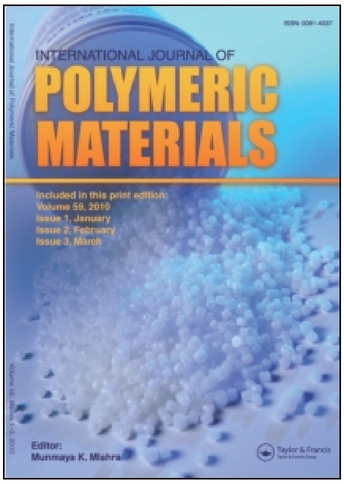

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Synthesis and Characterization of an Acrylamide-Based Resin for Coating Application

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To synthesize an acrylamide-based resin, two functional acrylamide monomers, N-methylolacrylamide and N-butoxymethylolacrylamide, were prepared and copolymerized separately with two methacrylate esters: methylmethacrylate and butylmethacrylate. The resin derived from N-methylolacrylamide proved to be inadequate due to its instability. To adjust the necessary amount of the reagents needed for the synthesis, different concentrations of the initiator, benzoyl peroxide, and various concentrations of the molecular weight regulator, tertio-dodecyl mercaptan transfer agent, were tested by monitoring the resulting viscosity and conversion. The paint formulation containing N-butoxymethylolacrylamide co-monomer was characterized in terms of hardness, impact and embossing resistance, gloss and adhesion to a metal substrate. The performance properties, which were compared with those of a commercial paint composition, considered as a reference, were overall satisfactory.

Keywords: acrylamide, acrylic resins, coatings, polymerization, synthesis

INTRODUCTION

The widespread usage of polymeric materials in different fields is attributable to their great performance, low cost and ease of processing,

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making them reliable engineering materials. The variety of polymeric materials also contributes to their great versatility of applications, including plastics, rubber goods, adhesives and coatings. Among the polymeric resins that have found success in the coating and paint industry are the acrylic resins. Although they have been used for more than 60 years, they are continuously developed to meet the changing and ever-increasing demands made on them in paint technology [1]. Moreover, the wide interest concerning the preparation and handling of acrylic resins results not only from the proper choice of adequate monomers to be copolymerized, but also from the pertinent chemical treatment required for the handling of their derivatives [2].

This article describes the step-by-step procedure that was followed to prepare a formulation for a self-curing acrylamide-based resin and the end use performance properties of the resulting paint composition.

A paint used for coating is a fluid substance which, once dried, forms a thin layer that could be a varnish if transparent, or an opaque spreadable paint film spread over a substrate to which it imparts qualities of a esthetics as well as physical and mechanical properties such as gloss and impact resistance [3]. A typical coating formulation includes a polymeric binder, solvents and plasticizers, colorant and other special purpose additives. The binder is the continuous matrix which represents the continuous phase throughout which the other ingredients are dispersed. The main properties of the coat film formed are strongly governed by the intrinsic characteristics of the resin. The solvents used in paint formulations are volatile liquids used mainly to fluidize a composition. Except for a few cases where the solvent reacts with the resin, it is generally eliminated by evaporation during the coating film formation. Plasticizers are also fluid substances but are non-volatile and are added to impart a plasticization effect in the composition of paints and varnishes. Other additives are used in order to impart specific properties. For example, surfactants help improve the wetting and the dispersion over the substrate. Thickening agents are another category of additives which are used to increase the viscosity of the paint and prevent the separation of the different ingredients [4].

The success of the preparation of the thermosetting grade of acrylamide-based resins depends largely on the control of polymerization conditions and kinetics. The kinetics of the polymerization of acrylamide are characterized by an unusually large rate constant for the propagation reaction, a relatively low rate constant for termination, and very low transfer processes to monomer and to solvent. As a consequence, high degrees of polymerization are possible, and the conversion of monomer to polymer can be nearly complete within relatively short reaction times. Extensive details concerning the chemistry of polymeric resins used in the paint industry, in addition to the general considerations in paint formulation, can be found in the literature [5–9].

EXPERIMENTAL

Materials

The different chemicals required for the polymerization, for the paint composition, and for testing, butanol, xylene, paraformaldehyde, and methacrylic acid (MAA), were all supplied by CYANAMID-France and were used as supplied. The monomers, acrylamide, methyl methacrylate (MMA), and butyl methacrylate (BMA), being of the highest purity grades, were used without any further purification.

The thermosetting polyacrylamide resin that was considered for the reference composition, trade name Uracron CS 103 XB, was obtained from DSM Resins, The Netherlands.

Monomer Preparation and Polymerization

The preparation of N-methylolacrylamide and N-butoxymethylolacrylamide, and their copolymerization with MMA and BMA, were carried out in a three-necked flask equipped with a stirrer and a reflux condenser. During each synthesis reaction, samples were taken at regular time intervals and were characterized in terms of evolution of free formaldehyde and hydroxyl group percentage for the monomer preparation, and in terms of viscosity and percentage conversion for the resulting resin.

The technical approach that was followed is explained in the Results section.

Testing Procedures

All the tests were carried out following the French standard AFNOR NF T-30 procedures [10].

Percentage of OH Groups

This method gives the weight of hydroxyl groups contained in 100 g of a sample. The experiment was performed for 3 tests among which one was the reference. A solution of 25 ml of acetic anhydride was added to a specimen and heated under agitation at 90°C for 40 min. To neutralize the excess acetic acid formed, distilled water was added to the solution, which was then titrated by a 1 N NaOH solution in the presence of phenol phthalein indicator. The percentage OH was calculated as

$$\%\text{OH} = \frac{(\text{V}_1 - \text{V}_2) \times 17{,}05 \times \text{f}}{\text{P}} \times 100 \qquad (1)$$

where V_1 is the volume (ml) of NaOH solution added for the reference. V_2 is the volume of the NaOH solution added for the test, f is a correction factor (usually taken as equal to 1), and P is the sample weight (g).

Free Formaldehyde

This method is based on the principle that in the presence of water the free formaldehyde reacts with sodium bisulphite, leading to the formation of sodium hydroxide, which is then neutralized by sulfuric acid solution. A sample of the methylolated monomer was put in an Erlenmeyer flask to which ice was added to 2/3 volume. After adding the color indicator under continuous agitation the mixture was neutralized by a 0.5 N H_2SO_4 solution until discoloration. Next, 50 ml of a molar solution of Na_2SO_3 was added and the mixture was titrated again by 0.5 N H_2SO_4 until a clear change in color occurs. The percentage of free formaldehyde was calculated as

$$\%\ \text{free formaldehyde} = \frac{\text{V} \times \text{N} \times 3}{\text{P}} \qquad (2)$$

where V is the volume (ml) of the 0.5 N H_2SO_4 added, N normality, and P the sample weight (g).

Iodine Index

The experiment, which is a measure of the double bonds in a molecule, was carried out for 3 tests among which one was the reference. A test sample was placed in a 250 ml Erlenmeyer flask and 25 ml. of carbon tetrachloride was added. While agitating, 25 ml of Wijs solution (iodide tetrachloride and iodine) was added and the mixture left in the dark for 2 h. Before performing titration by sodium thiosulfate, about 50 ml of distilled water was added in addition to starch powder as the color indicator. The iodine index was calculated as

$$\text{Iodine Index} = \frac{(\text{V}_1 - \text{V}_2)\ \text{N} \times \text{f} \times 126.9}{\text{P}} \times 100 \qquad (3)$$

where V_1 is the volume (ml) of the thiosulfate added for the reference, V_2 is the volume (ml) of the thiosulfate added for the test, f is the thiosulfate normality factor, N is the normality, and P is the specimen weight (g).

Solid Content

The percentage conversion was estimated from solid content measurements performed on samples withdrawn from the polymerization setup at regular intervals of time. It is calculated as the ratio of the initial weight (g) of the sample to the final weight (g) after drying.

Viscosity

The resin viscosity during the polymerization was measured by means of a Brookfield viscometer run at variable speeds. All measurements were carried out at room temperature.

Coat Film Perzos Hardness

A sample of a coat film, 20–30 microns thick, applied on a metal plate was placed resting horizontally on two steel balls and then a pendulum was freed to oscillate from an initial angle of 12°. The Perzos hardness is expressed in terms of the time (sec) it took for the pendulum to oscillate between 12° and 4°.

Impact Resistance

This test consists of determining the minimum height from which a given load of 1000 g falls freely and induces visual fracture on the coat film. The impact resistance is expressed as the ratio of height (cm) to the load (g).

Embossing Resistance

This test measures the resistance to fracture of a coat film subjected to slow deformation by embossing the metal substrate from its back side. The coated metal plate was tightely held between two steel rings perpendicular to a plunger axis. Then, the plunger, having a diameter of 20 mm was allowed to penetrate slowly at a constant speed until fracture occurs. The apparatus is fitted with an optical microscope that detects the appearance of cracks on the film surface. Embossing resistance is expressed in terms of the plunger penetration depth (mm) to cause fracture.

Gloss

Gloss was measured by means of a gloss meter at an angle of 60°. The apparatus was calibrated using a standard specimen with a gloss value of 93.

RESULTS AND DISCUSSION

Monomer Preparation

In order to functionalize acrylamide and provide a site for crosslinking, the monomer was prepared by a methylolation reaction, i.e., reaction of acrylamide with formaldehyde:

$$CH_2{=}CH{-}\overset{\overset{O}{\|}}{C}{-}NH_2 + HCHO \longrightarrow CH_2{=}CH{-}\overset{\overset{O}{\|}}{C}{-}NH{-}CH_2{-}OH \tag{4}$$

To follow the course of this reaction, the disappearance of formaldehyde and hydroxyl group formation were monitored. Figure 1 shows the variations of the free formaldehyde and OH groups' percentages with the methylolation reaction time. The trends of these curves are governed by kinetic considerations. They show that during the first

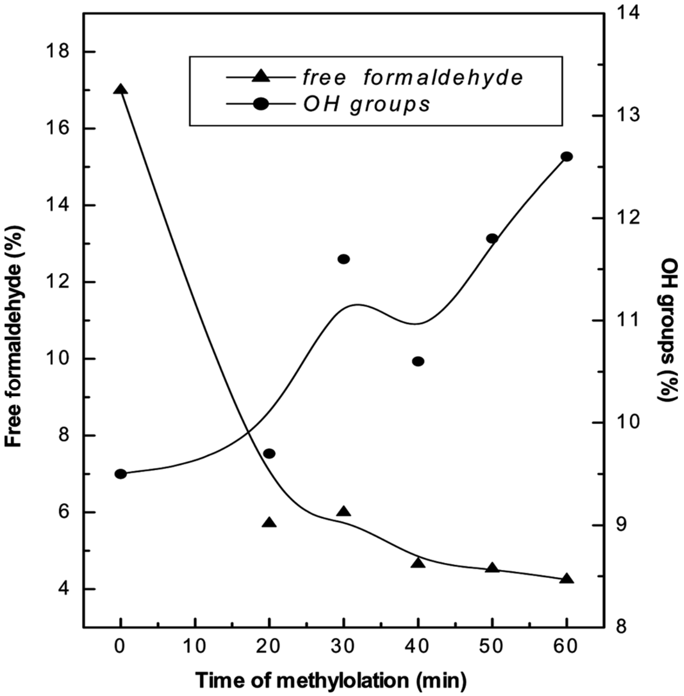
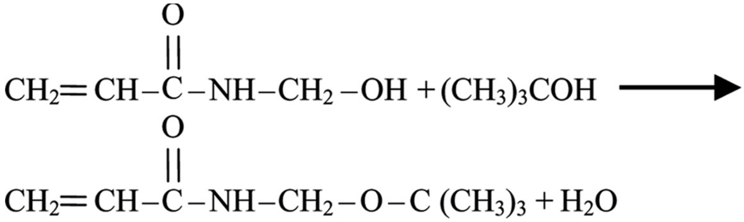


FIGURE 1 Evolution of the free formaldehyde and the hydroxyl groups with methylolation reaction time.

20 min, the reaction proceeds at a rate such that the formaldehyde is rapidly consumed and methylolacrylamide is slowly formed. Then for the rest of the reaction time, methylolation follows a steady rate before reaching a constant level. This leveling off did not correspond to a final state, since it turned out later that the functional monomer formed was not stable as was evidenced from the change in its appearance. Within two weeks' storage at room temperature, this monomer changed from a wax-like viscous liquid to a less-viscous milky one. This instability could be attributed to the reversibility of the methylolation reaction owing to the weakness of the $-NH-CH_2OH$ bond.

Conversely, since in the presence of a strong base such as NaOH, which was used to adjust the pH value to around 8, acrylamide may polymerize, it was therefore necessary to verify. But according to the Iodine index variation, from 1.89 to 1.96 for acrylamide and N-methylolacrylamide, respectively, it is clear that homopolymerization was far from being the predominant reaction.

Because of the instability of N-methylolacrylamide, another functional form of the monomer, N-butoxymethylolacrylamide, was prepared by the etherification of the former:



$$CH_2{=}CH{-}\overset{\overset{O}{\|}}{C}{-}NH{-}CH_2{-}OH + (CH_3)_3COH \longrightarrow$$
$$CH_2{=}CH{-}\overset{\overset{O}{\|}}{C}{-}NH{-}CH_2{-}O{-}C\,(CH_3)_3 + H_2O \quad (5)$$

This reaction was carried out using an excess of n-butanol in an inert acidic medium and driving out the formed water by means of an azeotropic distillation.

Both this functional monomer and the resin resulting from its polymerization were stable.

Polymerization with N-butoxymethylolacrylamide

The end-use performance of the resin and the appropriate choice of the synthesis conditions were the main considerations that dictated the selection of all ingredients, that is, the copolymerizing monomers, initiator, molecular weight regulator, catalyst, and solvents. For instance, the use of the methylmethacrylate (MMA) and buthylmethacrylate (BMA) combination was intended to result in a synergistic effect with respect to the resin hardness. Benzoyl peroxide was chosen as the initiator for practical reasons. It generally decomposes at a

TABLE 1 Initial Composition used to Estimate Initiator Concentration [I] and Transfer Agent Concentration [T.A] Needed

	[I] constant		[T.A.] constant	
Formulation with ingredient (g)	BMA	MMA	BMA	MMA
N-butoxymethylolacrylamide (50% in n-butanol)	20	20	20	20
Initiator	03	0.3	04–0.7	04–0.7
Xylene/butanol (60/40)	90	90	90	90
Transfer agent	0–0.7	0–1.4	0.5	1.2
MMA or BMA	83.3–82.6	83.3–81.9	82.7–82.4	82–81.4
MAA	3.2	3.2	3.2	3.2

moderate rate between 60°C and 80°C, a temperature range safe enough to help avoid premature crosslinking through the reaction between the methylol groups, and to avoid also the loss of the solvents and monomers through evaporation. Methacrylic acid (MAA) was used because it catalyzes curing and enhances adhesion to substrates. Finally, laurylic mercaptan was used since it is a common transfer agent for the control of molecular weight, a major structural factor that affects the resin properties.

Once the ingredients were selected, the next step was to find the optimum concentration of each of them. Taking into account the fact that viscosity and conversion, in addition to the mechanical and physical properties of the resulting resin, are the limiting factor, we have aimed to find the initiator concentration [I] and that of the transfer agent [T.A.] that would offer the required system viscosity with maximum conversion. In this context, the copolymerization of N-butoxymethylolacrylamide with MMA and BMA was carried out using the initial composition, which is shown in Table 1. In order to adjust the conditions and estimate the optimum [I] and [T.A.] the system viscosity and the corresponding conversion were monitored and the results are shown in Figures 2, 3, and Figures 4, 5 for MMA and BMA, respectively. The major comments to be made concerning the synthesis are as follow:

First, the N-butoxymethylolacrylamide that was prepared did not show any change throughout the entire progress of this work.

As for amido resins, the degree of etherification is the main factor that affects the resin stability and paint properties as well as viscosity and degree of polymerization. As the viscosity decreases, the degree of polymerization increases and so does stability, consequently, reactivity decreases and softer paint films would result. On the other hand,

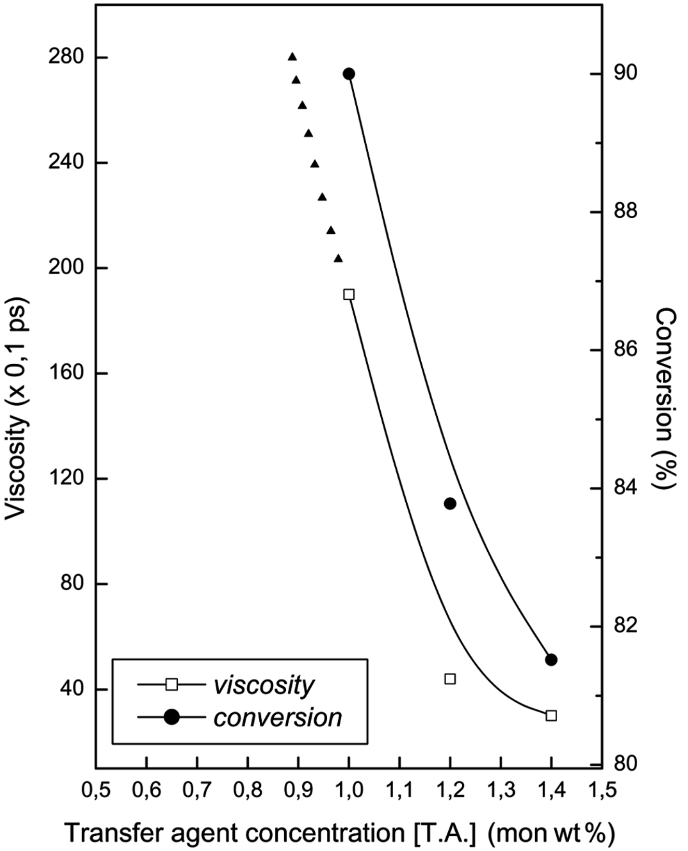


FIGURE 2 Copolymerization with MMA. Effect of transfer agent concentration [T.A.] on viscosity and conversion (constant initiator concentration [I] = 0.6 mon wt%).

increasing the degree of etherification gives better gloss but lower hardness. This is why a compromise should be found in order to produce balanced properties. In this study the etherification to 80% seemed to be adequate to achieve satisfactory resin characteristics.

Despite a slight reddish coloration, the resulting synthesized resin exhibited an aspect similar to that of the reference resin. This coloration actually originated from the methacrylic acid itself.

One of the drawbacks of the resin based on this monomer was the relative lower conversion compared to that obtained with N-methylolacrylamide. In fact, conversion above 90% was not possible as this limit marked the onset of gel effect (shown in Figure 2 with a

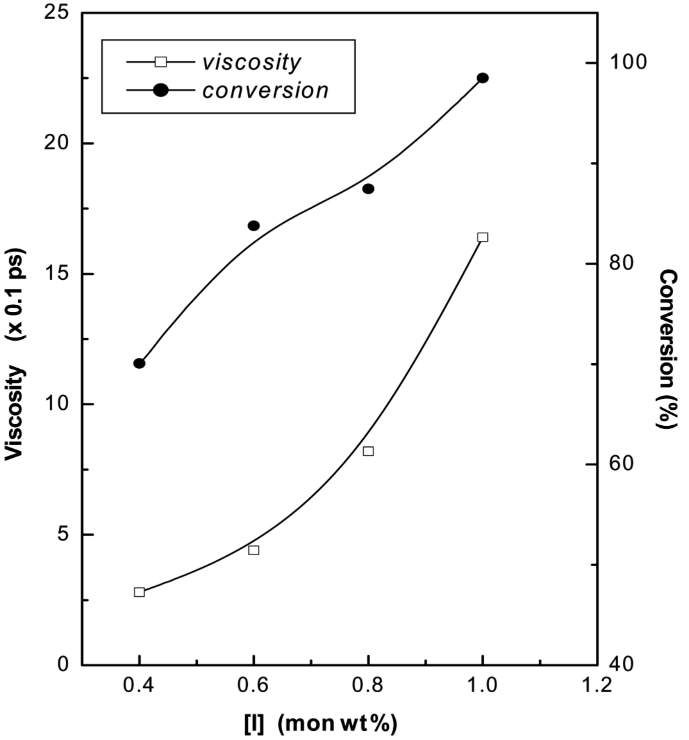


FIGURE 3 Copolymerization with MMA. Effect of initiator concentration [I] on viscosity and conversion (constant transfer agent concentration [T.A.] = 1.2 mon wt%).

dotted line). The maximum conversion (90%) that was reached corresponded to a 45% solid content, meaning that the residual monomers could have then affected drastically the performance of the resin once used in application. One of the problems linked to this aspect was in fact the appearance of orange skin due to the presence of volatile substances which broke the continuity and the regularity of the flow lines of the coating paint during its application. To remedy this problem different solutions are possible. These include the use of a heavier diluent, such as xylene or diacetone alcohol. Another solution reported by Savostianoff [4] and referred to as the "reflow" process, consists of drying the film at 80°C – 90°C and polishing in order to get rid of orange skin and redrying again at 140°C to get a smooth surface. The most reliable solution however, in order to avoid the formation of any residual substance, would be to carry out the polymerization

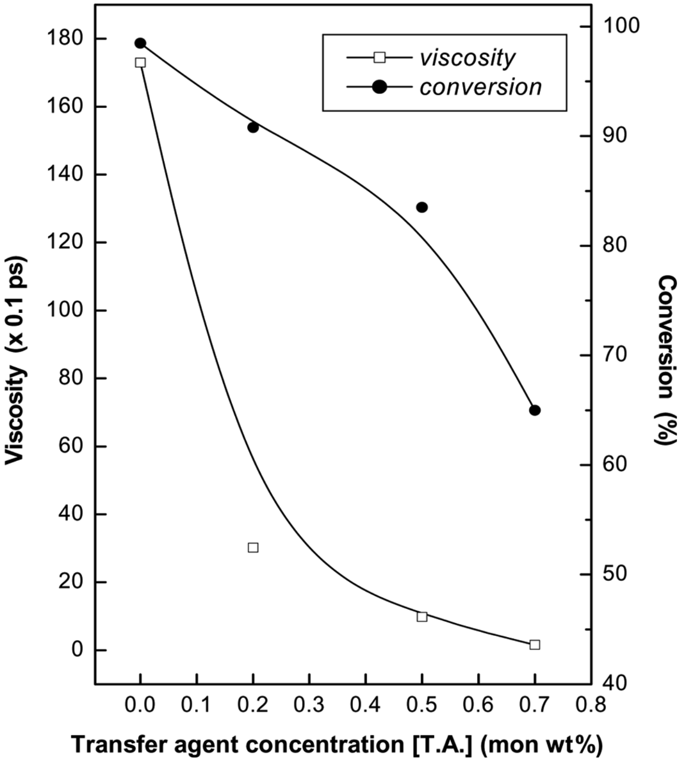


FIGURE 4 Copolymerization with BMA. Effect of transfer agent concentration [T.A.] on viscosity and conversion (constant initiator concentration $[I] = 0.6\,\text{mon wt\%}$).

to complete conversion (as near to 100% as possible) by adjusting the monomer and initiator concentrations as well as temperature.

Polymerization Formulation Optimization

Methacrylic acid is an important ingredient in the coat film formulation, for it catalyzes the curing reaction and participates also in the crosslinking formation. It was therefore necessary to find its adequate concentration that would give optimum mechanical properties in terms of hardness and impact resistance. Different concentrations were used, fixing the other components at the specified quantities, and the corresponding properties were monitored, as shown in Figure 6. It is shown that hardness and impact resistance vary contrarily with respect to methacrylic acid concentration, suggesting that a compromise should

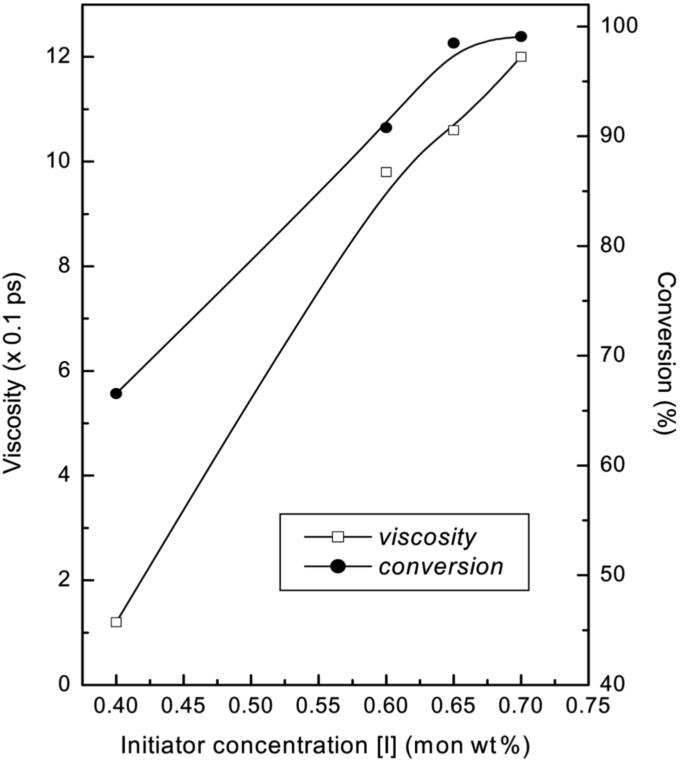


FIGURE 5 Copolymerization with BMA, effect of initiator concentration [I] on viscosity and conversion (constant transfer agent concentration [T.A.] = 0.5 mon wt%).

also be found. The optimum concentration of methacrylic acid that gave satisfactory properties, compared to those of the reference formulation was found to be 2 wt%.

The properties of the coat film that was made from the synthesized resin are shown in Table 2. In addition to a high degree of gloss, the coat paint showed a good adhesion to the metal substrate and a high detergent resistance. Nevertheless, a major drawback, worth to be pointed out, is that this resin was more sensitive to impact than the reference formulation. This property may be enhanced through the use of additives, including an external high molecular weight plasticizer such as an epoxy resin or even a urea/formaldehyde resin, that could be incorporated once the polymerization composition and conditions adjusted.

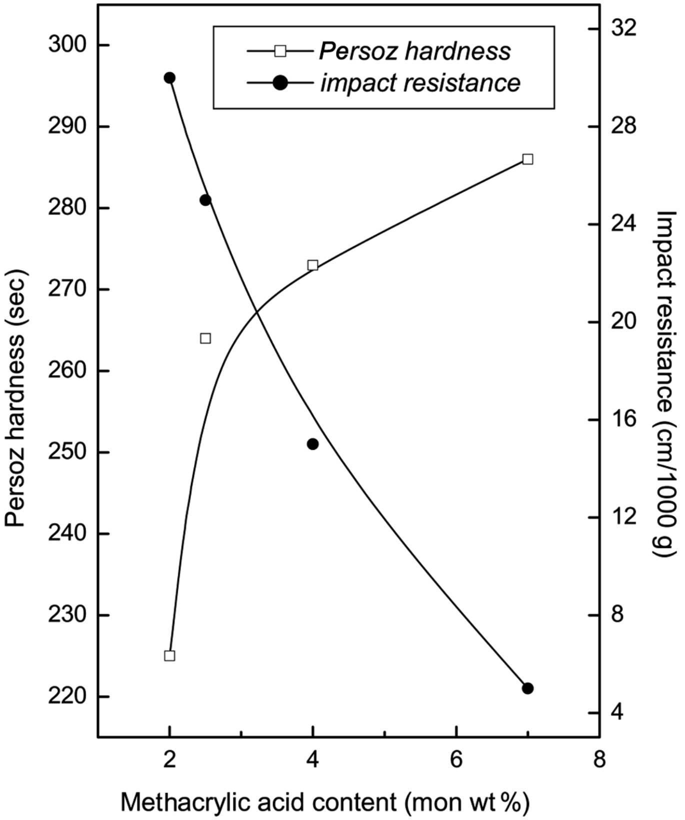


FIGURE 6 Effect of Methacrylic acid content on Hardness and Impact resistance of the coat film. Ingredients (g): N-butoxymethylolacrylamide-63% in n-Butanol (32.4), Xylene/n-Butanol 60/40 (60/27.7), Initiator (1), transfer agent (0.9), MMA (38), BMA (38).

TABLE 2 Butoxymethylolacrylamide-based Paint Properties Compared to those of the Reference Composition

Property	Synthesized resin	Reference resin
Persoz hardness (sec)	213	245
Embossing (mm)	8.6	9.6
Impact resistance (cm/1000 g)	30–35	40–45
Gloss (degree)	71.39	88.60
Adhesion to a metal substrate	Good	Good

CONCLUSION

This study dealt with the functionalization of acrylamide monomer and its copolymerization with methylmethacrylate and butylmethacrylate. Different compositions were prepared in order to adjust the initiator and molecular weight regulator concentrations.

The resulting resin was characterized in terms of paint property requirements and the results were compared to those of a commercial reference composition. After some adjustments in both the polymerization conditions as well as the paint formulation, the synthesized resin exhibited satisfactory properties including gloss, hardness, and resistance to impact and to embossing.

For further completion of this work, it is recommended to investigate the effect of the addition of an epoxydic or urea/formaldehyde resin, and to correlate quantitatively the synthesized resin molecular weight with the different ingredient concentrations.

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