

## Synthesis and Characterization of Nanostructured Polystyrene/ Polybutylacrylate Copolymer Coating

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**R**UBBERY and hard coating materials based on homo- and co-polymers of n-butylacrylate and styrene were developed. Miniemulsion polymerization technique was used to prepare nano-scale polymers which were fully characterized by gel permeation chromatography (GPC) and particle size analyzer (PSA). PS, PBA and PS/PBA copolymers were found to have average number molecular weights of 32300, 19900 and 24600 g/mol, respectively. Particle size distribution of PS, PBA and its copolymer which dispersed in aqueous medium presence relative particle diameter measurement are distributed over narrow range from 30 – 100 nm with percentage more than 90 % of particles by volume distribution. In addition, thermal gravimetric analysis (TGA) was used to study the thermal behavior of the prepared polymeric coatings. Polymerized coating solutions were applied over paperboard surface having a base weight of 285 g/m<sup>2</sup> with rapping roller. By morphological study, spherical polymer particles were detected with narrow particle size distribution ranging from 30-70 nm. The mechanical properties of coated paperboard were investigated to determine coating type effect on paperboard properties. The higher tensile strength of paper board was achieved by coating using polystyrene alone which give the higher coating weight 19 g/m<sup>2</sup>. PS/BA coating improve tensile strength of one face coated paperboard more than BA coating. Also, PS/BA coating improves wet tensile strength of coated paperboard. The measured WVTR of control paperboard was as high as 3075 g/m<sup>2</sup>/d. By coating on one surface, its WVTR was reduced to approximately half of magnitude in case of coating by PS/BA.

**Keywords:** Coating, Polybutylacrylate, Polystyrene, Miniemulsion, Nano-polymer and Paperboard.

Miniemulsion polymerization is a type of polymerization that is stabilized against coalescence by using an emulsifying agent. This technique requires high mechanical or sonification homogenization energy. The emulsified system usually yields stable emulsion with narrow distribution of droplets with an average size of < 500 nm<sup>(1)</sup>.

Paperboard is a very popular packaging material based on cellulose fibres. Usually, it is made from 100 % recycled or blended fibres containing percentage of virgin fibres. It is, therefore, considered as an environmental friendly

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material<sup>(2)</sup>. Technical requirement of paperboard for packaging include appearance and performance. Performance is related to strength, product protection and efficiency of all the production operations involved in making and using the packaging. Paperboard containers are widely used in all industries around the world. This is attributed to its functionality to be used as primary, secondary and tertiary packaging. The packaging paperboard produced with recovered paper has low quality due to its smell, color of the packaging material and poor strength. So, paperboard is coated in order to improve appearance and efficiency<sup>(3)</sup>. To a limited extent, paperboard usually has poor gas, moisture and grease resistance. Consequently, it is often coated to improve its barrier properties especially to water vapor, oxygen, aromas and grease by hydrophobic materials such as paraffin wax and polyethylene<sup>(2)</sup>. Acrylic lattices<sup>(4)</sup> have the ability to form strong films with low porosity, high gloss, good printability, adequate water resistance and ignore residual odour. So, these acrylic lattices were used for perfect barrier coating. The main disadvantage of this acrylic lattices is the high cost of synthesis in presence of surfactants<sup>(5)</sup>. Modified copolymer lattices were prepared using mono-vinyl aromatic monomers and acrylates or methacrylates<sup>(6)</sup> in the absence of surfactant<sup>(7)</sup>. The styrene-butadiene latexes copolymer prepared from aromatic mono-vinyl monomers, aliphatic conjugated dienes and dicarboxylic acids with<sup>(8)</sup> or without emulsifying agents<sup>(9)</sup> are characterized by its ability to deposit onto cellulose<sup>(10)</sup>. Recently, paperboard surface is modified by coating using nanoparticles produced from imidization of styrene-maleic anhydride copolymers<sup>(11)</sup>. Mechanical properties of coated paperboard were improved owing to the interaction of nanoparticles and cellulose fibres<sup>(12)</sup>.

In this work, different types of homo and copolymer coating were prepared through miniemulsion polymerization techniques. Polymerized coating solutions were applied over paper surface with rapping roller. Mechanical and morphological properties of coating and coated paper were investigated to determine coating type effect on paper properties.

## Experimental

### *Chemicals*

n-Butylacrylate and styrene were carefully purified with NaOH and distilled over CaH<sub>2</sub>. Potassium peroxodisulfate (KPS), methanol, sodium hydroxide calcium hydride, hexadecane, sodium n-dodecyl sulfate (SDS) and sodium chloride are used as received.

### *Synthesis of polymers*

Polymerization reactions were carried out in a round bottom double jacket reactor with four necked flasks equipped with adequate reflux condenser, mechanical stirrer, temperature sensor for automatic temperature control. The reaction mixture was layered with an inert gas inlet using self-sealing septum silicon rubber stopper, used in combination with hypodermic syringes. In the laboratory, a vacuum line was employed; all operations were conducted under

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high vacuum. A reduction of oxygen content was achieved by applying several vacuum/N<sub>2</sub> cycles (minimum 30 mbar at room temperature).

#### *Miniemulsion polymerization*

In a three-neck tube, 0.19 mol. of monomers and a solution of 172.8 mg of sodium dodecyl sulfate (SDS) were mixed and added in 63.36 g of water.

The mixture was degassed (vac/N<sub>2</sub>, followed by stirring 30 min under N<sub>2</sub> at 100 min<sup>-1</sup>). The mixture was stirred for 1hr at 800 min<sup>-1</sup>. After that, miniemulsion was prepared by ultra-sonication for 11 min (Amp. 90%) with an ultrasonic processor UP100H (100 watts, 30 kHz). A slight stream of nitrogen was applied and the emulsion was cooled with ice water. The formed miniemulsion was transferred into the reaction vessel. After short degassing, the temperature was raised to 72 °C. After reaching T, an aqueous solution of initiator (360 mg KPS in 5.75 g water, degassed under N<sub>2</sub> for 30 min) was added. The reaction was performed at 400 rpm for 4hr. Then the mixture was cooled to 25 °C. The reaction vessel was immersed in ice bath to decrease the temperature until room temperature. 5 ml of product uptake for particle size measurements. 40 g of the dispersion were precipitated in 300 ml MeOH (1 wt% HQ). The precipitation was done by dropping the latex solution drop by drop. Prepared polymers were filtrated and dried in vacuum oven overnight.

The styrene and butylacrylate were extracted twice with 0.1 N NaOH, followed by washing with water and brine in order to remove the stabilizer. Prior to use it was heated over CaH<sub>2</sub> to 80°C until the evolution of H<sub>2</sub> disappeared and then distilled under vacuum. It was stored under nitrogen in a refrigerator for no longer than one week.

#### *Measurements and analysis*

##### *Differential scanning calorimetry (DSC)*

DSC 8500 from PerkinElmer, USA was used to measure glass transition temperature (T<sub>g</sub>). Aluminum pan was filled with sample weighing between 5 and 15 mg. Nitrogen was used as the purge gas. Polymers were subjected to a Heat-Cool-Heat cycle to erase thermal memory. Samples were heated from -100 to 150 °C at a heating rate of 40 °C / min, then cooled to -100 °C at 50 °C / min and heated at 10 °C per min to 150 °C. The intersecting line method was used to determine T<sub>g</sub>.

##### *Thermogravimetric analysis (TGA)*

The thermogravimetric analysis (TGA) was carried out using a TGA machine (Perkin Elmer TGA7, USA) from ambient temperature up to 600 °C under nitrogen atmosphere at a heating rate of 5 °C /min.

##### *Scanning electron microscopy (SEM)*

The scanning electron microscope for PS, PBA and PS-co-PBA samples were investigated through using SEM Model Quanta 250 FEG (Field Emission Gun) attached with EDX Unit (Energy Dispersive X-ray Analyses), with accelerating voltage 30 K.V., magnification 14x up to 1000000 and resolution for Gun.1n).

*Gel permeation chromatography (GPC)*

GPC Agilent Series 1100, CHCl<sub>3</sub>; 1 mL/min, RI and UV detector, columns PL-MIXED-B-LS (300x7.5 mm) and 10mm PS-gel (Agilent Co., USA) was used.

*Coating application*

A standard grade of manilla paperboard having a gramage of 285 g/m<sup>2</sup>, thickness 0.52 mm and size 25x35 cm without any surface treatment, supplied by Simo Co., Egypt was used as substrates to apply the coatings. Sheets that were made without any coating were denoted as "REF", and used as the reference case for the coating treated sheets. The polymer coatings were applied on one surface from dispersions, by using a hand coater.

The applied coatings were air dried and subsequently conditioned for at least 24hr at 23 °C and 50% relative humidity before subsequent measurements were made. After conditioning, the coated paper sheets were tested and compared to non-coated paper sheets. Coating weights (g/m<sup>2</sup>) were obtained by subtracting the weight of uncoated paper sheet from the weight of coated paper sheet.

*Test series*

The sheets were tested for tensile strength according to the German Standard method by means of a Karl Frank 468 tester (Weinheim–Berkenauand). The tensile strength represents the load in kg at which a paper strip of 15mm width breaks. This can be converted to the tensile index (Nm/g) by considering the weight strip in gram .WVTR of paperboard was estimated according to ASTM E96-80 at 38C and RH 90 and by using WEISS TECHNIK.

**Results and Discussion***GPC results*

Molar ratios of prepared polymers coatings were measured. Relatively low polydispersities were detected with Unimodals chromatograph as shown in Fig. 1.

PS, PBA and PS/PBA copolymers have molecular weight Mn=32300, 19900 and 24600 g/mol, respectively. In addition, polydispersity of polymer chain distribution was states as 1.4, 1.2 and 1.25 for PS, PBA and PS/PBA copolymer.

*Particle size analyzer*

DLS can be considered as a main tool to understand and verify models pertaining to the dynamics of polymers in dilute solution. It allows determining the size and hydrodynamic radius of polymer molecules in solution.

As shown in Fig. 2, particle size distribution of PS, PBA and its copolymer which dispersed in aqueous medium presence relative particle diameter measurement distribution over narrow range from 30 – 100 nm with percentage more than 90 % of particles by volume distribution.

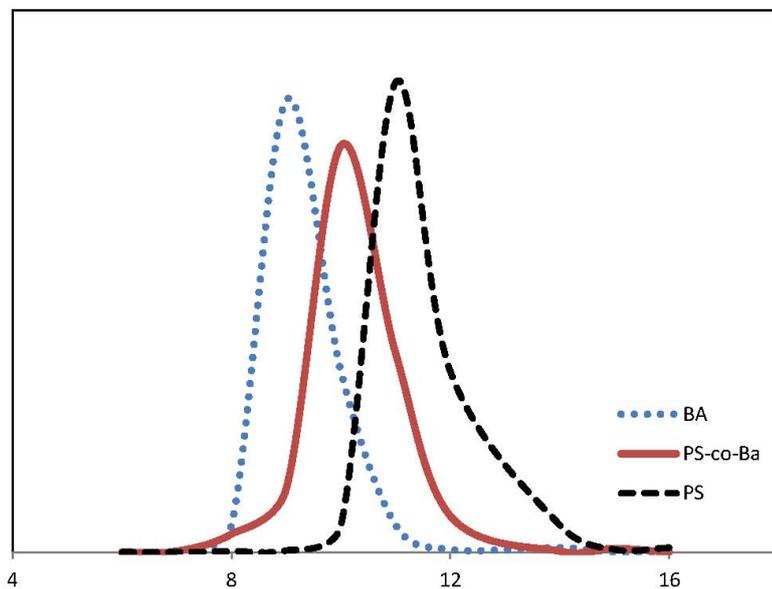


Fig. 1. GPC chromatographs of PS, PBA and PS/PBA prepared through miniemulsion polymerization technique.

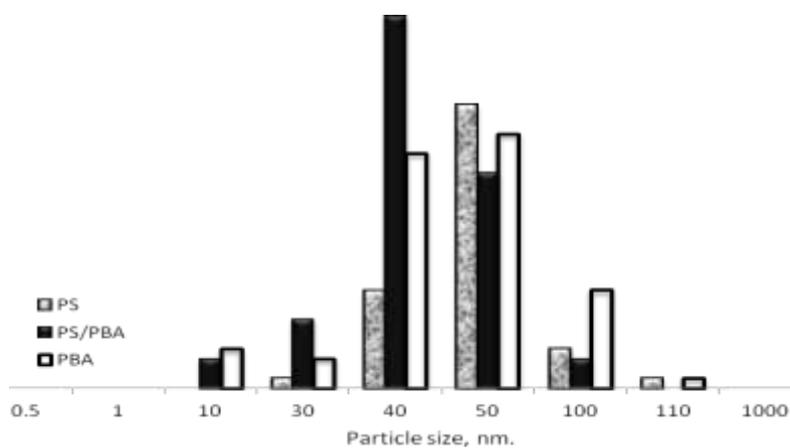
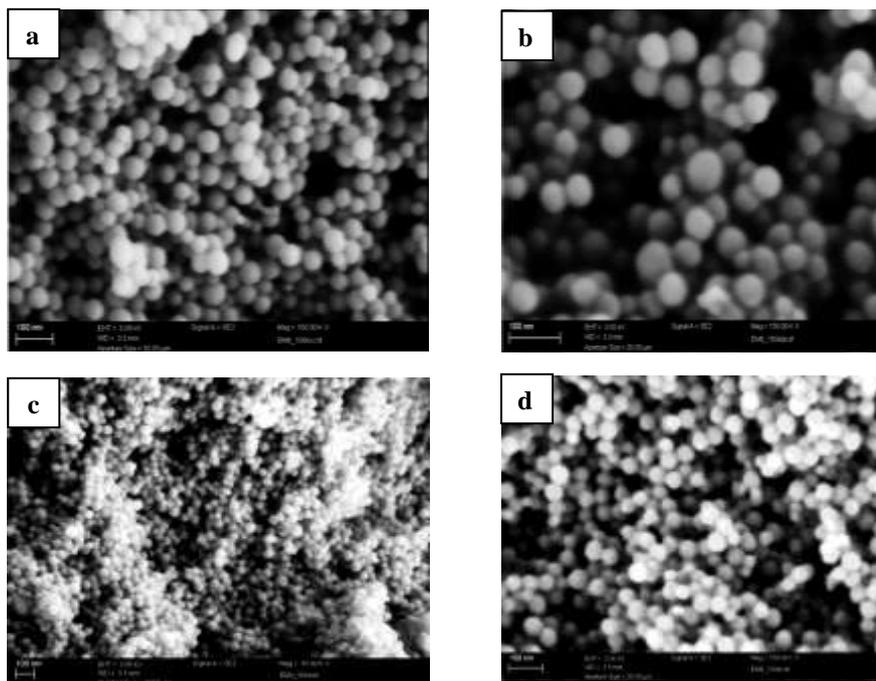


Fig. 2. PSA distribution of polystyrene, poly-n-butylacrylate and poly (styrene/ butylacrylate) copolymer particles prepared through miniemulsion polymerization technique.

*Scanning electron microscopy (SEM)*

Figure 3 shows SEM micrographs of miniemulsion polymerization coatings of PS, PBA and PS/PBA copolymer. Spherical polymer particles were detected with narrow particle size distribution with range from 30-70 nm.



**Fig. 3.** SEM micrographs of (a) PS, (b) PBA, (c) and (d) P(St/BA) copolymer with magnifications 100K, 100K, 50K and 100k, respectively, prepared through miniemulsion polymerization technique with average particle size 30-70 nm.

DLS and SEM results are in agreement in terms of particle size with little deviation due to difference of measurement state from solution in case of DLS to solid dry state in case of SEM imaging. Polymer particles can swell or shrink corresponding to nature of copolymer in solution during DLS measurement. In case of SEM, particle could be extrovert to give large size or highly dried under vacuum conditions to give small size.

*Thermal analysis**Thermal gravimetric analysis (TGA)*

TGA thermograms of polystyrene, polybutylacrylate (homopolymer segments) and PS/PBA (copolymer segments) which were prepared through miniemulsion polymerization are shown in Fig. 4.

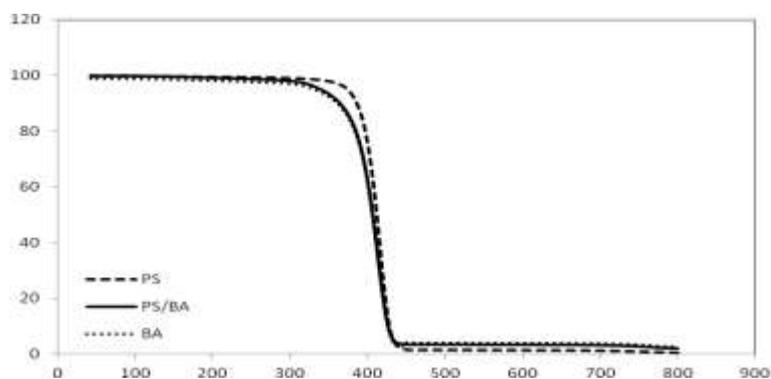


Fig. 4. TGA thermograms of polystyrene, n-butylacrylate and polystyrene-n-butylacrylate copolymer.

All measurements were carried out from room temperature to 800°C with a heating rate of 5 °C/min under nitrogen flow. The thermal stability data and the residues at 500 °C of polymers are summarized in Table 1.

TABLE 1. TGA data for PS, PBA and PS/BA copolymers.

Polymer	<sup>a</sup> T <sub>i</sub>	<sup>b</sup> T <sub>f</sub>	<sup>c</sup> T <sub>50</sub> %	Weight loss at 200°C (%)	Weight loss at 400°C (%)	Weight loss at 600°C (%)
PS	385	470	438	1	17	98
PS/PBA	335	472	427	3	23	96
PBA	315	460	425	2	24	94

a: initial decomposition temperature, b: Final decomposition temperature, c: Decomposition temperature at 50% weight

The thermal stability of polystyrene and polybutylacrylate are in agreement with thermal properties data from literature<sup>(13)</sup>. Furthermore, PS-b-BA copolymers have a good thermal stability with only (1-3 %) weight loss until 200°C<sup>(13)</sup>.

#### Differential scanning calorimetric (DSC)

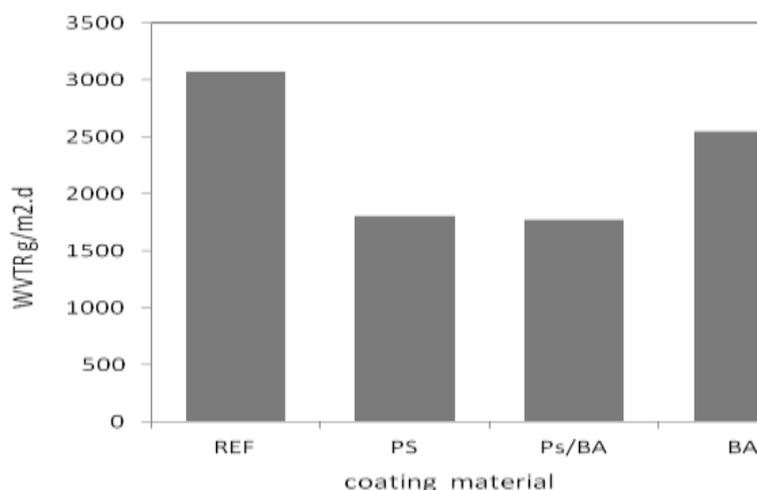
It is important to understand the concept of the glass transition temperature,  $T_g$ . As the temperature of a polymer drops below  $T_g$ , it behaves in an increasingly brittle manner. As the temperature rises above the  $T_g$ , the polymer becomes more rubber-like. Thus, knowledge of  $T_g$  is essential in the selection of materials for various applications. In general, values of  $T_g$  well below room temperature define the domain of elastomers and values above room temperature define rigid, structural polymers.

The glass transition temperature of polystyrene is in agreement with standard values of polystyrene and polystyrene *n*-butylacrylate copolymer at this composition.  $T_g \approx 108$  °C,  $-54$  °C and  $73$  °C for PS, PBA and PS-co-BA, respectively.

*Water vapor transmission rate (WVTR) of coated paperboard*

WVP is a measure of the amount of water vapor passing through unit area of material per unit time. The measured WVTR of control paper was as high as 3075 g/m<sup>2</sup>/d (Fig. 5).

This was attributed to the obvious pore structure of fiber-based paper and the hydrophilic fibers<sup>(14)</sup>. When these pores were filled with prepared polymers by coating on one surface its WVTR was reduced to approximately half of magnitude in case of coating by PS/BA. The high efficiency of PS/BA as a moisture-barrier is likely related to both of its chemical composition and physical structure. Since polymer could easily permeate into paper base, which resulted in a massive coating weight and good barrier property. The hydrophobic polymer polystyrene (PS) or PS/BA, improve WVTR of one side coated paperboard. Coated paper board was heterogeneous, which had a relatively denser coating layer and a porous base. However, natural materials are hydrophilic materials with polar groups in their molecular structures, and the interaction of polar groups with permeating water molecules causes the WVP to depart from ideal behavior<sup>(15)</sup>. The deviation from ideal behavior is attributed to the variation of structure of the materials. The deviation was believed to be governed by free volume theory<sup>(16)</sup>. Water increases the polymer free volume, allowing the polymeric chain segments to increase their mobility. Higher segment mobility results in higher WVP.



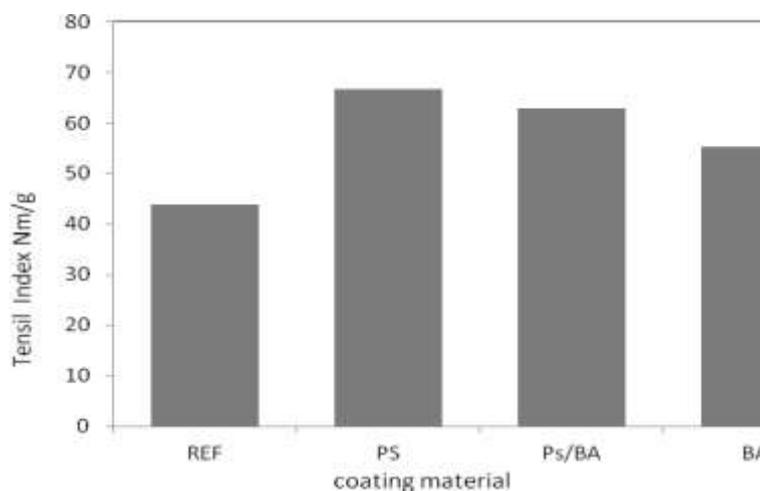
**Fig. 5. WVTR of control and paperboard samples coated with PS, PS/BA copolymers and PBA.**

*Tensile strength*

High mechanical properties are usually required to maintain packaging integrity during shipping, handling and storage. Tensile strength (TS) is the most commonly reported responses to describe mechanical properties of paper-based packaging materials. TS is a measure of the ability of coated paper board to resist breaking under tension, which is dependent on the strength of fibers, their surface area, and length, and also the bonding strength between them.<sup>(17)</sup> The TS values of polymer-coated papers board were positively affected by the linear terms of coating. It can be seen from Table 2 and Fig. 6 that the TS of coated papers increased with increasing the coating weight.

**TABLE 2. Coat weight and wet strength, for the paperboard and the coated paperboard .**

Sample	Coat Weight ,g/m <sup>2</sup>	Tensile index, Nm/g
Reff.	--	3.1
PS coated paperboard	19	5.2
BA coated paperboard	7	3.3
PS/BA coated paperboard	16	6.6



**Fig. 6. Effect of coating polymer type on tensile strength of coated paperboard.**

The higher tensile strength of paper board was achieved by coating using polystyrene alone which gives the higher coating weight 19 g/m<sup>2</sup>. PS/BA coating improve tensile strength of one face coated paperboard more than BA coating. In case of PS/BA, coating weight was 16 g/m<sup>2</sup> and 7g/m<sup>2</sup> for BA coating. Wet strength is the mechanical strength of paper remaining after complete soaking in water. It is clear from Table 2 that synthetic PS/ BA coating intended to reinforce mechanical properties of wet paper more than PS or BA coating.

### Conclusion

Miniemulsion polymerization technique was used to prepare nano-scale polymers which were fully characterized by gel permeation chromatography (GPC) and particle size analyzer (PSA). PS, PBA and PS/PBA copolymers were found to have average number molecular weights of 32300, 19900 and 24600 g/mol, respectively. TGA indicates that PS-b-BA copolymers have a good thermal stability with only (1-3 %) weight loss until 200 °C. Manila paperboard was coated on one surface by prepared polymers. Its WVTR was reduced to approximately half of magnitude in case of coating by PS/BA compared to control substrate. The TS values of polymer-coated papers board were positively affected by the linear terms of coating. The higher tensile strength of paper board was achieved by coating using polystyrene alone which gives the higher coating weight 19 g/m<sup>2</sup>.

PS/BA coating improves tensile strength of one face coated paperboard more than BA coating. In case of PS/BA, coating weight was 16 g/m<sup>2</sup> whereas the weight is 7g/m<sup>2</sup> for BA coating. Wet strength of manila paperboard was also improved on coating.

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## تحضير وتوصيف البوليستيرين والبولى بيوتيل اكريلات ذات البنية النانو مترية واستخدامهم كطلاء

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المركز القومى للبحوث – شارع التحرير – الدقى – الجيزة – مصر.

فى هذه الدراسة تم استخدام تقنية الأستحلاب الدقيق للبلمرة لتحضير بوليمرات ذات بنية نانومترية. تم توصيف البوليمرات المحضرة باستخدام GPC ومحلل حجم الجسيمات ووجد ان متوسط الأوزان الجزيئية هو 32300، 19900، و24600 جم / مول، أما التحليل الوزنى الحرارى TGA فقد استخدم لدراسة السلوك الحرارى للبولى ستيرين والبولى بيوتيل اكريلات وقد اظهر هذا التحليل الثبات الحرارى الجيد للبوليمرات المحضرة. عند تطبيق استخدام البوليمرات المحضرة فى طلاء وجه واحد من اوجه ورق المانيلا وجد ان التغطية كان لها تأثير ايجابى على خواص الورق المطلى بالمقارنة بالورق الغير مطلى. فمثلا نفاذية الورق لبخار الماء انخفضت الى قيمة النصف فى حالة التغطية بالبولى ستيرين/ والبيوتيل اكريلات. كذلك تحسنت قوة الشد الجاف وقوة الشد الرطب للورق المغطى بدرجة كبيرة مما يجعل الكرتون المغطى بهذه التقنية يستخدم فى اغراض التعبئة والتغليف الجافة والرطبة.