oil. The fatty acid compositions of tallow and coconut oil are quite similar to those of palm oil and palm kernel oil respectively. However, palm oil and palm kernel oil, are more flexible to use as they can be fractionated to olein and stearin. The higher C16 content in palm oil is advantageous over tallow, while the lower of C8 – C10 in palm kernel oil advantageous over coconut oil.

Various palm-based feedstocks can be used to produce esterquats including palm oil fatty acids, pure fractionated fatty acids and blends of palm-based fatty acids. An earlier study by MPOB indicated that the saturated hydrocarbon chains in the raw material will provide good softening power and lubricity as well as good water repellency (Zainab and Salmiah, 1999).

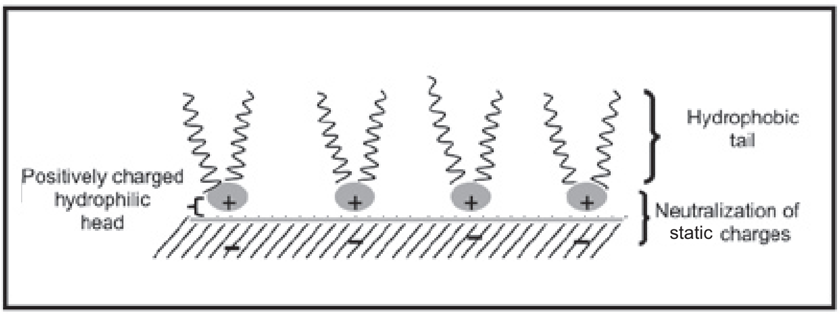


Figure 4. Anti-static and softening effects of esterquats.

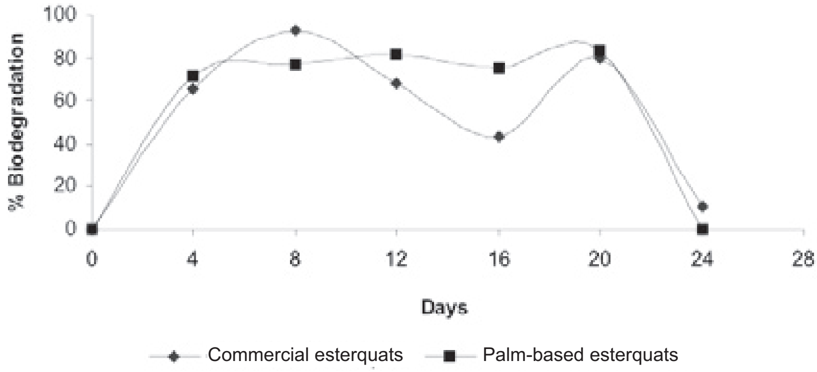


Figure 5. Esterquats biodegradability.

Nevertheless, as the percentage of saturated hydrocarbon chain in esterquats increased, the treated fabric becomes more hydrophobic making the rewetting property more difficult. Rewetting is required to facilitate easy penetration of water and detergent in the next wash. This drawback can be overcome by incorporating a degree of unsaturation in the raw material to enhance the rewetting power of the palm-based esterquats. The selection of raw material for esterquats production is crucial for the performance of fabric softeners. MPOB has found that a palm-based raw materials for esterquats for fabric softeners should have suitable ratio of saturated to unsaturated fatty acids to confer optimum rewetting characteristics, provide some water repellency and, at the same time provide good softening power. The palm-based esterquats produced were also found to be readily biodegradable with characteristics comparable to those of commercial esterquats derived from tallow (*Figure 5*).

In Malaysia, palm-based fatty acids are good alternative feedstocks for the production of environmental-friendly surfactants, since they are from a renewable source. In addition, their abundant supply from the large oleochemicals complex in the country ensures their competitive prices. From *Table 1*, it can be seen that palm oil is the fastest growing compared to other oils, making it the most reliable oil in terms of supply.

Generally, esterquats are produced via a two-stage process in which triethanolamine is esterified with palm-based fatty acids in the presence of a catalyst in the first stage, resulting in the formation of three major products - mono-ester, diester and triesteramine - with water as the by-product. However, tertiary amines are preferred over primary and secondary amines for esterquats because the latter two are also potential precursors for the formation of nitrosamine, a carcinogenic compound. Thus, the reaction mixture is quaternized with a quaternizing agent in isopropanol to introduce the positive charge to the esterquats molecule.

The colour of esterquats is one of the most important criteria in fabric softening formulations. Basically, the esterquats are adsorbed on the negatively charged surface of the fabric where they provide the softening effect. Any colour in the esterquats will therefore affect the colour of the fabrics and therefore, limit their application. Therefore, light-coloured esterquats is preferred to minimize the yellowing effect on white fabrics. The properties of the palm-based esterquats produced are comparable to those of commercial esterquats derived from tallow, particularly the colour of the products (*Table 2*). The colour of esterquats can be improved by incorporating hypophosphorous acid as a catalyst in the esterification stage (Haliza and Zainab, 2003). Besides, applying vacuum in the system and minimizing of exposure to heat also contribute to lighter colour products.

Palm-based esterquats were prepared using a 25 kg batch^{-1} reactor and their properties found comparable to commercial esterquats made from tallow, particularly in terms of colour (*Table 2*). The palm-based esterquats produced were used as active ingredients in fabric softeners (*Figure 6*).

TABLE 1. WORLD PRODUCTION OF OIL AND FATS ('000 t)

Source/year	1985	2000	2002	2003	2004	2005	2006 f
Annuals	**37 023**	**61 998**	**64 015**	**65 241**	**68 012**	**72 871**	**74 910**
Soyabean oil	14 026	25 531	29 857	31 291	30 677	33 491	34 462
Rapeseed oil	6 116	14 471	13 284	12 659	14 850	16 023	16 491
Groundnut oil	3 529	4 554	5 135	4 505	4 737	4 503	4 567
Sunflower oil	6 398	9 700	7 612	8 970	9 440	9 705	10 019
Corn oil	1 170	1 966	2 016	2 015	2 015	2 117	2 184
Caster oil	413	497	440	419	488	543	555
Linseed oil	786	705	626	596	630	628	642
Sesame oil	635	706	816	780	782	839	855
Cotton oil	3 950	3 868	4 229	4 006	4 393	5 022	5 135
Perennials	**12 488**	**30 386**	**34 205**	**37 548**	**39 885**	**43 537**	**43 835**
Palm oil	6 975	21 874	25 305	28 082	30 453	33 499	33 500
Palm kernel oil	903	2 691	3 021	3 331	3 524	3 924	4 094
Coconut oil	2 814	3 281	3 174	3 286	3 017	3 227	3 302
Olive oil	1 796	2 540	2 705	2 849	2 891	2 887	2 939
Animals	**19 381**	**22 321**	**22 180**	**22 494**	**22 862**	**24 300**	**23 791**
Tallow & grease	6 525	8 191	8 061	8 025	8 087	8 181	8 333
Lard	4 988	6 668	6 949	7 210	7 304	7 543	7 674
Butter as fat	6 379	6 040	6 231	6 275	6 330	6 678	6 786
Fish oil	1 489	1 422	939	984	1 141	998	998
Total	**68 892**	**114 705**	**120 400**	**125 283**	**130 759**	**139 808**	**142 536**

Note: f - forecast.
Sources: Oil World Annual 2005; 1988; Oil World Monthly March 2006.

Figure 6. Palm-based esterquats and fabric softeners.

MATERIALS AND METHODS

Materials

Distilled palm stearin fatty acid was obtained from Palm Oleo (M) Sdn Bhd. Triethanolamine (99.5%) was purchased from Euro Chemo-Pharma Sdn Bhd. Hypophosphorous acid (50%) was obtained from Fluka Chemicals, Switzerland.

Preparation of Esteramines

The fatty acid (1.8 mols) was mixed with triethanolamine (1 mol) in a 2-litre reaction vessel. Hypophosphorous acid (0.3%) was then added and the mixture heated to 150°C while stirring under a vacuum of 1 mbar. When the temperature reached 150°C, the pressure was increased to 40 mbar by introducing nitrogen gas and the temperature further increased to 160°C where it was maintained for 4 hr. The mixture was then cooled with stirring while maintaining the vacuum. At 60°C, the vacuum was released and at 40°C-50°C, the mixture purged with compressed air for about 15 min.

Preparation of Esterquats

The esteramines (1 mol) were

mixed with isopropanol to make 80% dispersion. Dimethyl sulphate (0.95 mol) was then added dropwise while the mixture was heated at 50°C. When the addition was complete, the reaction was maintained at 60°C with stirring for another 2 hr.

Formulation of Fabric Softeners

Fabric softeners based on esterquats were prepared. The oil and water phases of the formulations were heated to 70°C-75°C separately. The oil phase was then slowly poured into the water phase with stirring (1000 rpm), after which, the mixture was maintained in that condition for about 10 min. Then, the stirring was reduced to 500 rpm and, a dye solution and perfume added. Then the mixing speed was reduced to 250 rpm and maintained until the product cooled to room temperature.

Performance Evaluation

The esterquats performance was evaluated based on their softening property (ASTM D 5237-92, AATCC EP5 and in-house), rewetting property (ASTM D 5237-92) and foaming property (in-house method).

RESULTS AND DISCUSSION

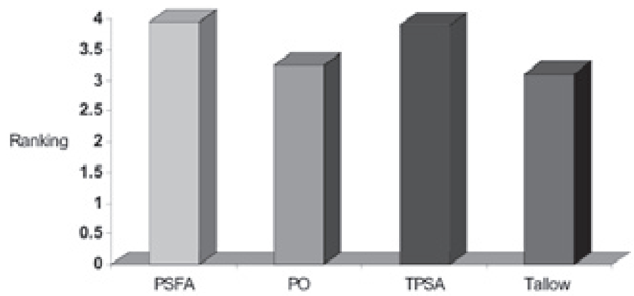
The properties of esterquats produced and those of commercial products are shown in *Table 2*.

Softening Property

The softening performances of the formulated fabric softeners using various palm-based and tallow-based esterquats were evaluated via the tactile method. The numbers in *Figure 7* indicate that the fabric softeners with palm-based esterquats exhibited better softening performances than a commercial softener formulated with tallow. This was due to the fact that the palm-based esterquats were more saturated than the tallow-based esterquats. Indeed, esterquats from triple pressed stearic acid, made from 100% saturated feedstock exhibited the best lubricity.

TABLE 2. PROPERTIES OF ESTERQUATS

Property	Palm-based	Commercial (tallow)
Appearance	Paste	Paste
Colour Lovibond (R)	3.0 - 4.0	2.9
Active matter (meq g^{-1} sample)	0.91- 0.95	0.95 - 1.05
Total solid content (%)	85 - 89	85
pH	2.7 - 3.5	2.5 - 3.5
Amine value (mg KOH g^{-1})	4.50 - 5.00	> 5.00



PSFA: palm stearin fatty acid, PO: palm oil, TPSA: triple pressed stearic acid.

Figure 7. Softening properties of formulated esterquats with different fatty acid compositions.

Rewetting Property

Besides having good softening and lubricity properties, esterquats in fabric softeners should be able to re-wet in order to facilitate penetration of water and detergent (anionic surfactant) during the subsequent wash. In tropical countries, where the humidity is high, the rewetting property of the garment is also important to enable it to absorb sweat. In cold countries, however, water repellency is desired for more rapid drying of the fabric during winter, making the rewetting power unnecessary. The rewetting properties of fabric softeners (measured by the distance wetted by a dye solution) formulated from palm-based esterquats at different percentages of unsaturated fatty acids are shown in *Figure 8*, where the rewetting power enhanced with the degree of unsaturation in the esterquats feedstock.

The fabric softeners using palm-based esterquats had better rewetting power than the commercial fabric softener with distearyl dimethyl quaternary ammonium compound (conventional quats). Although the palm-based esterquats had better softening power than the tallow esterquats (*Figure 8*), their rewetting power was found to be the converse (*Figure 9*).

Anti-static Property

Electrostatically charged fabrics unpleasantly cling to the skin especially in dry climates or in an air-conditioned room. The charge also attracts dirt onto the fabric. Esterquats often have an anti-static property to neutralize the static charge on the fabrics. Experimentally, the static charges can be measured as a function of resistance to flow of electricity at a fixed voltage created on the as shown in *Figure 10*.

All the formulations offered good static reduction on polyester cloth

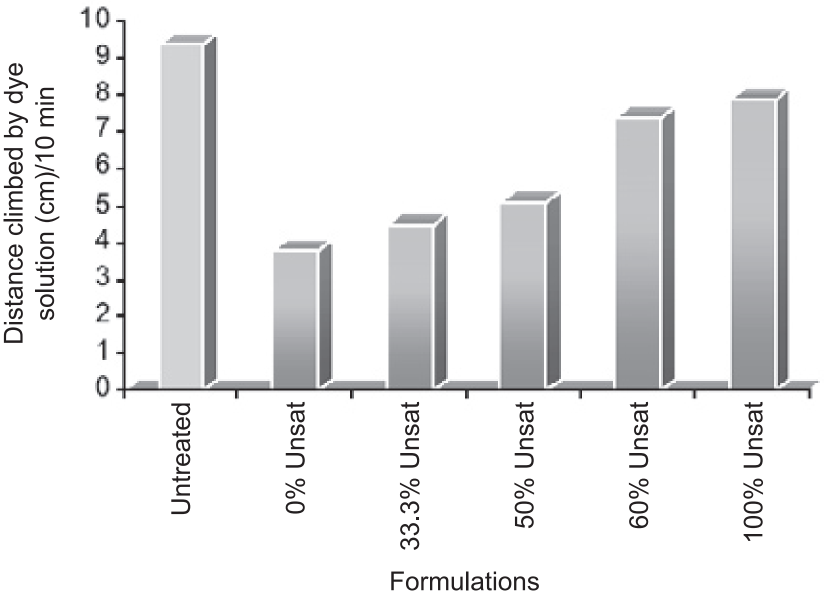
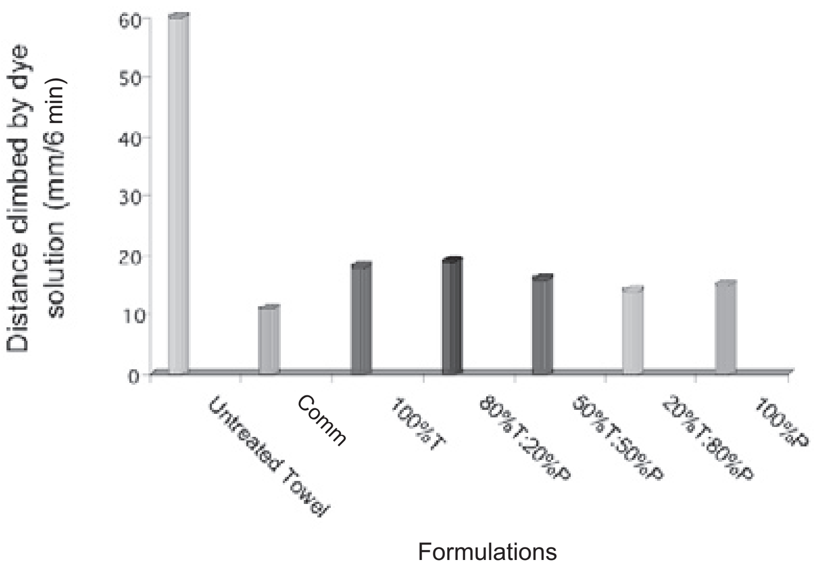


Figure 8. Rewetting power of formulated esterquats at various degrees of unsaturation.



Comm.: Commercial Softener, T: Tallow, P: Palm Oil

Figure 9. Rewetting properties of fabric softeners.

and moderate reduction on acrylic cloth. Overall, the fabric softeners formulated from palm-based esterquats exhibited comparable anti-static properties to those of the tallow-based esterquats.

Foaming Power

A high foam volume is undesirable in fabric softeners as they are added in the last rinse of the washing cycle. *Figure 11* indicates that the fabric softener formulated with fully saturated palm-based fatty acids yielded the highest foam volume whereas no foam was observed with fully unsaturated fatty acids. Using palm-based esterquats with a blend of saturated and unsaturated palm-based fatty acids, however, minimized the foam volume, making it comparable to the commercial softener.

CONCLUSION

Nowadays, esterquats are becoming the surfactants of choice over conventional distearyl dimethyl ammonium compounds due to the former's excellent environmental-friendly profile. Moreover, palm-based esterquats are also gaining acceptance over the animal-based raw materials. In MPOB, the process to produce palm-based esterquats has been scaled up from the laboratory scale to a 25 kg batch^{-1} pilot plant. The properties of the palm-based esterquats were found comparable to those of a commercial esterquats derived from tallow, and therefore would be suitable for use in fabric softeners. The palm-based esterquats produced from the pilot plant were used as active ingredients in fabric softener formulations and their softening performance found to be better than that of tallow esterquats. In their anti-static property, the palm-based esterquats exhibited comparable performance to the tallow-based esterquats towards polyester and acrylic fabrics. Some unsaturation in the hydrocarbon chains in the raw material is required to enhance the rewetting power of the palm-based esterquats without reducing their softening property.

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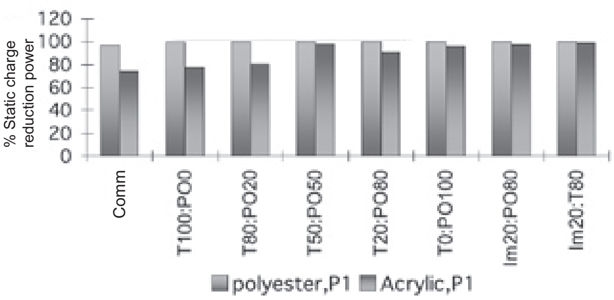
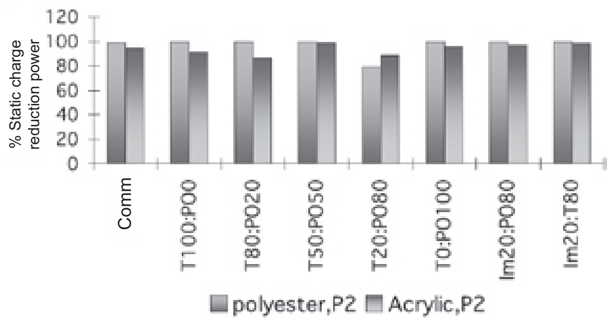
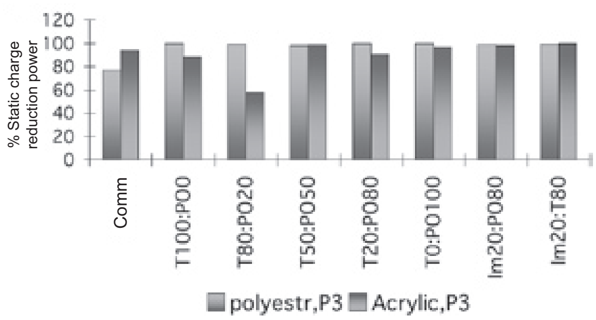


P1: Position measuring anti-static property: at 3 cm cloth width



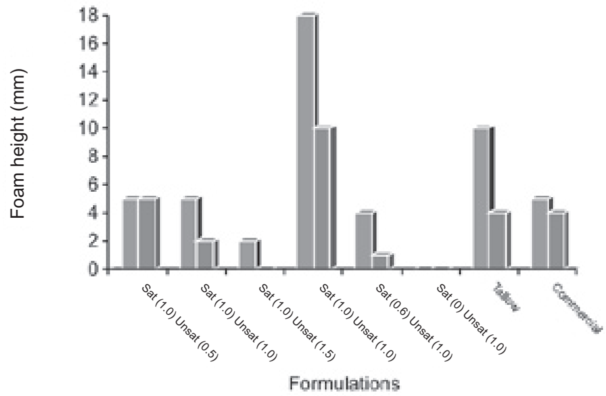
P2: Position measuring anti-static property: at 5 cm cloth length



P3: Position measuring anti-static property: at 6 cm cloth diagonal

T: tallow, PO: palm oil, Im: imidazoline

Figure 10. Static reduction power of formulations with different esterquats blends against commercial softener and imidazoline quats.



Sat: saturated palm-based fatty acid, unsat: unsaturated palm-based fatty acid

Figure 11. Foam volume of various fabric softeners.