

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 ($^1\text{H-NMR}$). The grafted resins obtained were incorporated in the anti-fouling 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 50°C under reduced pressure.

Benzalkonium chloride (BCI)^[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]

¹H-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 (BCI) 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 $-\text{CCl}$ and $-\text{CH}$ (stretch) appeared at 2950 cm^{-1} . Un-conjugation ester $\text{C}-\text{CO}-\text{O}-\text{C}$ 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 $-\text{CH}$ (stretch), while the broad band at 3550 cm^{-1} in spectrum (B, C) was attributed to $-\text{OH}$ of carboxylic acid.

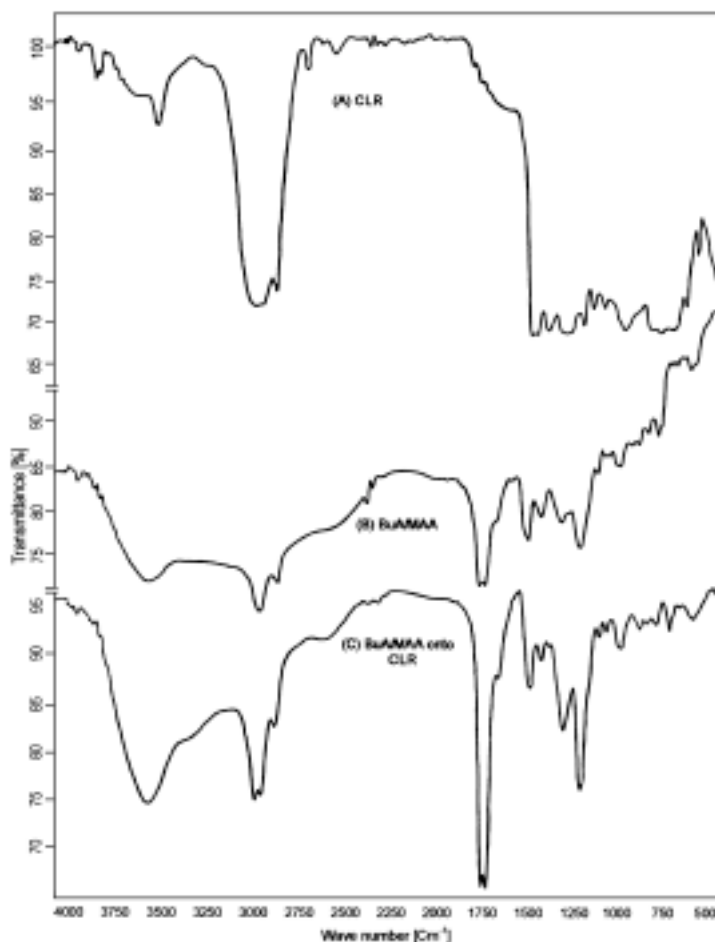


Fig. 1. FT-IR spectra of : (A) Chlorinated rubber (CLR), (B) Linear copolymer of BuA/MAA and (C) Grafted copolymer of BuA/MAA onto CLR (at CLR/M = 23.2%).

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

In Fig. 2 ¹H-NMR spectrum (A), range of chemical shift $\delta = 2-4$ 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 $-\text{CH}_2$ (doublet) at $15\delta = 2.1, 2.3$ and 2.6 ppm, while the signal at $\delta = 3.6$ ppm could be the $-\text{CH}$ proton which disappeared in spectrum (C) because of the substitution of hydrogen atom during the grafting polymerization. The broad signals at $\delta = 4.2-5.6$ ppm may be due to presence of attached chlorine.

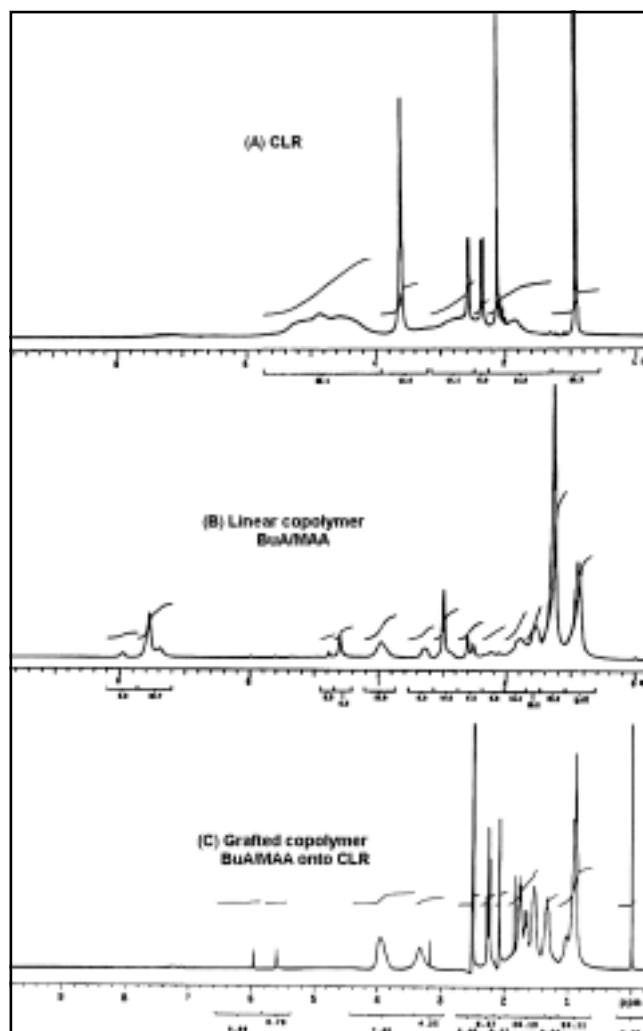


FIG. 2. ¹H-NMR spectra of: (A) Chlorinated rubber (CLR), (B) Linear copolymer of BuA/MAA and (C) Grafted copolymer of BuA/MAA onto CLR (at CLR/M = 23.2%).

In spectrum (B), the integration ratio at the range of the chemical shift $\delta = 1.2$ -2.6 ppm was found 2:1:2:9 that meaning the proton signal at $\delta = 1.2$ -1.87 ppm (multidoublet) of butyl group protons $-C_4H_9$, $\delta = 2.1$, 2.5 ppm (single) of $-CH_2$ and (triplet) at $\delta = 2.49$ ppm $-CH$ polybutyl acrylate. The broad signals at $\delta = 3.3$ 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)	1.1	1.0	1.7
Remarks on bonding strength*	15% (AF) 85% (CF)	0.0% (AF) 100% (CF)	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.

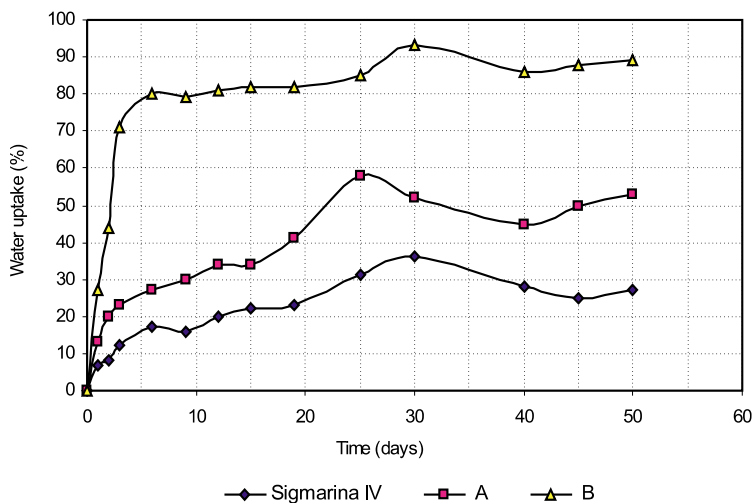


FIG. 3. Water uptake of the new non polluting antifouling coatings using BCI (A) and Parmetol PF95 (B) comparing with Sigmarina IV.

Evaluation of the Antifouling Activity on Natural Site

Steel panels ($120 \times 80 \times 1.2$ 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 23-28°C, 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 (BCI), 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 BCI 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 BCI (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

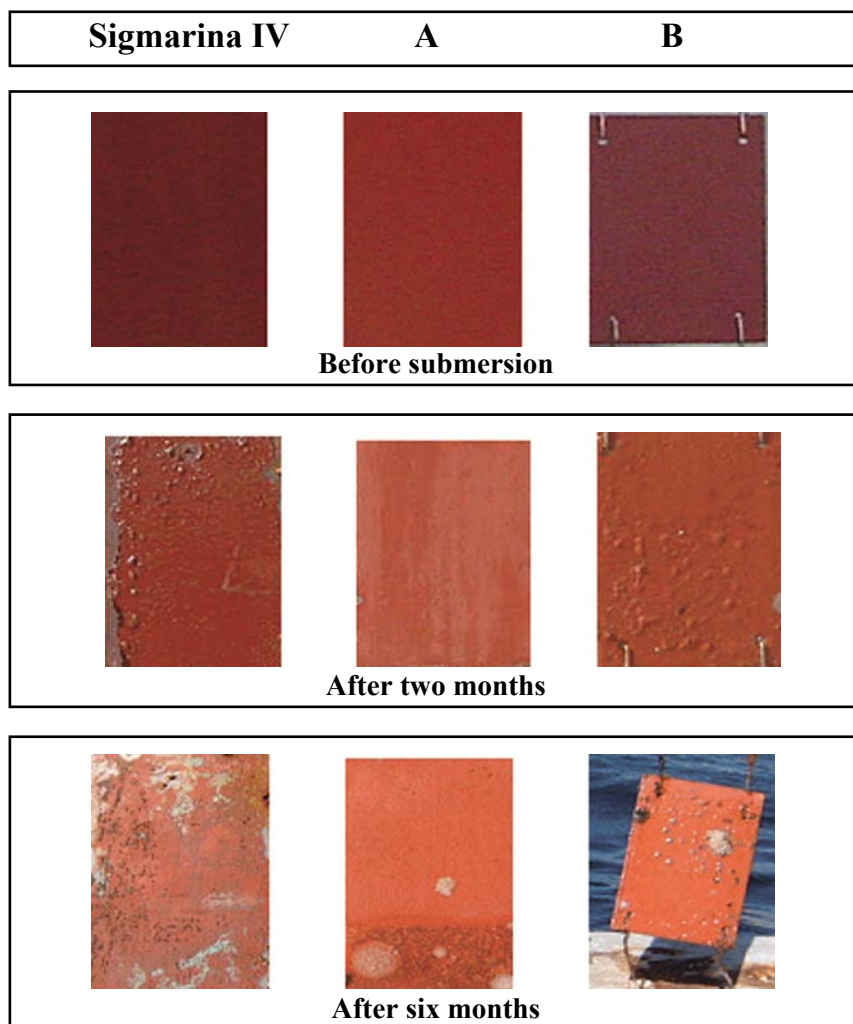


FIG. 4. Photograph of testing antifouling coating through one year exposed in Obhor Bay, Red Sea, Saudi Arabia. Sigmarina IV: Antifouling paint from market taken as a reference, A: Nonpolluting antifouling coatings based on BCI and grafted copolymers of BuA/MAA onto CLR, B: Nonpolluting antifouling coatings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

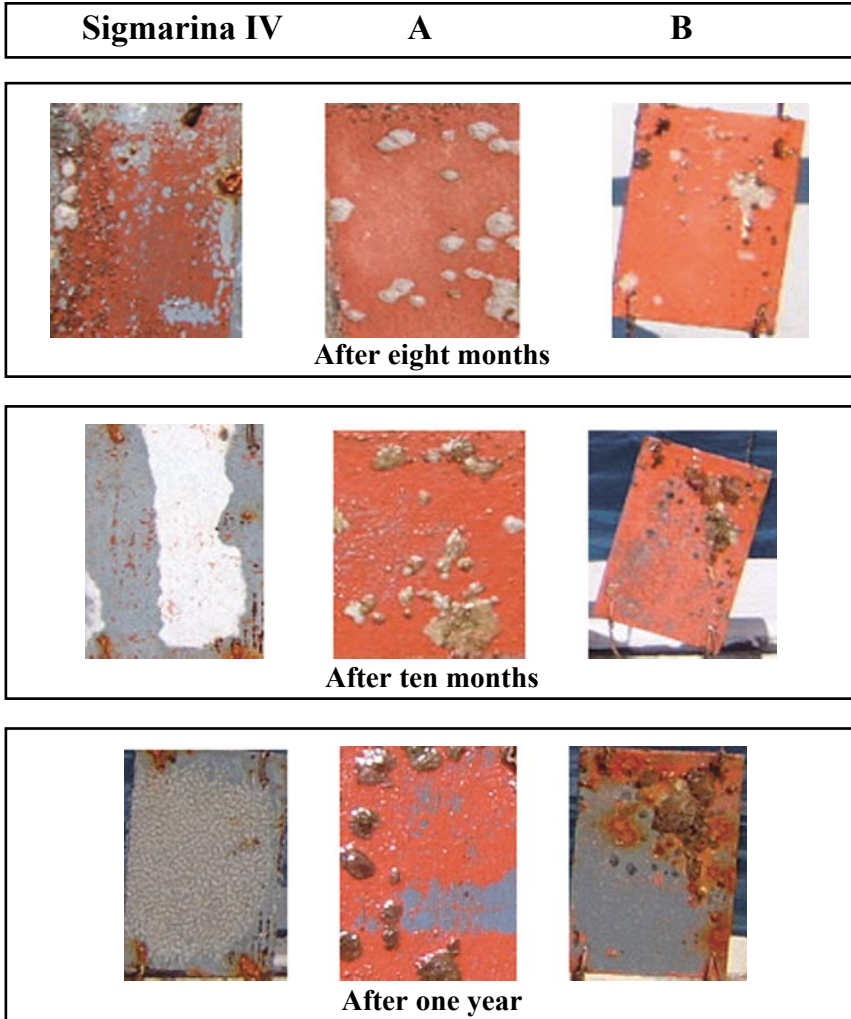


FIG. 4. Contd.

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

References

- [1] **Thompson, M.F., Sarojini, R., Nagabhushanum, R. and Balkemal, A.A.**, *Marine Biodegradation Advanced Techniques Applicable to the Indian Ocean*, Rotterdam, p. 781 (1988).
- [2] **Gurvich, E.S., Manatsakanov, S. S. and Frost, A. M.**, *Biologiya Morya*, **5**: 66-70 (1981).
- [3] Similar Bans on used of TBT paints were imposed in the United Kingdom (1987) and U.S.A. and NZ (1988).
- [4] **Kjer, E.B.**, *Prog. Org. Coat*, **20**: 339-352 (1992).
- [5] **Huttinger, K.J.**, *Fouling Science Technology*, Kluwer Amsterdam, pp: 233-239 (1988).
- [6] **James, D.**, *Adking Prog. Org. Coat*, **29**: 1-5 (1996).
- [7] **Brady, R.F.**, *J. Coating Technology*, **59**: 755 (1987).
- [8] **Sankholkar, S. and Deb, P.C.**, *J. Applied Polymer Science*, **39**: 1681-1688 (1990).
- [9] **Deb, P.C. and Sankholkar, S.**, *J. Applied Polymer Science*, **43**: 1007-1010 (1991).
- [10] **His, E., Beiras, R., Quiniou, F., Parr, A.C.S., Smith, M.J. Cowling and Hodgkiess, T.**, *Water Research*, **30**(11): 2822-2825 (1996).
- [11] **American Society Testing and Materials (ASTM)**, D 2621-87, 06.01 (1992).
- [12] **Vallee-Rehel, K., Guerin, P., Langlois, V. and Langlois, Y.J.**, *J. Coating Technology*, **70** (880): 55-63, May (1998).
- [13] **American Society Testing and Materials (ASTM)**, D 4541-85, 06.01 (1989).

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

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

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 للحشَف. تمت دراسة خواصها الطبيعية والميكانيكية ، ودراسة التحلل المائي وتحرر المادة الفعالة المقاومة للحشَف 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 بالاشترَك مع مادة كلوريد البنز الكونيوم (Benzalkonium Chlo-) ride أكثر قربا لدهان سيجمارينا من الدهان المحضر من نفس البوليمر مع مادة البرميتول بي أف 95 Parmetol PF95 والأكثر امتصاصا للماء (Henzalkonphilic) من مادة كلوريد البنز الكونيوم (Hydrophobic). ثم تقييم مقاومة هذه الدهانات للحشَف ، وذلك بتعريضها في أماكن بحرية طبيعية. فبعد تعريض هذه الدهانات لمدة سنة في منطقة خليج أبهر

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