JKAU: Mar. Sci., **vol. 15,** pp: 73-84 (2004 A.D. / 1424 A.H.)

Synthesis of Marine Resin by Graft Copolymerization of Some Acrylic Monomers onto Poly (Vinyl Chloride). Part I

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Abstract. A graft copolymer of methyl methacrylate (MMA) and methacrylic acid (MAA) onto poly (vinyl chloride) (PVC) with benzoyl peroxide (BPO) as initiator in cyclohexanone was prepared. The formation of grafted copolymer was verified by infrared spectra FT-IR and ^{1}H-NMR. The linear and grafted copolymers have been used in formulation of antifouling coatings free from tributyl tin derivatives. After one year immersion in Obhor Bay, Red Sea, in Saudi Arabia, study indicates longer shelf life of the antifouling coating formulated by grafted copolymer compared to antifouling coating based on linear copolymer.

Introduction

Up to the present, antifouling paints contain either Copper or organometallic compounds such as tributyltin oxide (TBT)[1]. TBT based antifouling paints have been banned after demonstrating toxic effects to non-target marine invertebrates, and in particular on the embryo genesis[2-4].

International maritime organization (IMO) agrees that the global measures to be developed by the Marine Environment Protection Committee (MEPC) should ensure a global prohibition on the application of organotin compounds which act as biocides in antifouling systems on ships by 1 January 2003, and a complete prohibition by 2008[5].

Grafting is basically a cationic chain transfer step in the course of which a growing polymer is linked to a preformed polymer chain. However, chain transfer not only links the growing chain to a preformed polymer but also produces an independent initiating species. To render efficient grafting, the grafting attack must be terminated (as contrasted to chain transfer), *i.e.*, propagation must cease at the instant grafting onto the preformed backbone has been completed.[6]

Graft copolymerization of methyl methacrylate onto halogen-containing polymer chain has been utilized for grafting of methyl methacrylate/methacrylic acid monomer pair onto polyvinyl chloride[7]. The objective of the present work is to prepare such a resin, and to explore its use in antifouling paint formulations free from TBT.

Experimental

Materials

Methyl methacrylate (MMA) and methacrylic acid (MAA) were supplied from Merck GMB, Germany and Acros Organics Co. USA, respectively. The monomers were freed from inhibitor and purified by distillation under reduced pressure of N_2. Benzoyl peroxide (BPO) was obtained from BDH Chemicals Ltd, Poole (England), and was dosed as received.

Polyvinyl chloride (PVC), Evipol EP 7050, was obtained from European Vinyls Corporation Acrol Ltd. (Italy), and was purified by dissolving in methyl ethyl ketone and precipitating by methanol then drying at 50ºC under reduced pressure.

Benzalkonium chloride (BCl), supplied by Sigma Chemical Co. (Switzerland) and Parmetol PF95 from Schulke & Mayer, Norderstedt (Germany) were used as nontoxic antifouling agents[8].

Sigmarina antifouling IV is from Sigma Paint Company (KSA). It is based on cuprous oxide with tributyl tin fluoride (TBTF) and was taken as a reference.

FT-IR spectra were carried out by using Bruker IR spectrometer using KBr[9].

^{1}H-NMR spectra were obtained by a Varian-Mercury spectrometer (Germany) operating at 300 MHZ, dimethyl sulfoxide (DMSO) was used as solvent.

Copolymer Synthesis

Graft copolymerization reactions were carried out by solution polymerization using benzoyl peroxide (BPO) as a free radical initiator. A 250 ml three-necked round bottom flask under nitrogen with a water condenser was used as a kettle. The temperature of solution was maintained at 70 ± 2ºC, and controlled by Labmaster Isopad heating mantel.

Copolymers of MMA/MAA were made by mixing the monomers in appropriate molar ratios and adding gradually to a solution of BPO and PVC in the reaction flask during mixing at 600 rpm[7].

The viscosity of the solution increased by the time and the colour also converted from transparent to yellowish to off white. The gelatinous grafted copolymers were precipitated by aqueous methanol (10/90 v/v) and then dried at 50ºC under reduced pressure.

Marine Resins

The yield was quantified and the product was kept in glass bowls. When it solidified, the crude product was grinded to small granules. The granules were dissolved in a mixture of cyclohexanone and tetrahydrofuran (2:1) by volume and used in the antifouling coating formulations.

Paint Formulations

Four antifouling coating formulations were prepared based on linear copolymer (**L**) and on grafted copolymer (**G**) with nontoxic biocides as shown in Table 1.

The formulations were prepared by mixing together, the resin solution, rosin, and petroleum resin solutions, then adding the other ingredients of each formulation in the ratios given in Table 1. The mixture was milled until a high fineness of the paint was obtained. The viscosity was controlled by Brookfield viscometer model RVF.

TABLE 1. Nonpolluting antifouling coatings using linear and grafted copolymers of MMA/MAA onto PVC with BCl (A) and Parmetol PF95 (B).

Components	L-A	L-B	G-A	G-B
Acrylic resin solution 40% (in cyclohexanone)	9	9	9	9
Rosin solution 70% (in cyclohexanone)	19	19.3	19.8	19.4
Petroleum resin 50% (in cyclohexanone)	8	8	8	8
Colloidal silica	0.4	0.3	0.4	0.3
Red iron oxide	8.9	7.6	7.9	7.6
Cyclohexanone	7.4	6.8	7	6.5
Baysolvex (plasticizer)	0.0	3.6	0.0	3.6
Baryte	14	13	14	14
Kaolin	9	9	8	8
Dowanol PM	9.3	9.4	10.9	9.6
Biocide (A)*	15	....	15	....
Biocide (B)**	....	14	....	14
Total	100	100	100	100

*BCl = Benzalkonium chloride **Parmetol PF95

Evaluation of Antifouling Activity

The fouling resistance of submersion panels was investigated by visual and biological examination of the films in Obhor Bay, Red Sea, Jeddah, K.S.A.[10].

Results and Discussion

Characterization of Copolymer

FT-IR spectra of grafted copolymer

The compositions of graft copolymers were ascertained from vinyl group and chlorine content. Figure 1 shows the FT-IR spectrum of PVC, linear copolymer of MMA/MAA and grafted copolymer of MMA/MAA onto PVC. In the spectrum (A), the sharp bands at 630-650 cm^{-1} were attributed to –CCl which were reduced to small weak bands after grafting MMA/MAA copolymer onto PVC as shown in spectrum (C). –CH appeared as sharp absorption bands at 1350 cm^{-1} and 2950 cm^{-1} in spectrum (A) then disappeared after grafting as showing in spectrum (C). As will as the sharp bands in the region 1200-1500 cm^{-1} in spectrum (A) disappeared in spectrum (C) also may be due to the graft polymerization process. The bands at around 1750 cm^{-1} in (B, C) could be attributed to the carbonyl of the ester group. The broad strong absorption band of –OH appeared at 3460 cm^{-1} in spectra (B, C) due to the presence of MAA.

1H-NMR spectra of grafted copolymer

Figure 2 illustrates the ^{1}H-NMR spectra of PVC, linear copolymer of MMA/MAA and grafted copolymer of MMA/MAA onto PVC. The resonance peak of vinyl group protons were at δ = 3.2-3.4 ppm (doublet) for $–CH_2$ and the signal at δ = 2.2-2.6 ppm for –CH proton (triplet) were shown in spectrum (A). The signal of –CH (triplet) disappeared in spectrum (C) and this was attributed to the probability of the grafting has taken place on this location. Hence the grafting was proved by this result. The resonance peak of CH_3 proton was at δ = 1.6-2.55 ppm (multiple single), spectrum (B, C). The broad signal at chemical shift δ = 4.478 ppm in spectrum (A, C) may be attributed to the presence of halogen.

Technical Properties of Nonpolluting Antifouling Coatings

The mechanical properties[11] given in Table 2 show that, **G-A** (50% cohesive failure) demonstrates more strength than **L-A** (20% cohesive failure). **G-B** based on grafted copolymer exhibits higher binding strength (100% cohesive failure, *i.e.*, high bonding strength) than antifouling **L-B**, based on linear copolymer (90% cohesive failure). This improvement may be attributed to the branched structure of grafted copolymer. Also the Pull-off property was affect-

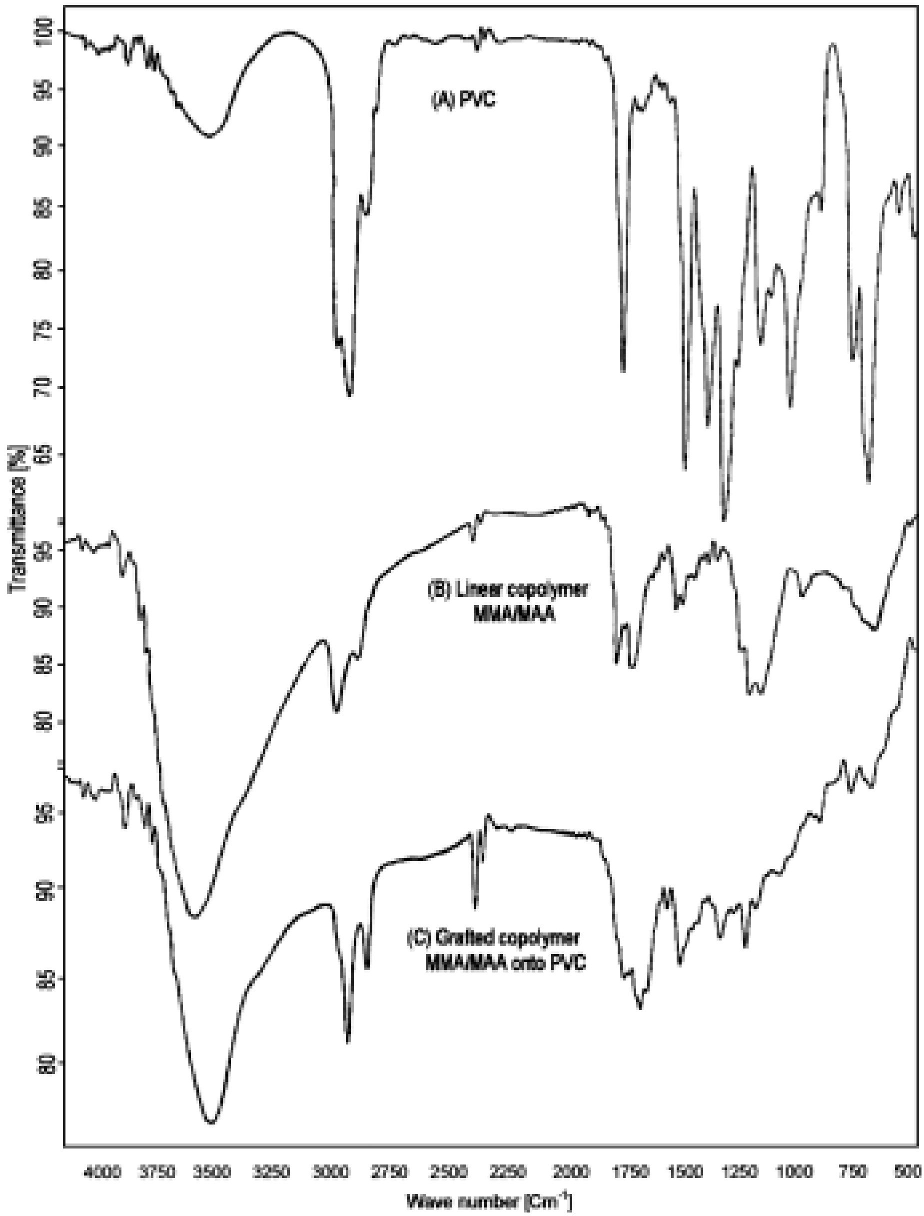

FIG. 1. FT-IR spectra of: (A) PVC, (B) Linear copolymer of MMA/MAA and (C) Grafted copolymer of MMA/MAA onto PVC at PVC/M = 15.8 %.

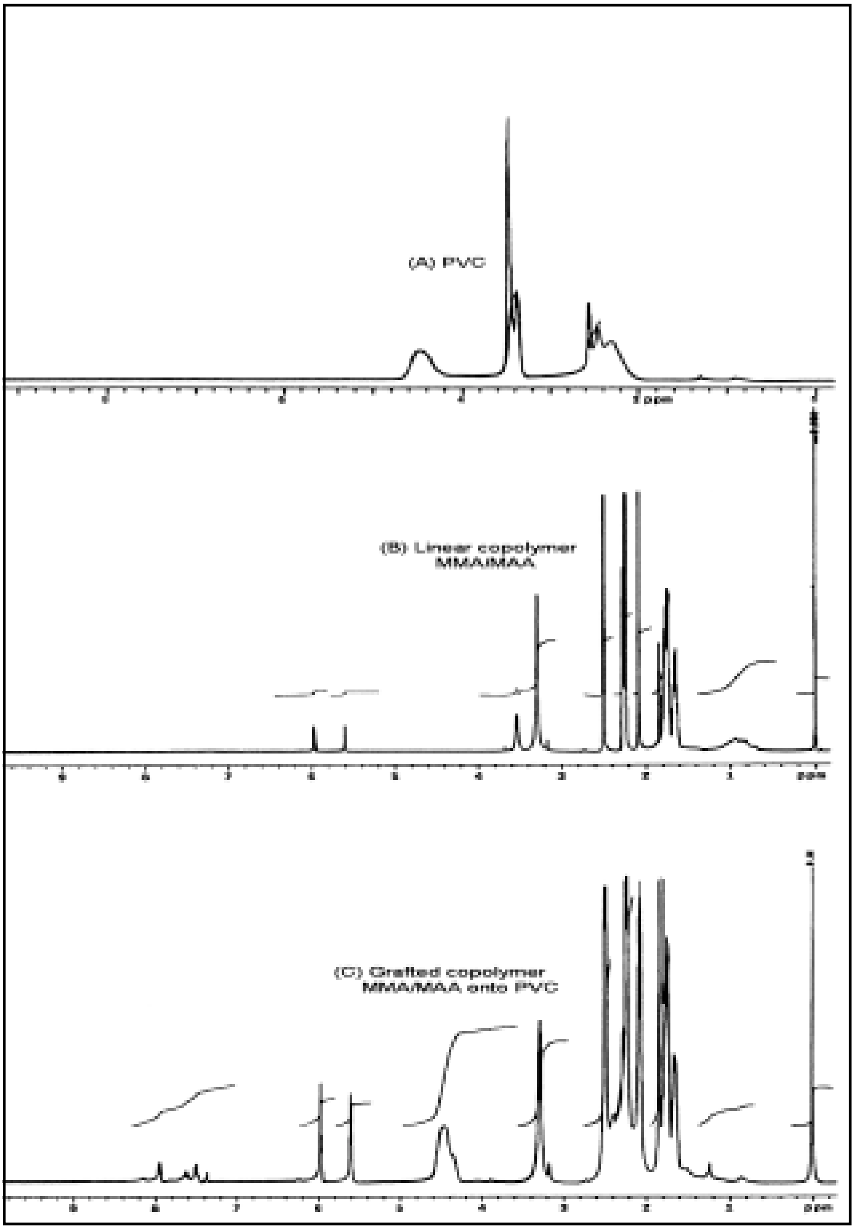

FIG. 2. ^{1}H-NMR of: (A) PVC, (B) Linear copolymer of MMA/MAA and (C) Grafted copolymer of MMA/MAA onto PVC at PVC/M = 15.8%.

ed by the biocide whereby **L-B** and **G-B** (with Parmetol PF95) show more bonding strength than **L-A** and **G-A** (with BCl) as the biocide.

TABLE 2. Technical properties of nonpolluting antifouling coatings based on linear and grafted copolymers of MMA/MAA onto PVC.

Test	Sigmarina IV	L - A	L - B	G - A	G - B
Specific gravity (g/cc)	1.54	1.31	1.29	1.11	1.18
Viscosity (cps)	1400	2000	2500	1500	1600
Touch drying time (min)	60	150	35	170	50
Solid content (%)	76	73	68	63	62
Pigment / binder ratio	N/A**	2.14	2.42	1.51	2.03
Pull-off test (kg/cm^2)	1.1	0.45	0.50	1.10	1.30
Remarks on bonding	15% (AF)	80% (AF)	10% (AF)	50% (AF)	0.0% (AF)
Strength*	85% (CF)	20% (AF)	90% (CF)	50% (CF)	100% (CF)

*AF = Adhesive failure and CF = Cohesive failure ** N/A = not available

Hydrolysis and Biocides Release

The ability of antifouling coating to uptake seawater depends on the nature of binder and biocides used in the formulation. Figure 3 shows that **L - formula** (linear copolymer) reaches the maximum water uptake in a short time, while grafted copolymer paint **G - formula** (grafted copolymer) and Sigmarina IV have a lower rate of water uptake. By studying the rate of water uptake, the hydrolysis and leaching rate of biocide and consequently the paint life time could be estimated for further possible product optimization[12].

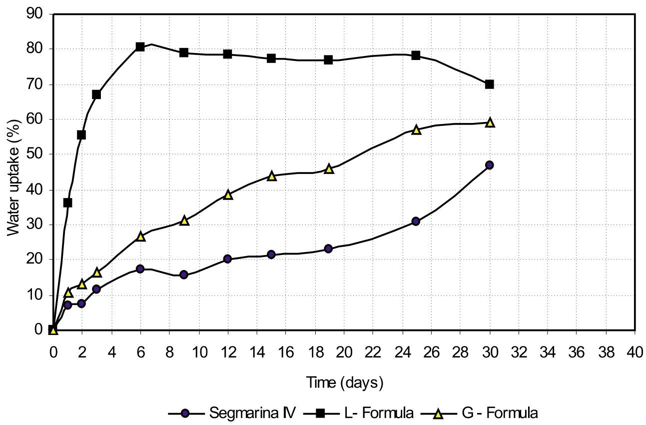

FIG. 3. Water uptake of nonpolluting antifouling coatings based on linear and grafted copolymers compared to Sigmarina IV.

Evaluation of the Antifouling Activity on Natural Site

Test steel panels (120 × 80 × 1.2 mm) were cleaned and freed from rust. The steel panels were painted with anticorrosive coating. After completely dry, non-toxic antifouling coatings were applied on two sides of the panels in two coats with 24 hours intervals between them. The panels were allowed to cure under ambient conditions. The dry film thickness was 100-150 µm per coat. Coated panels were located in a steel frame and submerged in the Red Sea at Obhor Bay, Jeddah, Saudi Arabia. Water temperature was 23-28ºC, salinity, 39.8-40.2‰ and pH was 8.5-9.1. Under these conditions the results in Table 3 show that **G**-formulations are more resistance to fouling than **L**-formulations possibly because the branched or graft polymer has a tendency to attain a more compact structure than does the linear polymer.

TABLE 3. Results of experimental surfaces of nonpolluting antifouling coatings based on linear copolymer of MMA/MAA and grafted copolymers of MMA/MAA onto PVC at environmental conditions of submersion place have water temperature 23-28ºC, pH 8.5-9.1 and salinity 39.8-40.2‰ at Obhor Bay in Red Sea, North Jeddah, Saudi Arabia for one year immersion.

	Submersion experiment (days)					
	15	30	60	150	240	360
L - A	No fouling,	Deformed with few detritus	Deformed completely	Covered by algae and larvae	100% erosion, primer appeared	Small barnacles and algae found
L - B	No fouling,	Some deformation and no fouling	A few of algae and barnacle	50% deformed, no more fouling	15% fouled and 20% erosion	40% deformed and big barnacles
G - A	No fouling,	No fouling	A few algae appeared	Good fouling resistance	No fouling, still in good condition	60% deformed and, big barnacles
G - B	No fouling	No fouling	A few of algae and barnacles	10% fouled, film in good condition	15 covered by small barnacles	Coat covered by gelatinous layer

From Fig. 4, which shows the periodical changes of steel panels, it is seen that the formulation based on grafted copolymer have more durability in seawater than formulations of the linear copolymer.

Conclusion

On the basis of the results presented, it has been shown that grafted copolymer of MMA/MAA onto PVC has improved the mechanical properties (pull-off) of antifouling paints. Nontoxic antifouling paints formulated by grafted acrylic

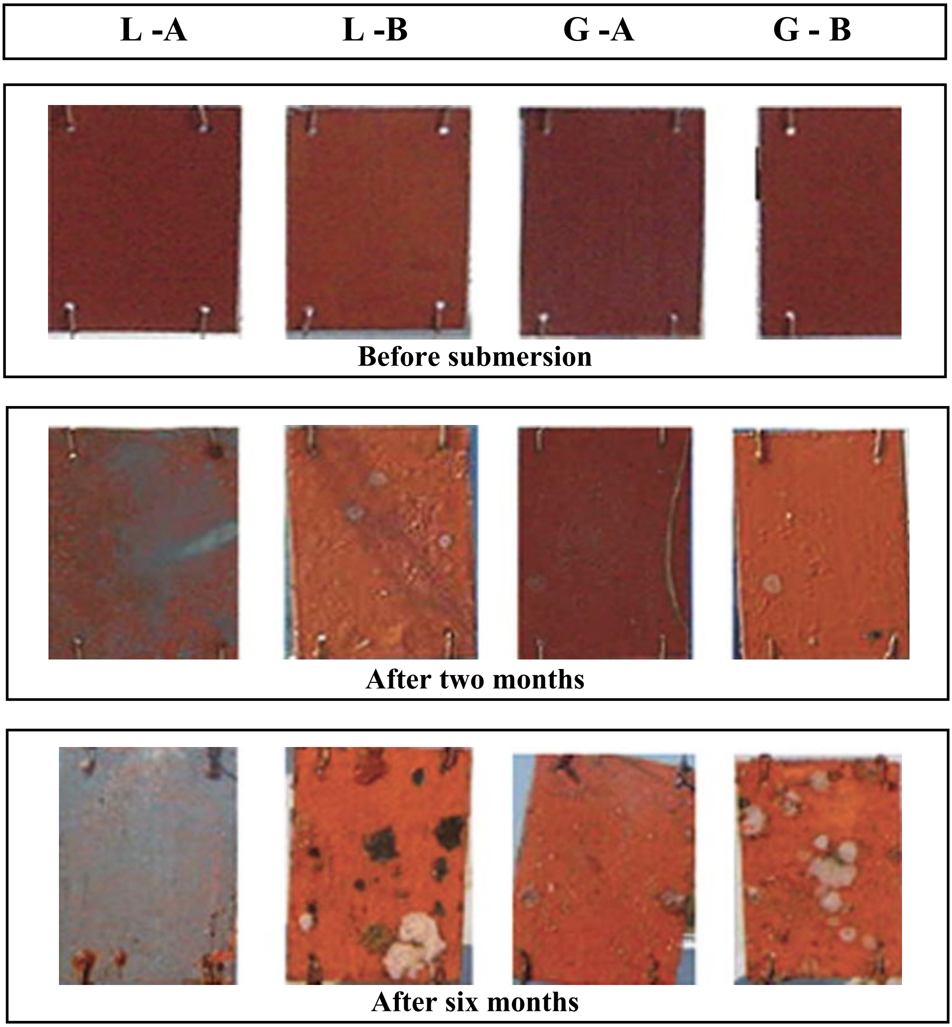

FIG. 4. Photographs of testing nonpolluting antifouling coatings through one year exposed in Obhor Bay, Red Sea, Jeddah, Saudi Arabia. L-A and L-B were based on linear copolymer with BCl and Parmetol PF95 respectively while G-A and G-B were based on grafted copolymer of MMA/MAA onto PVC with BCl and Parmetol PF95 respectively.

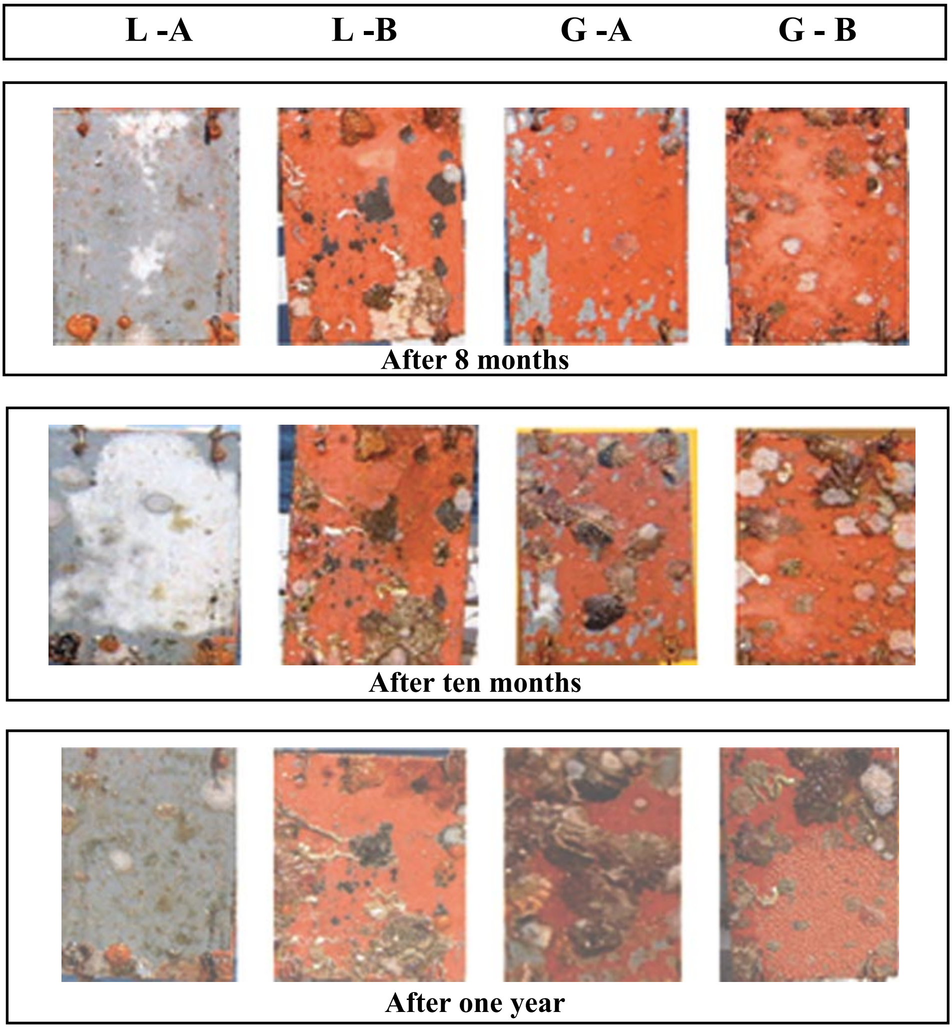

Fig. 4. Contd.

copolymer onto PVC are more resistant to erosion than the paints formulated by linear copolymer. Hydrolysis of biocide from grafted copolymer paint is less than for linear copolymer paint. Paints based on grafted copolymer demonstrated more fouling resistance and are more protective to steel from marine corrosion than linear copolymer.

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تخليق راتنج للأغراض البحرية باستخدام البلمرة بالتطعيم لبعض مونمرات الأكريليك على عديد كلوريد الفينيل . الجزء الأول

معروف م. علي ، و مجدي م. أيوب*

شركة فوسروك الشرق الأوسط العالمية ، جدة ، المملكة العربية السعودية ،
*و *قسم البلمرات والمخصبات بالمركز القومي للبحوث ، القاهرة*
جمهورية مصر العربية

المستخلص. تم تحضير بوليمر مطعم مشترك من ميثاكريلات الميثيل مع حمض الميثاكريليك على عديد كلوريد الفينيل (PVC) في وسط مذيب من السيكلوهكسانون وفي وجود فوق أكسيد البنزويل كبادئ للتفاعل ، تم التحقق من التركيب الجزيئي للبوليمر الخطي والمطعم على عديد كلوريد الفينيل (PVC)، وذلك بدراسة الطيف الناتج من تعرض جزيئات البلمرات المختلفة للأشعة تحت الحمراء وأشعة الرنين النووي المغنطيسي ، ومنها تم التأكد من حدوث التطعيم على سلسلة عديد كلوريد الفينيل . ولتحضير دهانات مقاومة للحشف وغير ملوثة للبيئة ، تم إدخال هذه البوليمرات الخطية ، وأيضا المطعمة على عديد كلوريد الفينيل (PVC) في دهانات غير سامة ومقاومة للحشف . تمت دراسة التحلل المائي وتحرر المادة الفعالة المقاومة للحشف بالمقارنة بدهان سيجمارينا (منتج في السوق المحلي لشركة سيجما للدهانات). ومن الدراسة وجد أن الدهان المصنع من بوليمر ميثاكريلات الميثل مع حمض الميثاكريليك على عديد كلوريد الفينيل (PVC) أكثر قربا لدهان سيجمارينا من الدهان المحضر من نفس البوليمر الخطي غير المطعم والأكثر امتصاصا للماء . تم تقييم مقاومة هذه الدهانات للحشف ، وذلك بتعريضها لمدة سنة في منطقة خليج أبحر بالبحر الأحمر شمال ميناء جدة بالمملكة العربية السعودية ، وقد لوحظ أن الدهانات المصنعة من بوليمر ميثاكريلات الميثيل مع حمض الميثاكريليك المطعم على عديد كلوريد الفينيل (PVC) أكثر مقاومة للحشف ، وأكثر مقاومة للتآكل من سيجمارينا والدهانات المصنعة من البوليمر الخطي لميثاكريلات الميثيل مع حمض المياكريليك.

JKAU: Mar. Sci., **vol. 15,** pp: 85-97 (2004 A.D. / 1424 A.H.)

Synthesis of Marine Resin by Graft Copolymerization of Some Acrylic Monomers onto Chlorinated Rubber. Part II

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ABSTRACT. Some marine resins were prepared by graft copolymerization of butyl acrylate (BuA) and methacrylic acid (MAA) onto chlorinated rubber (CLR) in cyclohexanone using benzoyl peroxide (BPO) as free radical initiator. The prepared copolymers were characterized by infrared spectra (FT-IR) and proton nuclear magnetic resonance (^{1}H-NMR). The grafted resins obtained were incorporated in the antifouling paint formulations as marine binders free from TBT, and their physical and mechanical properties were investigated. The results revealed that the water uptake by the coatings was found to depend on the hydrophilic or hydrophobic properties of the biocides used in the formulations. Raft test performed at Obhor Bay, Red Sea, in Saudi Arabia, showed that the surfaces of the testing panels of some formulations are not affected by marine organisms after one year of immersion.

Introduction

The fouling of ships results in increasing cost due to reduction of speed and increasing fuel consumption. For many years, copper arsenate[1] and mercuric oxide yellow were widely used in antifouling paints up to the 1950s. The Japanese have used phenyl compounds of lead[2]. Tributyl tin (TBT) has been described as the most toxic substance introduced into the marine environment[3]. Therefore alternatives have been eagerly pursued in research laboratories around the world[4-7].

Grafting copolymerization of acrylic monomers onto polymer chain containing halogen has been utilized to give a good erosion resistance characteristic, because a branched polymer, is normally more coiled than linear polymers[8]. The paint based on a grafted copolymer is characterized by having a lower leaching rate and reduced time for attainment of steady state leaching compared to linear chain copolymer[9]. The purpose of this work is to prepare of TBT-free antifouling coatings by using new grafted copolymer.

Experimental

Materials

Butyl acrylate (BuA) and methacrylic acid (MAA) were supplied from Merck GMB (Germany) and Acros Organics Co. USA, respectively. The monomers were freed from inhibitor by repeated distillation under reduced pressure of nitrogen gas. Benzoyl peroxide (BPO) from BDH Chemicals Ltd, Poole (England) was dosed as received.

Chlorinated rubber (CLR): Alloprene CR – 20 V from Zenca Resin (England) with chlorine content 65% was purified by dissolving in benzene then precipitated by methanol and dried at 50ºC under reduced pressure.

Benzalkonium chloride (BCl)[10] lab grade from Sigma Chemical Co. (Switzerland) and Parmetol PF95 from Schulke & Mayr, Norderstedt (Germany) were used as non-toxic antifouling agents.

Sigmarina IV, an antifouling paint based on cuprous oxide and tributyl tin fluoride (TBTF) and manufactured by Sigma Paints Company (Saudi Arabia) was used as a reference.

FT-IR spectra were carried out by using Bruker IR spectrometer using KBr.[11]

^{1}H-NMR spectra were obtained by a Varian-Mercury spectrometer (Germany) operating at 300 MHZ, dimethyl sulfoxide (DMSO) was used as solvent.

Copolymer Synthesis and Antifouling Resins

Graft copolymerization reactions, and preparation of antifouling resins by solution polymerization, were explained in **part I**[8].

Paint Formulation

Two formulations based on grafted copolymer of BuA/MAA onto CLR were prepared as shown in Table 1. Formulations **(A)** and **(B)** were made using benzalkonium chloride (BCl) and Parmetol PF95 as biocides, respectively.

Table 1. Nonpolluting antifouling coatings based on new marine resin of grafted copolymer of BuA/MAA onto CLR with BCl (A) and Parmetol PF95 (B).

Components	A	B
Copolymer resin 40% (in cyclohexanone)	16.3	16.3
Rosin solution 70% (in cyclohexanone)	16.2	16
Petroleum resin 50% (in cyclohexanone)	8.1	5.1
Colloidal silica	0.4	0.3
Red iron oxide	6	5.6
Cyclohexanone	6.5	6.5
Baysolvex (plasticizer)	4	0.0
Baryte	13	12.8
Kaolin	13	13.1
Dowanol PM	6	8.3
Biocide (A)*	10.5	....
Biocide (B)**	....	16
Total	100	100

*Benzalkonium chloride **Parmetol PF95

The paint was made by first adding the copolymer resin; rosin and petroleum resin solutions then the other ingredients. The mixture was milled until a high fineness of the paint was achieved. The viscosity was adjusted by adding cyclohexanone and controlled with Brookfield viscometer model RVF equipment.

Water Uptake Percent

Painted glass plates were immersed in sea water at lab temperature, sea water was changed day by day with fresh sea water. Water uptake was determined quantitatively as follow:

$$\text{Water uptake \%} = \frac{(\text{Weight of coat after submersion} - \text{Weight of coat before submersion}) \times 100}{\text{Weight of coat before submersion}}$$

Evaluation of Antifouling Activity

Coated panels with antifouling paints were placed in a steel frame and submerged at Obhor Bay, Jeddah, Red Sea, Saudi Arabia. Fouling resistance of submersion panels was investigated by both visual and biological examination of the films[12].

Results and Discussion

Characterization of Copolymer

FT-IR spectra of grafted copolymer of BuA/MAA onto CLR

Figure 1 shows in the spectrum (A), band at 735 cm^{-1} was attributed to –CCl and –CH (stretch) appeared at 2950 cm^{-1}. Un-conjugation ester C – CO – O – C from BuA appeared only in spectra (B, C) at absorption 1200 cm^{-1}. Strong band at 1750 cm^{-1} in spectra (B, C) was attributed to the carbonyl group of MAA. The bands at 3000 cm^{-1} in spectra (B, C) were attributed to –CH (stretch), while the broad band at 3550 cm-1 in spectrum (B, C) was attributed to –OH of carboxylic acid.

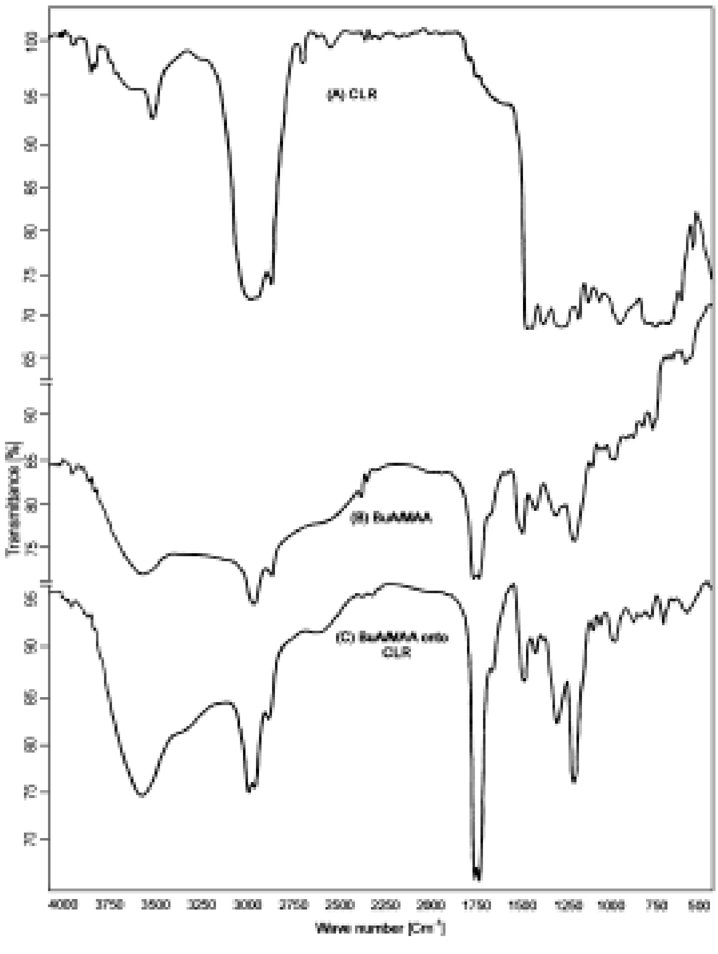

FIG. 1. FT-IR spectra of : (A) Chlorinated rubber (CLR), (B) Linear copolymer of BuA/MAA and (C) Grafted copolymer of BuA/MAA onto CLR (at CLR/M = 23.2%).

[1]H-NMR spectra of grafted copolymer of BuA/MAA onto CLR

In Fig. 2 ^{1}H-NMR spectrum (A), range of chemical shift δ = 2-4 ppm shows the behavior of chlorinated rubber protons and the integration ratio was found 2:2:1:2. These signals were attributed to protons of $–CH_2$ (doublet) at 15δ = 2.1, 2.3 and 2.6 ppm, while the signal at δ = 3.6 ppm could be the –CH proton which disappeared in spectrum (C) because of the substitution of hydrogen atom during the grafting polymerization. The broad signals at δ = 4.2-5.6 ppm may be due to presence of attached chlorine.

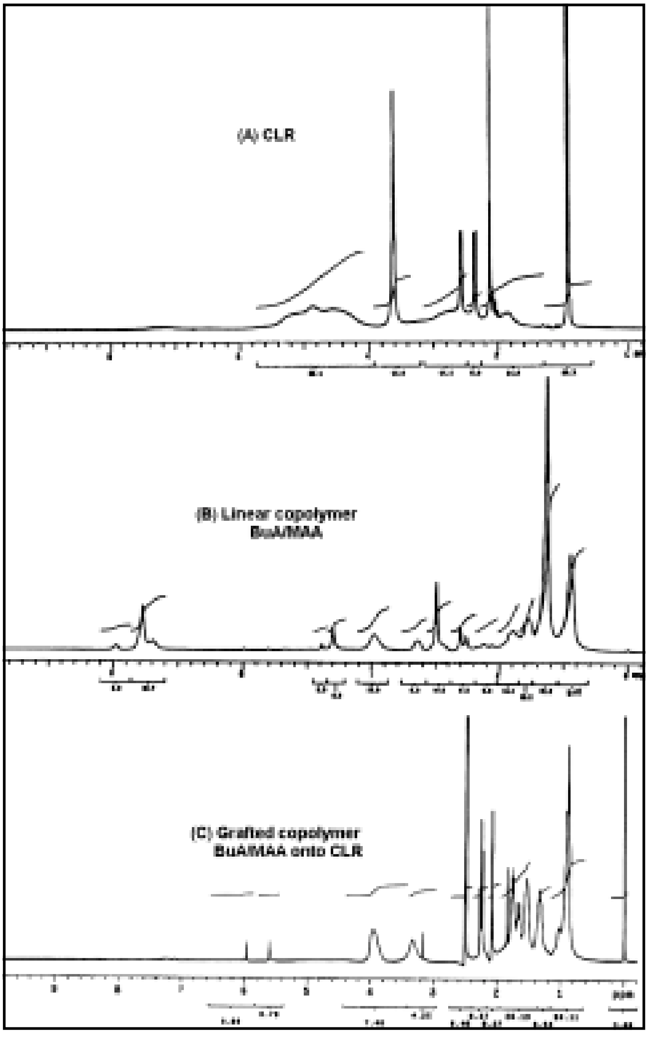

FIG. 2. ^{1}H-NMR spectra of: (A) Chlorinated rubber (CLR), (B) Linear copolymer of BuA/MAA and (C) Grafted copolymer of BuA/MAA onto CLR (at CLR/M = 23.2%).

In spectrum (B), the integration ratio at the range of the chemical shift δ = 1.2 -2.6 ppm was found 2:1:2:9 that meaning the proton signal at δ = 1.2-1.87 ppm (multidoublet) of butyl group protons $–C_4H_9$, δ = 2.1, 2.5 ppm (single) of $–CH_2$ and (triplet) at δ = 2.49 ppm –CH polybutyl acrylate. The broad signals at δ = 3.3 and 4.0 ppm may be due to presence of attached chlorine.

Physical and Mechanical Properties of Coatings

Table 2 shows, the mechanical properties[13] of the two formulations (A and B) as compared to the reference. Both (A) and (B) have higher bonding strength (100% cohesive failure) than Sigmarina IV (15% adhesive failure).

TABLE 2. Technical properties of nonpolluting antifouling coatings by grafted copolymer of BuA/MAA onto CLR.

Properties	Sigmarina IV	A	B
Specific gravity (g/cc)	1.54	1.44	1.13
Viscosity (cps)	1400	2000	1800
Touch drying time (min)	60	25	150
Solid content %	76	63.8	69
Pigment / binder ratio	N/A	2.28	1.41
Pull-off test (kg/cm^2) Remarks on bonding strength*	1.1 15% (AF) 85% (CF)	1.0 0.0% (AF) 100% (CF)	1.7 0.0% (AF) 100% (CF

*AF = adhesive failure and CF = cohesive failure

Hydrolysis and Biocides Release

Figure 3 shows the water uptake of antifouling coatings **A** and **B**. The maximum amount of water uptake for (**A** = 58%) occurred after 25 days of submersion then decreased gradually to an almost fixed value of 50%. In contrast, the water uptake of antifouling coating (B), which contains biocide (B), increased linearly then reached a maximum of 80% through a period of 5 days. This high water uptake which occurred within a short period time causes faster erosion of the coating film. Such difference between (**A**) and (**B**) may be attributed to the hydrophilic and hydrophobic character of the biocide, respectively. The rate of water uptake affects the rate of release of the biocide from the matrix “leaching rate”. A lower leaching rate would extend the antifouling life.

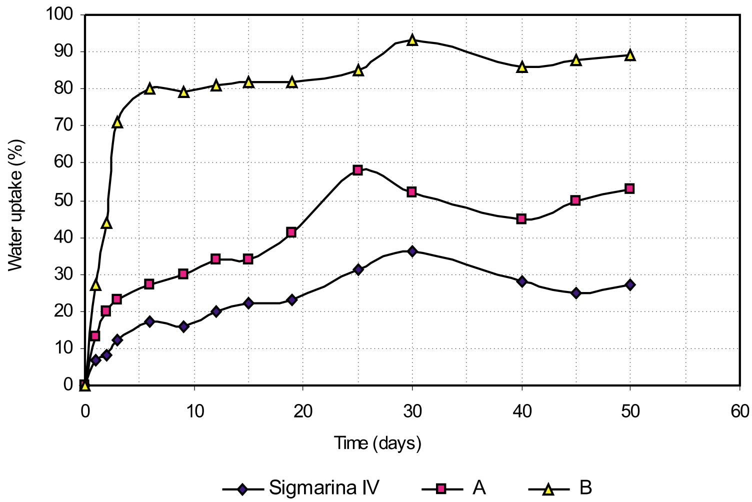

FIG. 3. Water uptake of the new non polluting antifouling coatings using BCl (A) and Parmetol PF95 (B) comparing with Sigmarina IV.

Evaluation of the Antifouling Activity on Natural Site

Steel panels (120 × 80 × 1.2 mm) were cleaned properly and freed from rust then, painted with anticorrosive paint. After completely dry, the antifouling coatings were applied to both sides of the test panels with two coats with 24 hours between them. The panels were left to dry under ambient conditions. Dry film thickness was 100-150 µm per coat. Coated panels were placed in a steel frame and submerged in the Red Sea at Jeddah, Saudi Arabia. Water temperature was 23-28ºC, salinity ranged from 39.8-40.2‰ and pH was 8.5-9.1. Under these conditions the formulations (**A**) and (**B**) showed more fouling resistance than Sigmarina IV, as given in Table 3.

Figure 2 shows the periodical changes of the steel panels. The formula (**A**) and (**B**) have more durability in sea water than Sigmarina IV. By comparing the results of formulation (**A**) and (**B**), it is found that formulation (**A**), based on biocide (BCl), has more fouling and erosion resistance than either (B), based on the Parmetol PF95, or Sigmarina IV.

Conclusion

Non polluting antifouling coatings based on grafted copolymer of BuA/MAA onto CLR and BCl or Parmetol PF95 have more erosion resistance than Sigmarina IV. Water uptake of antifouling coatings depends on the hydrophilic or hy-

Table 3. Results of experimental surfaces of non polluting antifouling coatings using BCl (A) and Parmetol PF95 (B) at Obhor Bay, Red Sea, Jeddah, Saudi Arabia.

Formulation code #	Submersion experiment (days)					
	15	30	60	150	240	360
Sigmarina IV	No fouling, small erosion trapped silt	Some deformation with few detritus and small longitude white shells	10% deformation few barnacles appeared in all the surface	25% deformed with small cracks and exfoliation of the surface	A few of white barnacles and 100% dissociation of coating	100% dissociation of coating and covered by gelatinous layer of fouling
A	No fouling, trapped silt and detritus	No fouling	A few algae and barnacles appeared	Good fouling resistance but covered by gelatinous layer	Some growth of barnacles and algae but film still in good adhesion	A little of growth barnacles and algae
B	No fouling trapped silt	No fouling and still in good condition	Some fill down of topcoat, few barnacles, good fouling resistance	5% fouling area and blistering in 15% of the film	Some growth of barnacles with some blistering	Some growth barnacles, 100% deformation of the film and 30% rusted area

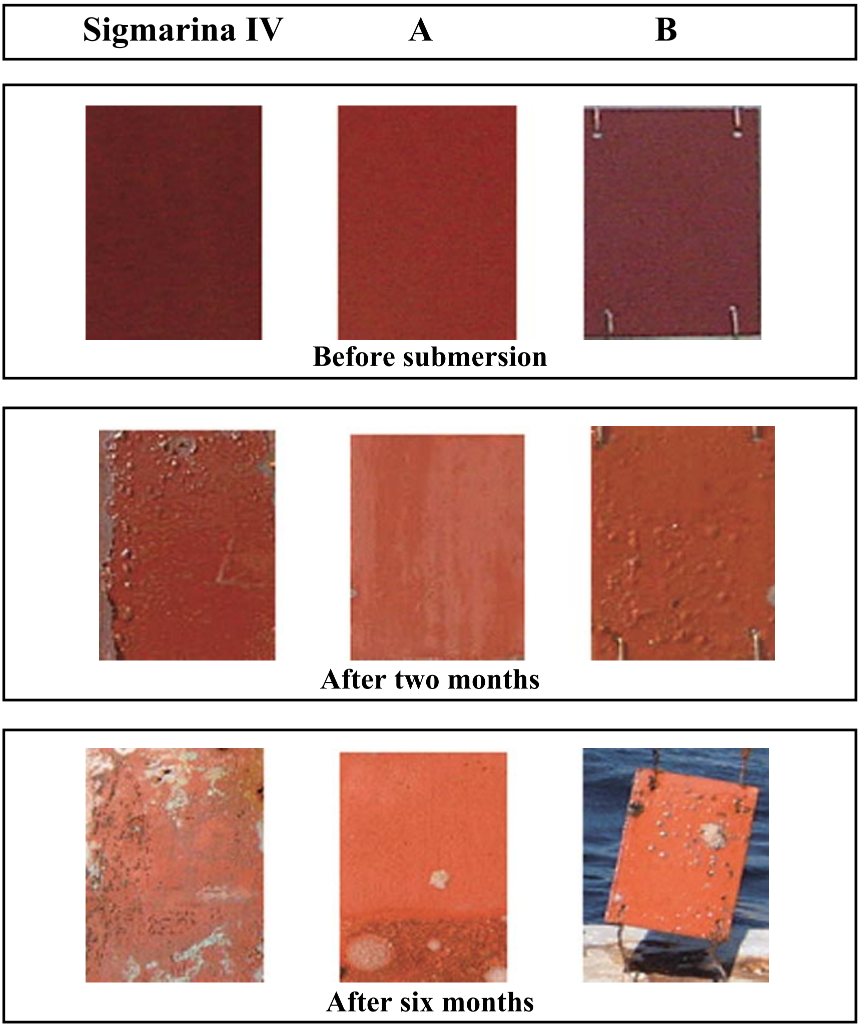

FIG. 4. Photograph of testing antifouling coating through one year exposed in Obhor Bay, Red Sea, Saudi Arabia. Sigmarina IV: Antifouling paint from market taken as a reference, A: Nonpolluting antifouling coatings based on BCl and grafted copolymers of BuA/MAA onto CLR, B: Nonpolluting antifouling coatings based on Parmetol PF95 and grafted copolymers of BuA/MAA onto CLR.

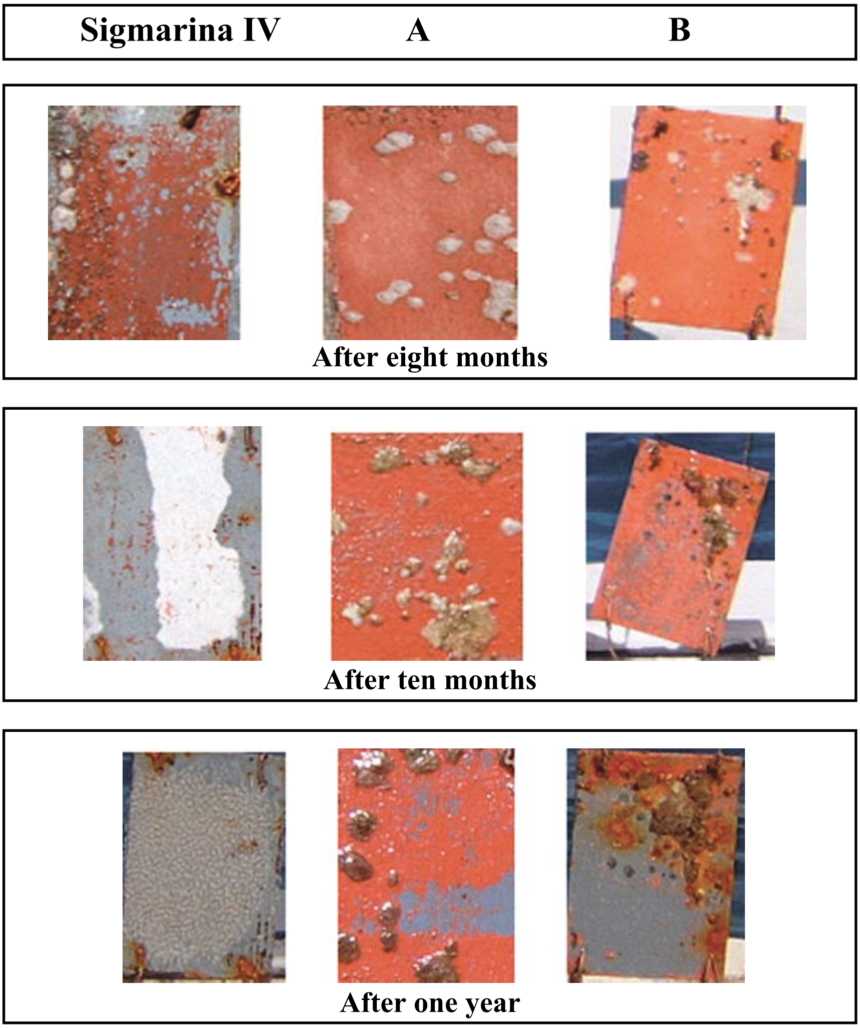
Sigmarina IV
A
B
After eight months
After ten months
After one year

FIG. 4. Contd.

drophobic nature of biocide. Antifouling coating based on BCl has more fouling resistance than either Sigmarina IV (based on TBTF and cuprous oxide) or the antifouling paint based on Parmetol PF95.

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تخليق راتنج للأغراض البحرية باستخدام البلمرة بالتطعيم لبعض مونمرات الأكريليك على المطاط المكلور. الجزء الثاني

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المستخلص. تم تحضير بوليمر مطعم مشترك من أكريلات البيوتيل مع حمض الميثاكريليك على المطاط المكلور (CLR) في وسط مذيب من السيكلوهكسانون ، وفي وجود فوق أكسيد البنزويل كبادئ للتفاعل .تم التحقق من التركيب الجزئي للبوليمر المطعم على المطاط المكلور ، وذلك بدراسة الطيف الناتج من تعرض جزئيات البوليمرات المختلفة للأشعة تحت الحمراء وأشعة الرنين النووي المغنطيسي ، ومنها تم التأكيد من حدوث التطعيم على سلسلة المطاط المكلور . تم إدخال هذه البوليمرات المصنعة من أكريلات البيوتيل مع حمض الميثاكريليك المطعم بمادة المطاط المكلور في دهانات غير ملوثة للبيئة ومقاومة للحشف . تمت دراسة خواصها الطبيعية والميكانيكية ، ودراسة التحلل المائي وتحرر المادة الفعالة المقاومة للحشف بالمقارنة بدهان سيجمارينا (منتج في السوق المحلي لشركة سيجما للدهانات) . ومن الدراسة وجد أن الدهان المصنع من بوليمر أكريلات البيوتيل مع حمض الميثاكريليك المطعم على المطاط المكلور بالاشتراك مع مادة كلوريد البنزالكونيوم (Benzalkonium Chlo-ride) أكثر قربا لدهان سيجمارينا من الدهان المحضر من نفس البوليمر مع مادة البرميتول بي أف ٩٥ Parmetol PF95 والأكثر امتصاصا للماء (Henzalkonphilic) من مادة كلوريد البنزالكونيوم (Hydrophobic). تم تقييم مقاومة هذه الدهانات للحشف ، وذلك بتعريضها في أماكن بحرية طبيعية . فبعد تعريض هذه الدهانات لمدة سنة في منطقة خليج أبحر

بالبحر الأحمر شمال ميناء جدة بالمملكة العربية السعودية ، لوحظ أن الدهانات المصنعة من بوليمر أكريلات البيوتيل مع حمض ا لميثاكريليك المطعم على المطاط لها خاصية مقاومة الحشف .