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Short communication

## A method for polymethymetacrylate coating via self-curable unsaturated polyester primer on metal and glass surfaces

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### Abstract

A method was developed for protective coating of steel and glass surfaces with poly(methylmethacrylate) (PMMA). In this method, first, a primer coating was formed on the flat surfaces using self-curable polyester, poly(2-hydoxypropyl maleate) (Polymer-1). The polyester was applied onto polished surfaces and heated at 180  $^{\circ}$ C for 15–120 min to obtain transparent and crosslinked primer layer without using additional crosslinker.

Extent of the crosslinking was followed by real time IR methodology, based on decreasing intensity of the maleate double bond vibration at  $1640 \text{ cm}^{-1}$ . Experiments revealed that the crosslinking (15.4% within 1 h) occurs by addition of hydroxyl groups to the double bonds in the curing process.

The top coating with PMMA was performed by crosslinking photo polymerization of methylmethacrylate on the primer in presence of functional polyester (Polymer-2) having methacrylate pendant units. Thus UV irradiation at  $350 \text{ nm} (1.03 \times 10^{-3} \text{ mW cm}^{-2})$  for 30 min gave crosslinked PMMA coating layer with a Rocker hardness of 4. Real time IR studies revealed that more than 84.6% of the methacrylate groups disappear within 1 h of irradiation. Excellent adhesiveness of the top coating (5B) was ascribed to possible grafting of MMA through the residual maleate double bonds on the primer. Standard coating tests (contact angle, adhesion, hardness, flexibility and acid–base resistance) indicated that the method presented is versatile in coating of metal or glass surfaces with smooth PMMA layer. © 2007 Elsevier B.V. All rights reserved.

Keywords: Surface coating; Photo curing; Thermal curing; Poly(methylmethacrylate); Functional polyester; Unsaturated polyester

## 1. Introduction

Surface coating was and still is one of the major tasks in modern industry. Many excellent coating formulations have been developed, so far, for decorative and protective purposes [1]. However, in recent years, the technology has slightly changed due to increasing demands for better performance and stringent environmental regulations.

Among various coating materials poly(methylmethacrylate) (PMMA) has found less attention, although it exhibits high transparency, reasonable photo stability and good mechanical strengths. Moreover, PMMA has an outstanding hydrolytic stability against acid and base hydrolysis which is scarcely encountered in other vinyl ester polymers and polyesters. PMMA has found uses in medicine as bone template [2] and as coating material for titanium based implants in surgery [3,4].

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0300-9440/\$ - see front matter © 2007 Elsevier B.V. All rights reserved. doi:10.1016/j.porgcoat.2007.06.005 Solid PMMA surface is known as significantly inert to many chemical reactions. It is sluggish even in aminolysis reaction under ordinary conditions. However, its very low reactivity against amines allows grafting of poly(ethylene imine) and DNA onto flat PMMA surfaces [5,6]. Relatively low scratch resistance of PMMA coatings is an important drawback which deters their extensive use [7]. One solution is the use of pigmented PMMA. PMMA–silica hybrid coatings obtained by surface modification of the colloidal silica with trimethoxysilyl propyl methacrylate and followed polymerization of MMA through the surface has been demonstrated to enhance the scratch resistance [8].

Recently Chibowski et al. [9] demonstrated that, spin coating in the presence of polypropylene nanoparticles as fillers (1.7-5%) produces super hydrophobic surfaces with the contact angles as high as  $145^{\circ}$ .

However, another important limitation is weak adhesion of PMMA to underlying substrates. The use of tetramethylammonium formate has been demonstrated to increase adhesion of PMMA to various substrates [10]. An alternative route to improve the adhesion strengths is the use of copolymers with epoxy or hydroxy functional monomers such as 2-hydroxyethylmethacrylate or glycidylmethacrylate [11].

The present work is aimed at developing a method for highly adhesive PMMA coatings on metal and glass surfaces. In this method the coating was performed via well-adhered primer layer. New self-curable polyester, poly(2-hydroxy propylene maleate) (Polymer-1) was used for the primer coating. It was demonstrated that, this polyester with hydroxy groups in each repeating unit undergoes rapid crosslinking upon heating above 150 °C, without using additional crosslinker [12]. In the present study this chemistry was employed to create robust primers on glass and metal substrates.

The top coating with PMMA was achieved by photo curing of polyester (Polymer-2) with methacrylate pendant groups, using MMA as reactive diluent. In the study thermal curing for the primer layer was investigated in various time–temperature conditions and progress of the photo curing for the top coating was followed by real time IR spectroscopy technique. Typical coating characteristics such as flexibility, adhesiveness, hardness, acid–base resistances and contact angles were determined by standard procedures both for the primer and for the resulting bilayer coatings.

## 2. Experimental

## 2.1. Materials

Commercial glycidol partially polymerizes spontaneously upon standing especially when stored at room temperature. To obtain pure substance it was distilled under reduced pressure, before use. Methylmethacrylate (Aldrich), glycidylmethacrylate (Aldrich), cyclohexene oxide (Aldrich), dimethoxyethane (Acros) were distilled for purification. All the other chemicals were analytical grade products: Maleic anhydride (E. Merck) and succinic anhydride (E. Merck) were used as supplied.

## 2.2. Methods

## 2.2.1. Gel permeation chromatography (GPC)

GPC traces were taken by using an Agillant 1100 series apparatus consisting of a pump, a RI detector, and Waters styrogel (HR 4, HR 3, and HR 2) columns. Tetrahydrofuran was used as the eluent, and the flow rate was  $0.3 \text{ mL min}^{-1}$ .

#### 2.2.2. FT-IR spectra

FT-IR spectra were recorded on a Perkin-Elmer FT-IR Spectrum One B spectrometer.

## 2.2.3. Determination of the film characteristics

The film samples aforementioned were subjected to flexibility (the DIN 53 152), adhesion (ASTM D 3359-90 Test method B.), water resistance (ASTM D 1647-89), alkaline resistance (ASTM D 1647-89), and acid resistance (ASTM D 1647-89) and Rocker hardness (ASTM D 2134-66) tests. Glass tubes were used for the alkaline and acid resistance tests, as explained in the related standard methods.

## 2.2.4. Contact angle

The contact angles were measured according to the sessile drop technique by Goniometer (KSV Instruments Model CAM 101). A drop of distilled water with a tight syringe was placed on the surface. Advancing contact angles associated with the hydrophobic character and receding contact angles indicating hydrophilic character of the surface were measured at both left and right sides of the drop. The contact angles of surfaces were calculated from the average of the measured values.

## 2.3. Preparation of poly(2-hydroxy propylene maleate) (Polymer-1)

This polymer was prepared by stepwise condensation of maleic anhydride with glycidol (see Scheme 1) as reported before [12]. Viscous solution of the polymer  $(M_n = 16,400 \text{ gmol}^{-1})$  with 38.1% (w/w) dimethoxyethane was used in coating applications. The resulting polymer was found to be soluble in, ethanol, acetone, dimethylformamide (DMF), THF and insoluble in benzene, toluene, ether, *n*-heptane and slightly soluble in water.

# 2.4. Preparation of the polyester with methacrylate pendant groups (Polymer-2)

This polyester was prepared by reaction of succinic anhydride with equimolar amounts of epoxy compounds in presence of zinc succinate as catalyst as described elsewhere [13]. The polyester with 10% mol of glycidyl methacrylate pendant units was obtained by polymerization of glycidyl methacrylate (0.01 mol)–cyclohexeneoxide (0.09 mol)–succinic



Scheme 1. Preparation of the unsaturated polyester with hydroxy groups (Polymer-1) for the primer coating.

anhydride (0.10 mol) mixture (see Scheme 1). Herein glycidyl methacrylate was chosen as the main epoxy component while cyclohexeneoxide was the secondary epoxy component in order to dilute GMA component.

## 2.5. Coating with polymer-1 (primer formation)

The specimens  $(50 \text{ mm} \times 100 \text{ mm} \times 2 \text{ mm})$  were prepared from appropriate commercial materials. Surfaces of the glass and steel were cleaned by successive washing with detergent and distilled water before coating.

Polymer-1 solution was applied onto flat surfaces of glass or metal substrates by means of a Bird applicator with  $60 \,\mu m$  of aperture. They were transferred into an oven and heated at  $50 \,^{\circ}$ C for 2 h to remove solvent residues. Then they were cured at  $180 \,^{\circ}$ C for predetermined times.

Extension of the crosslinking reaction in the curing process was assigned by FT-IR spectra of the samples. This was carried out simply by monitoring the intensity ratios of stretching vibration bands of the maleate double bond at  $1640 \text{ cm}^{-1}$  to those of the carbonyl group vibrations at  $1715 \text{ cm}^{-1}$ .

## 2.6. Top coating with poly(methylmethacrylate)

Polymer-2 (1 g) was dissolved in 7.5 mL methylmethacrylate and 55 mg (0.3 mmol) benzophenone, 37 mg(0.3 mmol) *N*,*N*-dimethylaniline were added to this solution. The resulting solution was applied onto the primer (60  $\mu$ m) as described above. The films were irradiated in a Rayonet Merry-go-Round type photometer equipped with 16 lamps emitting light nominally at  $\lambda = 350$  nm and a cooling system. Extent of the photo curing reactions was followed by real-time IR spectroscopy methodology.

This was achieved by monitoring variation of the ratio of peak area of C=C stretching vibration band at  $1640 \text{ cm}^{-1}$  to that of the carbonyl vibration band at  $1715 \text{ cm}^{-1}$  during UV exposure (15–120 min). The data collected were used to build Fig. 2.

## 3. Results and discussion

In this work, a method was developed for coating of glass and metal surfaces with poly(methylmethacrylate). Coating those surfaces with (PMMA) is attractive due to its outstanding stability against acid-base hydrolyses and optical properties. However, direct coating with PMMA suffers from low adhesion which deters its extensive use in coating. In order to attain better surface adhesiveness, in this work, a suitable primer was formed, prior to application of PMMA.

For the primer new unsaturated polyester (Polymer-1) with hydroxy pendant groups was chosen, due to its good film forming ability and excellent adhesion to various substrates. This was obtained by stepwise ring opening of maleic anhydride and glycidol (Scheme 1), as described in our previous paper [12].

It was demonstrated that this polymer undergoes rapid crosslinking upon thermal curing above 150 °C to give a hard transparent mass. By taking this advantage into consideration



Fig. 1. FT-IR spectra of the primary coating layer before and after curing at 180  $^{\circ}\mathrm{C}$  for 1 h.

Polymer-1 was employed to form primer on steel and glass surfaces. For this purpose, the solution of the polyester ( $M_n$ : 16,400) was prepared using dimethoxyethane (38.1%, w/w) as solvent.

The viscous solution was applied onto the surfaces by means of Bird applicator with 60  $\mu$ m aperture. After removal of the solvent, the samples were heated in an oven at 180 °C for 1 h. This treatment gave hard and transparent coating layers on the surfaces. Fig. 1 shows FT-IR spectra of the surface coating layer before and after the curing. In the IR spectrum of noncured sample, the peaks at 1715 and 1640 cm<sup>-1</sup> are associated with carbonyl and carbon–carbon double bond vibrations of the unsaturated polyester, respectively. Thermal curing at 180 °C resulted in self-crosslinking of the polyester. The crosslinking occurs by addition of hydroxy groups to double bonds of the maleate component at this temperature (Scheme 2).

This mechanism was confirmed by diminishing intensity of the stretching vibration of the double bond at  $1640 \text{ cm}^{-1}$  after curing (Fig. 1). Extension of the crosslinking was assigned based on variation of ratio of the peak areas by the following relationship.

Conversion (%) = 
$$\frac{A_2^0 / A_1^0 - A_2 / A_1}{A_2^0 / A_1^0}$$

where,  $A_1^0$  and  $A_1$  are integrals of the carbonyl band at 1715 cm<sup>-1</sup> before and after curing, respectively.  $A_2^0$  and  $A_2$  are integrals of the double bond vibration at the beginning and at anytime. This assignment gave 15.4% conversion of the double bonds for the cured sample with the glass substrate.

The curing was studied at 170, 180 and 190 °C in order to determine the optimal cure temperature. The temperature, 180 °C was determined as optimal for the curing. However, curing at 190 °C gave slightly colored coatings, most probably due to partial dehydration of the polyester itself. Curing at 170 °C, on the other hand, gave a coated surface showing the same FT-IR spectra. But the resulting sample gave 3.6% of non-crosslinked polyester when soaked into acetone for 3 h, as observed in our previous work [12]. The films cured for 1 h at 180 °C gave no detectible acetone soluble portion.

Some physical characteristics of the surface films so obtained are listed in Table 1. The results showed that the surface layer



Scheme 2. Self-crosslinking of Polymer-1 by thermal curing.

Table 1	
Some film properties of the primer coating layer	

Substrate	Flexibility <sup>a</sup>	Adhesion <sup>b</sup>	Rocker hardness <sup>c</sup>	Acid resistance <sup>d</sup>	Alkali resistance <sup>e</sup>	Water resistance
Glass	No change	5B	4	No change	4 min (partial peeling)	No change
Steel	No change	5B	5	No change	3 min (partial peeling)	No change

<sup>a</sup> Test was positive when the cylinder with 2 mm diameter was used.

<sup>b</sup> Test method B was applied.

 $^{c}\,$  Dry film thickness was measured as 5  $\mu m$  (by elcometer).

<sup>d</sup> Test was carried out at 25 °C with 9% H<sub>2</sub>SO<sub>4</sub> solution.

 $^{e}\,$  Test was carried out at 25  $^{\circ}C$  with 3% NaOH solution.

exhibits excellent adhesion to the underlying surface. High adhesiveness of the surface film might stem from the hydroxy functionality of the unsaturated polyester. In another words, role of the hydroxy groups is to provide surface adhesion and crosslinking by addition to the double bonds in the cure conditions.

The primer showed excellent flexibility, adhesion and water resistance and very good acid resistance. Surface coating with common polyesters, on the other hand, are known to give surface cracks in some cases due to brittleness of the films obtained. Oil modification of the polyester is most common way to impart flexibility to avoid such surface defects. Excellent flexibility was attained by using Polymer-1 without additional softening component.

Adhesion of the primer is of prime importance for success of the whole coating process. High adhesion (5B) of this layer to the substrate material revealed that the unsaturated polyester is suitable as the primer although it showed somewhat low alkaline resistance (Table 1).

## 3.1. Top coating by UV curing

This was achieved by photo induced radical polymerization of MMA in the presence of new polyester possessing methacrylate pendant groups. The polyester (Polymer-2) used was obtained by zinc succinate catalysed ring opening reaction of the epoxy group of GMA (0.1 mol) with succinic anhydride (1.0 mol), in the presence cyclohexeneoxide (0.9 mol) as diluting comonomer, as reported before [13] (Scheme 3)

This procedure gave low molecular weight polyester (oligoester) with  $M_n = 1400$ ,  $M_w = 1450$ . Although, <sup>1</sup>H NMR spectrum of the resulting polymer indicated somewhat less methacrylate pendant group content (0.092 mol), it was demonstrated that solution of the polymer itself gives crosslinked materials by UV irradiation at 350 nm in the presence of benzophenone as activator.

In the present study this polyester was exploited as crosslinking agent in the polymerization of methylmethacrylate on the primer layer. To the solution of the polyester (12.5%, w/w) in



Scheme 3. Preparation of the polyester with methacrylate pendant units (Polymer-2) as crosslinker in photo polymerization of MMA.



Fig. 2. FT-IR spectra of the primer which was produced by thermal curing (1 h) of Polymer-1 (a), MMA–Polymer-2 mixture on the primer before (b) and after UV curing for 30 min (c) on glass substrates.

MMA, there were added catalytic quantities of benzophenone and *N*,*N*-dimethyl aniline and the resulting viscous solution was applied onto the primer on metal or on the glass substrates.

Viscosity of the solution was considered to provide easy processing and allows making patterned surfaces. Irradiation at 350 nm for 30 min resulted in hardening of the surface. FT-IR spectra of the surface showed significantly less intense methacrylate double bond vibration at 1640 cm<sup>-1</sup>, as expected (Fig. 2).

The double bond consumption in the photo polymerization was estimated by comparing peak areas of the double bond and carbonyl groups as in the case for the primer and the conversions were calculated based on the same formula.

Conversion–irradiation time plot in Fig. 3 shows that polymerization is fast at the beginning. 62.5% of the double bonds is consumed within 15 min and leveled off around 85% after 1 h of the irradiation.

However this estimation might not be correct, because it is highly probable that, maleate double bonds at the outer side of the primer may also involve in the photo polymerization. Although maleate esters are known to be reluctant to copolymerization with MMA [14], their fumarate isomers formed during the heating at 180 °C may have reasonable tendency of



Fig. 3. Percentage double bond consumption in photo curing of MMA–Polymer-2 mixture on the primer for the formation of top coating.

Some characteristics of the top coatings formed within different irradiation times

Irradiation time (min)	Flexibility <sup>a</sup>	Adhesion <sup>b</sup>	Rocker hardness <sup>c</sup>	Acid resistance <sup>d</sup>
15	No change	5B	4	No change
30	No change	5B	4	No change
60	No change	5B	6	No change
120	No change	5B	4	No change

<sup>a</sup> Test was positive when the cylinder with 2 mm diameter was used.

<sup>b</sup> Test method B was applied.

<sup>c</sup> Dry film thickness was measured as 9 µm.

<sup>d</sup> Test was carried out at 25 °C with 9% H<sub>2</sub>SO<sub>4</sub> solution.

copolymerization with this monomer [15]. Hence, graft copolymerization of MMA through surface of the primer is more likely to occur.

This means that the top PMMA layer is covalently linked to the primer and such linking must induce strong adhesion between the two layers.

Reasonably high adhesion (5B) and hardness of the top coating support this consideration (Table 2).

Obviously in such case calculations based on above formula will not be correct, because slight decrease in the initial double bond content by the copolymerization will cause great deviation in the conversions assigned by the above formula. However, it is almost impossible to make more precise assignment for the conversions in these conditions. Consequently the data shown in Fig. 3 must represent, at least, lower limits of the double bond conversions.

### 3.2. The contact angles

Contact angles of the substrates were measured  $19.7^{\circ}$  and  $22.2^{\circ}$  for naked surfaces of steel and glass samples, respectively. After coating with the unsaturated polyester the contact angle rised up to  $39.8^{\circ}$ . A drastic contact angle increment was observed for the case of the top coating with crosslinked PMMA (Table 3).

In another words the contact angles of the samples increase in accordance with increasing hydrophobicity of the surfaces in each step. Relatively small contact angle for the sample irradiated for 15 min (46.7°) indicated that the cure time is not enough. Maximum contact angle is observed for 30 min of cure time (74.9°). Slight decrease for 2 h irradiation can be ascribed to partial damage of the surface by prolonged UV exposure. These results revealed that, optimal irradiation time is around 30 min for the formation of the top coating.

Table 3

Contact angles of the support, primer and top coatings (PMMA) obtained by UV curing in different irradiation times

Surface	UV irradiation time (min)	Contact angle (°)	
Steel	_	19.7	
Glass	-	22.2	
Primer	0	39.8	
Top coating	15	46.7	
Top coating	30	74.9	
Top coating	60	74.6	
Top coating	120	69.7	



Primer layer

Scheme 4. Schematic illustration of the entire coating process.

#### 3.3. Other characteristics of the top coating

This process gives smooth, transparent and homogenous surface coatings either on steel or on glass supports. Regarding with other physical characteristics (Table 2) such as adhesion, hardness, flexibility and hydrolytic stability of the top coating, the procedure presented is satisfactory for coating with PMMA. Rocker hardness (4) attained within 30 min of irradiation which is in accordance with that implied by the contact angle measurements.

Overall bilayer coating process consists of two main steps as depicted in Scheme 4. The process yields smooth and transparent PMMA as top coating having typical luster of common acrylic surfaces.

## 4. Conclusion

Coating of steel and glass surfaces with the self-curable polyester (Polymer-1) by thermal curing at  $180 \degree$ C for 1 h gives

highly adherent primer. Followed photo curing of MMA solution of Polymer-2 on the primer yields crosslinked PMMA as top coating layer. Resulting bilayer coatings were found to be tightly adhered to the supports and exhibit typical surface characteristics of crosslinked PMMA. Considering with its peculiarities one can expect that the method presented might be of interest for preparing PMMA based super hydrophobic coatings in combination with suitable additives.

## References

- [1] E. Staring, A.A. Dias, R.A.T.M. van Benthem, Prog. Org. Coat. 45 (2002) 101.
- [2] J.W. Byun, J.U. Kim, Y.S. Lee, V.J. Chung, Macromol. Biosci. 4 (2004) 512.
- [3] A.W. Mccaskie, J.B. Richardson, P.J. Gregg, J.R. Coll, Surg. Edinb. 43 (1998) 37.
- [4] R. Kumazawa, F. Watari, N. Takashi, Y. Tanimura, M. Uo, Y. Totsuka, Biomaterials 23 (2002) 3757.
- [5] J. Liu, T. Pan, A.T. Woolley, M.L. Lee, Anal. Chem. 76 (2004) 6948.
- [6] F. Fixe, M. Dufva, P. Telleman, C.B.V. Christensen, Nucleic Acids Res. E9 (32) (2004) 1.
- [7] W. Tanglumlert, P. Prasassarakich, P. Supaphol, S. Wongkasemjit, Surf. Coat. Tech. 200 (2006) 2784.
- [8] E. Rubio, J. Almaral, R. Ramirez-Bon, V. Castano, V. Rodríguez, Opt. Mater. 27 (2005) 1266.
- [9] E. Chibowski, L. Holysz, K. Terpilowski, M. Jurak, Coll. Surf. A. 291 (2006) 181.
- [10] C. Li, G.L. Wilkes, J. Inorg. Organomet. Polym. 8 (1998) 33.
- [11] J.C. Kenny, T. Ueno, K. Tsutsui, J. Coat. Technol. 68 (855) (1996) 35.
- [12] N. Bicak, B. Karagoz, U. Tunca, J. Polym. Sci. Polym. Chem. 41 (2003) 2549.
- [13] N. Bicak, B. Karagoz, Polym. Bull. 56 (2006) 87.
- [14] D. Braun, G. Cei, Macromol. Chem. Phys. 187 (7) (1986) 1699.
- [15] G.M. Burnett, J.M. Pearson, J.D.B. Smith, J. Polym. Sci. Polym. Chem. 4 (10) (2003) 2543.