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Effect of methyl methacrylate and butyl methacrylate copolymer on the physico-mechanical properties of acryl syrup for paints

Abstract: The present study deals with the physico-mechanical properties of acryl syrups paint, which are made from copolymer powder and methyl methacrylate (MMA) monomer. Copolymer powders were used based on MMA and butyl methacrylate (BMA). The effect of copolymer powder to MMA- monomer ratio on the physico-mechanical properties acryl syrup mixes for paint applications was investigated. Testing included pot-life, curing time, viscosity, tensile strength, elongation, water absorption and hardness shore A. The results showed that, not only monomer composition of the copolymer but also the ratio of copolymer to MMA-monomer affected the physico-mechanical properties of acrylic films. The tensile strength, hardness, pot-life, curing time and hardness of the acrylic film increased with the increase of the MMA ratio in copolymer and decrease content of copolymer in acrylic syrup mixes. In conclusion, low copolymer content and high MMA ratio in copolymer (MMA/BMA) powders are desired to produce paint with physico-mechanical properties.

Key words: polymethyl methacrylate, syrups, self-curing, acrylic paint

Introduction

Poly(methyl methacrylate), PMMA, a kind of thermoplastic materials and self-curing for short, is an important polymer in the building industry as well as in other industries due to its excellent properties, such as transparency, lightness and safety. Typical applications are in architectural coatings, additives and polishing agents, binder, sealer, transparent neutron stopper, optical fiber, high-voltage application, and outdoor electrical application [1-5]. PMMA is classified as a hard, rigid, but brittle material, with a glass transition temperature of 105°C. PMMA has good mechanical strength, acceptable chemical resistance, and extremely good weather resistance [6]. PMMA has favorable processing properties, good thermoforming, and can be modified with pigments, flame retardant additives, UV absorbent additives, and scratch resistant coatings [7-10]. However, the physical and mechanical properties of PMMA limit its applications due to its brittleness nature [11-14]. Thus, modification of PMMA has attracted a great amount of attention from researchers all over the world, and the study of poly (methyl methacrylate) (PMMA) is a representative work in this research field. In order to enhance its mechanical properties, scientists have developed various methods to prepare different types of PMMA through the copolymerization of MMA monomer with various types of vinyl monomers [15-17]. Self-curing PMMA are materials formulated by the mixing of two-component, one solid (powder) based on PMMA spherical beads and another liquid includes monomer and an initiator to enable the polymerization reaction to occur at room temperature and a high level of heat being generated during the exothermic reaction. In self-curing, the polymerization reaction of methacrylate monomers is initiated by the activation reaction of BPO, with an amine accelerator at room temperature, which gives free radicals for addition to monomer molecules [18]. A high level of heat being generated during the exothermic reaction [9]. Authors [19] prepared copolymer latexes based on methyl methacrylate (MMA) and butyl methacrylate (BMA) using macro-radical initiator technique. Different ratios of acrylic monomers were designed to investigate the effect of monomer compositions on physico-mechanical properties of acrylic films for paint application. The results showed that, physico-mechanical properties increased with increasing the ratio of MMA in the copolymer. The work was further extended to include the application of the obtained copolymer latexes to make acrylic syrups containing varying content of MMA-monomer to be self curing and modify physico-mechanical properties of paint solvent free.

Experimental

Materials

Methylmethacrylate (MMA) monomer (supplied by Fluka), benzoyl peroxide (BPO) (supplied by Melbourne), N,N-dimethyl-p-toluidine (DMPT) (supplied by Fluka) and hydroquinone (HQ) (supplied by Merck) were used as purchased.

Synthesis and Characterization of Copolymer Latexes.

The preparation of copolymer latexes and the methods of analysis (^{1}H NMR, FT-IR, DSC, TGA and SEM) have been previously described [19]. The mix proportion of monomers in the copolymer and basic properties of synthesized copolymer are shown in Table 1.

Table 1 – Properties of P(MMA-co-BMA) [19]

Sample No.	MMA	BMA	T_H	T_{max}	T_k	T_c^a	T_c^b	Appearance
			°C					
M1	10	90	325	425	450	34.15	43.30	Powder
M2	50	50				57.12	63.10	
M3	90	10				94.34	98.40	

T_H Initial decomposition temperature.

T_{max} Maximum rate of temperature for weight loss.

T_K The final temperature of the decomposition.

^{a}Predicted using Fox equation.

^{b}Measured using DSC.

Preparation of copolymer syrups

Copolymer syrup was produced by dissolving copolymer (MMA/BMA) and BPO into MMA monomer at normal temperature (25°C). Then, a liquid component was produced using MMA monomer, DMPT and HQ. BPO and DMPT were added at 1.5 and 0.75 parts per hundred (pph) to syrup to act as initiator and accelerator, respectively. HQ was added in the syrup as an inhibitor. Paraffin wax was as added 1% wt. of syrups. This copolymer syrup was then placed into the liquid component mixed with ratio 10/90, 15/85 and 25/75% wt/wt to maintain the mixing ratio at 100% as shown in Table 1.

Table 2 – Formulation of copolymer syrup for acrylic paint

Group	Syrups	Copolymer (Powder, gm)	MMA (Liquid, gm)
Group 1	Syp10/M1	10	90
	Syp10/M2	10	90
	Syp10/M3	10	90
Group 2	Syp15/M1	15	85
	Syp15/M2	15	85
	Syp15/M3	15	85
Group 3	Syp25/M1	25	75
	Syp25/M2	25	75
	Syp25/M3	25	75

Film preparation

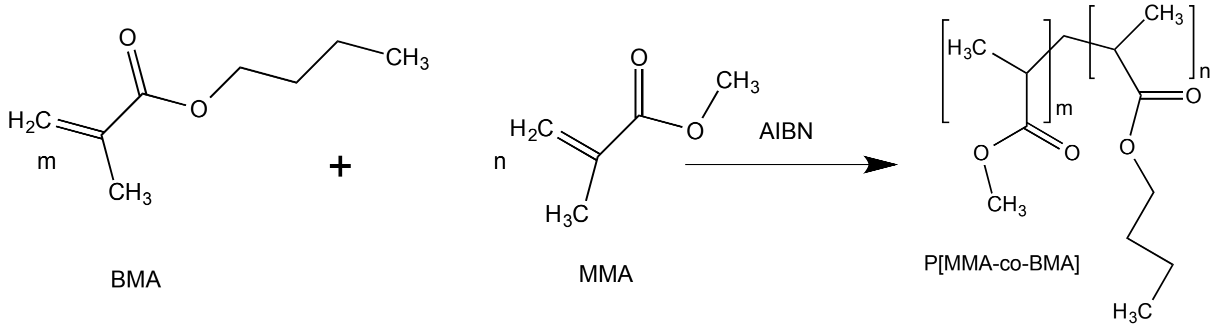
Films were prepared by casting the acryl syrups on leveled surfaces and allowing them to dry at room temperature for 3 hours. The films were stored in a desiccator at room temperature for further characterization and measurements.

Tests

The pot-life of fresh copolymer syrup was determined at 25 °C according to the finger-touching method prescribed in KS F 2484. The curing time of acrylic films was determined according to ASTM D5895. The viscosity (η) of the dispersions was measured using a Brookfield viscometer (Model LVTDV-II) at a shear rate of 100 S^{-1} at 25 °C. The contact angle formed between the water drops and the surface of the sample was measured using contact angle measuring system CAHN DCA-322 analyzer operated at 25 °C with water drop, and a velocity of 100 μm/s. The drop of water was mounted on the surface to be tested with a micro-syringe and contact angle was measured from the view of water drops as observed on monitor. Results are the mean value of three measurements on different parts of the film. The tensile properties of the acrylic syrup films were measured by using MTS 10/M tensile testing machine at a crosshead speed of 50 mm/min. An average of at least 4 measurements was taken and the 1-kN load cell was used. Shore A and D hardness was measured using an indentation hardness tester according to ASTM D2240-75. Water absorption test was according to BS 1881-122:2011.

Results and their discussion

Structure of copolymers. The structure of the copolymer latexes based on methyl methacrylate (MMA) and butyl methacrylate (BMA) is shown in Scheme 1. The copolymer latexes were synthesized with different ratios (M1=10/90, M2=50/50 and M3=90/10 respectively) using azobisisobutyronitrile (AIBN) as free radical initiator. The properties of the prepared copolymer latexes have been previously reported by authors [19]. The results showed that physico-mechanical properties of the copolymer were increased by increasing the ratio of MMA in the copolymer latexes.



Scheme 1 – General reaction for the synthesis of MMA/BMA copolymer [19]

Pot-life and curing test

Pot-life of acrylic films is the length of time in which the flow properties (such as, viscosity) of catalyzed syrup will no change within an acceptable for application. Pot-life and cure time of acrylic films (M1, M2 and M3) are measured in the lab at an ambient temperature of 25°C. Figure 1, shows a sharp decrease in pot-life and cure time of acrylic films with increasing MMA in copolymers backbone. Acrylic film (Syp25/M1) with (10% MMA) in group 3 where the content of copolymer 25% gave longest pot-life and cure time, while acrylic syrup (Syp10/M3) with (90% MMA) in group 1 where the content of copolymer 10% gave shortest pot-life and cure time. It is well that the pot-life and cure time of acrylic syrups are affected by fee composition of acryl syrups such as copolymer and MMA monomer. The same behavior was reported by Jaafar and Hamizad [8] when they studied the effect of PMMA powder to liquid monomer on the properties of PMMA cement.

Viscosity. The effect of content of copolymer (MMA/BMA) with different composition (M1, M2 & M3) on the viscosity of syrups is shown in Figure 2. The results showed that the viscosity increased with increasing of BMA in copolymer backbone. However, the viscosity increased with increasing content of copolymer from 10% to 25%. With respect to the content of monomers and copolymer used in different composition ratios with MMA monomer to prepare paint syrups, it is evident that viscosity values for [Syp10/M3], which contain 10% wt.% of copolymer M3 (MMA/BMA, 90/10) in group 1 is lowest one (30 cps), whereas [Syp25/M1] which contain 25% wt.% of copolymer M1 (MMA/BMA, 10/90) in group 3 is the highest one (190 cps). These results reflect differences among copolymer studied with respect to chemical structure, average molecular weight, configuration and orientation of the molecules, molecular weight distribution, polarity and chain branching. Acrylic syrups are mainly used in coatings. In acrylic, viscosity is important parameter. A suitable viscosity range is required to avoid sagging (in case of low viscosity) and practical difficulty in application (encountered with high viscosity).

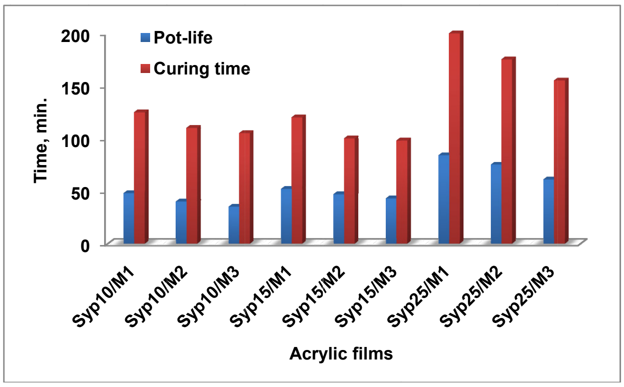


Figure 1 – Pot-life and curing time of acrylic films containing different content of copolymers M1, M2 and M3.

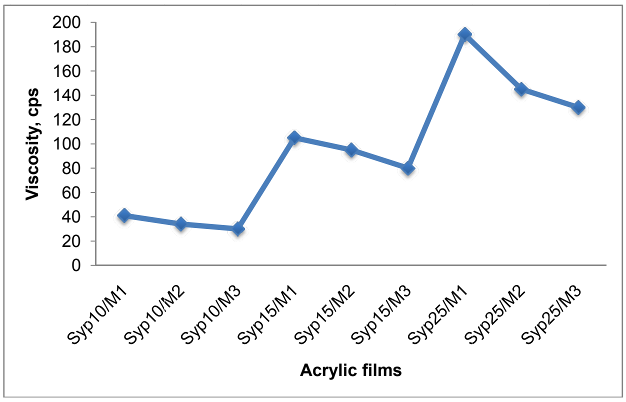


Figure 2 – Viscosity of acrylic syrups with different content of copolymer M1, M2 and M3.

Contact angle. Advancing and receding contact angle measurements of the films cast from acrylic could provide more information on the hydrophilicity of dried cast films [20-23]. A better understanding of the hydrophobicity of the cast films could be obtained from dynamic contact angle studies rather than from swelling studies. Figure 3 shows the measured contact angle for a drop of water on acrylic surfaces increase with increasing MMA in copolymer backbone. Syp10/M3 with 90% MMA gave the highest contact angle with 125 deg. while Syp10/M1 with 10% MMA gave contact angle of 100 deg. in-group 1. The hydrophobicity increased with the decreasing amount of copolymer in acrylic syrup. The results confirm that chain rigidity is a more significant factor in controlling the contact angle, because chain rigidity does not allow the ionic groups to come near the particle surface. Generally, if the water contact angle is smaller than 90°, the solid surface is considered hydrophilic and if the water contact angle is larger than 90°, the solid surface is considered hydrophobic.

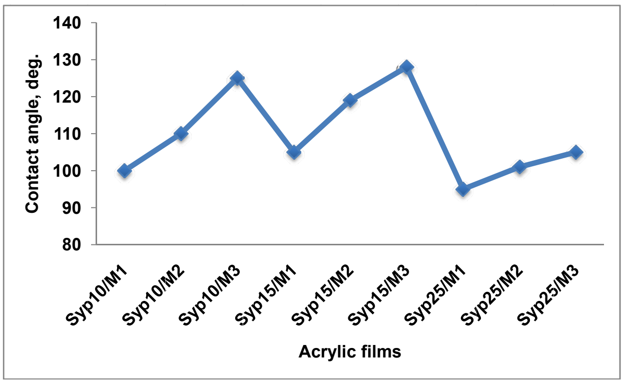


Figure 3 – Contact angle of acrylic films containing different content of copolymers M1, M2 and M3

Water absorption. Dynamic wetting tests were performed on a Camtel CDCA-100F dynamic adsorption apparatus (Camtel, UK). Each sample was cut to a size of 1 cm× 5 cm with sharp scissors. When the specimen was immersed into water for 2 months, the weight of adsorbed water was detected and recorded. The dynamic water adsorption was plotted as a function of feed composition of monomers. The results of the water adsorption tests reveal the dynamic wetting behavior of the acrylic films. The acrylic films show a very low adsorption, as shown in Figure 4. However, the water absorption of acrylic films decreased with increasing the amount of MMA in copolymer backbone in acrylic syrup. For example, the water absorption for Syp10/M3 (90% MMA) is 0.01mg and for Syp10/M1 (10% MMA) is 0.07 mg in-group 1. Also, water absorption of acrylic films in-group 1 is lower than that of group 3 as shown in Figure 4. The water absorption of Syp25/M3 (90% MMA) in-group 3 is 0.02 mg.

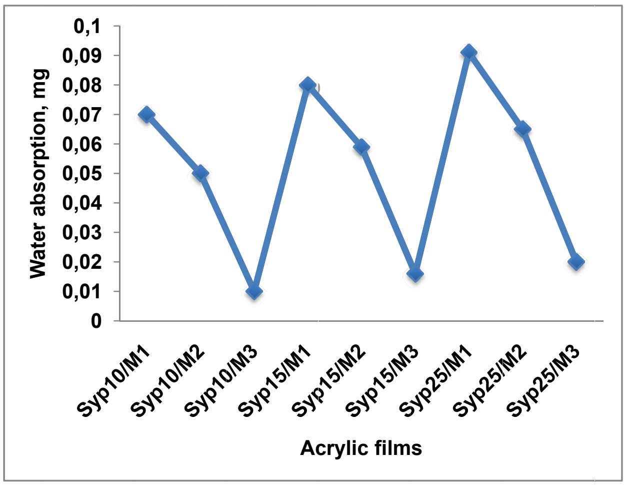


Figure 4 – Water absorption of acrylic films containing different content of copolymers M1, M2 and M3

Tensile and elongation. Figure 5 shows that the tensile strength increased with increasing the content of MMA in copolymer backbone. For example the tensile strength of Syp10/M3 (90% MMA) is 90 MPa and this drops down to 55 and 35 MPa for the Syp10/M2 (50% MMA) and Syp10/M1(10% MMA) containing 10% copolymer in-group 1. This is presumably due to the increased hard segment contents (MMA) in acrylic film. However, tensile strength of acrylic films decreases with increasing the content of copolymer in acrylic film. Syp25/M3 containing 25% copolymer shows substantially lower tensile strength than the Syp10/M3 containing 10% copolymer. Also, tensile strength of acrylic films affected by viscosity of acrylic syrup, whereas tensile strength decreased with increasing viscosity of acrylic syrup.

On the other hand the elongation of acrylic films decreased with increasing MMA in the copolymer backbone as shown in Figure 6. This is attributed to the increasing of flexible chain (BMA) with low T_g in the copolymer backbone. However, elongation increased with increasing the content of copolymer (MMA/BMA) in acrylic syrups. Also viscosity of acrylic syrup affected the elongation tests where the acrylic syrup with high viscosity (Syp25/M1) has longest elongation as shown in Figure 6.

Hardness. The results in Figure 7 show increase in hardness shore (D) with increasing of MMA in copolymer backbone of acrylic films. However, the hardness is affected by the content of copolymer. The surface hardness for acrylic film produced by Syp10/M3 in-group 1 (10%, 90/10 MMA/BMA) was found ca. 79, while that for acrylic film produced by Syb10/M3 in-group 3 (25%, 90/10 MMA/BMA) was found ca. 71.

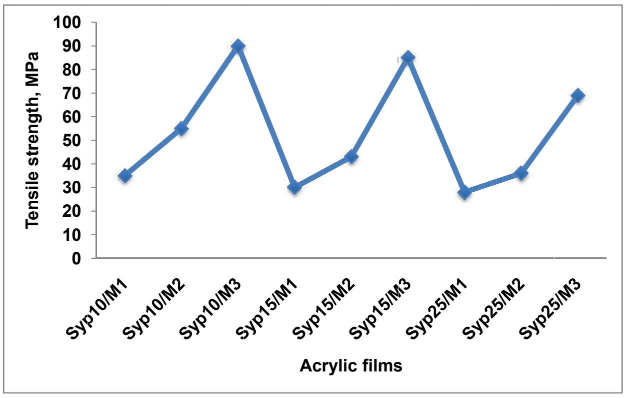


Figure 5 – Tensile strength of acrylic films containing different content of copolymers M1, M2 and M3.

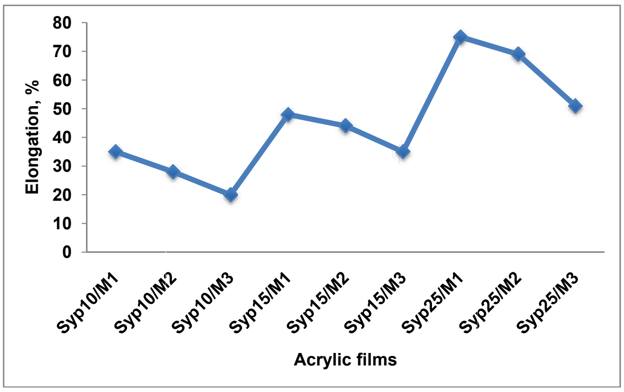


Figure 6 – Elongation of acrylic films containing different content of copolymers M1, M2 and M3

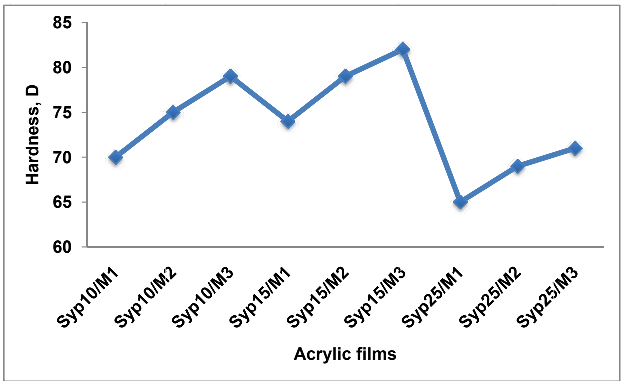


Figure 7 – Hardness of acrylic films containing different content of copolymers M1, M2 and M3

Conclusion

In this study, acrylic syrups with an MMA solution of copolymer (MMA/BMA) as a resin and physico-mechanical properties of the syrups were evaluated. The results obtained in this study are summarized as follows:

The pot-life, cure time, tensile, hardness shore D and water absorption of the syrup films increased with increasing MMA in copolymer backbone and decreasing the content of copolymer in syrup mixes. This is presumably due to the increased hard segment contents (MMA) in acrylic film.

The viscosity and elongation of the syrups increased with the increase BMA in the copolymer backbone and content of copolymer in syrup mixes. This attributed to the increased soft segment contents (BMA) in syrup mixes.

Monomer compositions of polymers played important role in specific characteristics of polymer films used in paint applications.

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