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NOVEL POLYURETHANES AS ANTIFOULING PAINT MATRICES

ABSTRACT

The new poly(ester-ether urethane)s (PEEUR) were prepared in two stage synthesis from formerly obtained oligo(alkylene ester-ether)diols (OAE) and 4,4'-diphenylmethane diisocyanate (MDI). PEEUR samples were subjected to crosslinking with styrene in the presence of radical polymerization initiators: methyl ethyl ketone peroxide (MEKPO) or cobalt 2-ethyl cyclohexanoate (EtHCo). Crosslinked PEEUR were characterized by their physicochemical and mechanical properties. Tensile strength of crosslinked PEEURs was in the range 63-29 MPa, hardness values were from 92 to 97°ShA, and glass transition temperature was in the range 59-74°C. For PEEURs filled with biocides tensile strength was in the range 6,8-8,5MPa, hardness values were from 82 to 92°ShA, and glass transition temperature was in the range 57-72°C. Optical microscopic observations showed that the materials obtained were homogeneous in micrometric scale.

Keywords: *polyurethane, antifouling protection, unsaturated oligo(alkylene ester-ether)diols, poly(ester-etherurethane)s, styrene crosslinking*

INTRODUCTION

In this paper we present the results of study on new polyurethanes, which have been used as antifouling coatings. The reasons for taking up the research in this field was the widespread use of antifouling coating systems, as a security for the underwater part of the hull of ships and for hydraulic structures operated in seawater, against the harmful effects of marine micro- and macroorganisms (accumulation on the hull surface) of animal and vegetable origin. [1-6] The application of antifouling protection should take into account some very important factors, both economic and environmental. The overgrowth of hull reduces the ship speed and its maneuverability. It also generates a significant increase in fuel consumption. Important from the environment protection point of view is that higher consumption entails increased emissions of CO_x, NO_x and SO_x into the atmosphere. So far, many research centres and companies are doing studies on vinyl and silicone antifouling systems. In the market are available products based on these polymers [5-10], but in the literature poly (ester-ether-urethane)s as antifouling coatings are not described.

SUBSTRATES AND SYNTHESIS

Substrates

Adipic acid $M_w=146,06$ (Aldrich); Maleic anhydride $M_w=98,06$ (Aldrich), poly(oxyethylene) (POE) $M_w=300$ (Aldrich), propane-1,3-diol $M_w=76$ (Aldrich), 4,4'-methylenebis(phenyl isocyanate) (MDI) $M_w=250$ (Borsdochem), styrene(S)-cda $M_w=104,1$ (Aldrich), solution of cobalt 2-ethyl cyclohexanoate (EtHCo/ILT) (10% cobalt) in white spirit, 36% solution of methyl ethyl ketone peroxide (MEKPO) (ILT) in dimethyl phthalate, 0,5% of organic biocide (zinc pyrithione), 5% of inorganic biocide (copper monoxide (I)).

Synthesis

The synthesis of poly(ester-ether urethane) matrix was conducted in three steps. Firstly, the unsaturated oligo(alkyleneester-ether) diols (OAEE) were obtained in polycondensation reaction of adipic acid, maleic anhydride, propane-1,3-diol and poly(oxyethylene) (POE). Secondly, the urethane quasi-prepolymers (QPRE) were obtained from unsaturated OAEE and 4,4'-methylenebis(phenyl diisocyanate). The third step was the synthesis of urethane prepolymers (PRE), which were obtained by chain extension of urethane quasi-prepolymers by formerly synthesized oligo(alkyleneester-ether)diols. Urethane prepolymers were obtained at different ratios of NCO/OH, in the range of 1,5:1 to 3,0:1.

ANTYFOULING COATING SYNTHESIS

Obtained PRE were subjected to crosslinking at room temperature with the use of styrene in amount of 25% wt towards mass of unsaturated OAEE, performed in the presence of methyl ethyl ketone peroxide (MEKPO) and cobalt 2-ethyl cyclohexanoate (EtHCo) or PRE were blended with biocides and then subjected to crosslinking with styrene. This way poly(ester-ether urethane)s (PEEUR) and poly(estro-ether urethane) (PEEUR) antifouling coatings were obtained.

DISCUSSION

Properties of obtained unsaturated oligo(alkyleneester-ether)diols

Obtained oligo(alkyleneester-ether)diols were characterized by acid, hydroxyl and iodine number and also by calculating its molecular weight. The results are presented in the Table (1).



Table 1. Physicochemical properties of oligo(alkylene ester-ether)diol

Sample symbol	Synthesis time	Acid number	Hydroxyl number	Molecular weight	Iodine number	
	[h]	[mgKOH/g sample]	[mgKOH/g sample]	[g/mol]	Theoretic	Determined
Oligo(alkylene ester-ether)diols synthesized with propane-1,3-diol and other comonomers						
OAEE	33,5	1,1	131	900	22	20

The study results presented in Table 1 has showed that obtained unsaturated OAEE have acid number of about 1 mgKOH/g. Hydroxyl number of unsaturated OAEE is in the range of 131 mgKOH/g. Based on hydroxyl number an average molecular weight of studied oligomerol was calculated (900 g/mol).

The iodine number of obtained unsaturated oligo(alkylene ester-ether)diol was estimated as 22 gI₂/100g and based on this value the number of unsaturated linkages present in the synthesized compound was calculated. Iodine number calculated theoretically was not much higher than that estimated experimentally and that confirm that only small amount of double bonds takes part in chemical reactions of polycondensation process. Decrease of unsaturation level of OAEE, determined that theoretical value was the result of glycol addition to the double bonds coming from maleic anhydride, what in consequence led to chains branching.

Poly(ester-ether urethane)s physicochemical properties

Table 2 contains experimental data for saturated (25% wt styrene to the molecular mass of OAEE) poly(ester-ether urethane)s obtained from MDI isocyanate and for unsaturated OAEE containing in their structure residues of propane-1,3-diol and other comonomers.

Table 2. Physicochemical properties of crosslinked poly(ester-ether urethanes) synthesized from MDI isocyanate and of unsaturated OAEE

Sample symbol	Tensile strength T _{SB} [MPa]	Hardness [°Sh A]	Glass transition temperature T _g [°C]	Mass loss after 6 months exposition to sea water [%]
PEEUR-1,5/1*	16	92	59,4	0,2
PEEUR-2,0/1	25	96	66,7	0,1
PEEUR-2,5/1	23	97	74,1	0
PEEUR-3,0/1	29	97	73,8	0

*Poly(ester-ether urethane) symbol: number after dash is ratio of NCO/OH

Poly(ester-ether urethane)s differ in their tensile strength, estimated in the range 16-29 MPa, which depend on NCO/OH ratio. The lowest T_{SB} value was determined for PEEUR synthesized at NCO/OH ratio of 1,5:1. PEEUR hardness was in the range of 92°ShA (NCO/OH 1,5/1) - 97°ShA (NCO/OH 3,0:1).

As a result of crosslinking copolymerisation between styrene and unsaturated linkages in quasi-prepolymer a high crosslinked structure was formed, what significantly affected the



tensile strength values of PEEUR samples. Moreover, PEEUR differ in glass transition temperatures (depending on molar ratio of NCO/OH changed in the range of 1,5:1 – 3,0:1), measured between 59°-74°C. Based on this differences it can be pointed out that the increase of hard segment content in the PEEUR structure have an impact on glass transition changes (higher NCO/OH ratio, from the range of 1,5:1-3,0:1, caused the increase in glass transition temperature of 10-20°C)

Physicochemical and mechanical properties of poly(ester-ether polyurethane)s filled with biocides

Physicochemical and mechanical properties of obtained antifouling coatings were studied by measurements of tensile strength, hardness, glass transition temperature and mass loss of PEEUR containing 0,5% of organic biocide and 5% of inorganic biocide after 6 month exposure to the sea water. Analysis of obtained data showed that polyurethanes tensile strength was in the range of 6,8-8,59 MPa, hardness values were of 82°-92°ShA and glass transition temperature was in the range of 57-72°C depending on molar ratio of NCO/OH. Obtained coatings were found as resistant to sea water and their mass loss didn't excess 0,4%, independently to the hard segment content. In the Tab (3) data for PEEURs containing biocides are presented

Table 3. Physicochemical and mechanical properties of PEEURs blended with biocides

Sample symbol	Tensile strength Tsb[MPa]	Hardness [°Sh A]	Glass transition temperature T _g [°C]	Mass loss after 6 months exposure to seawater [%]	Tensile strength after 6 months exposure to seawater Tsb [MPa]
PEEUR-1,5/1*	6,8	82	57,4	0,4	6,5
PEEUR-2,0/1	6,9	86	61,3	0,3	6,7
PEEUR-2,5/1	7,3	87	71,5	0,2	7,1
PEEUR-3,0/1	8,5	92	72,7	0,2	8,5

Efficacy evaluation of obtained PEEUR antifouling coatings with the use of optical microscopy

Poly(ester-ether urethane) coatings and poly(ester-ether urethane) coatings filled with biocides (antifouling cover) after hardening were subjected to the sea water exposure in a 6 months period. Optical microscope analysis of PEEUR materials was carried out before and after sea water exposure.

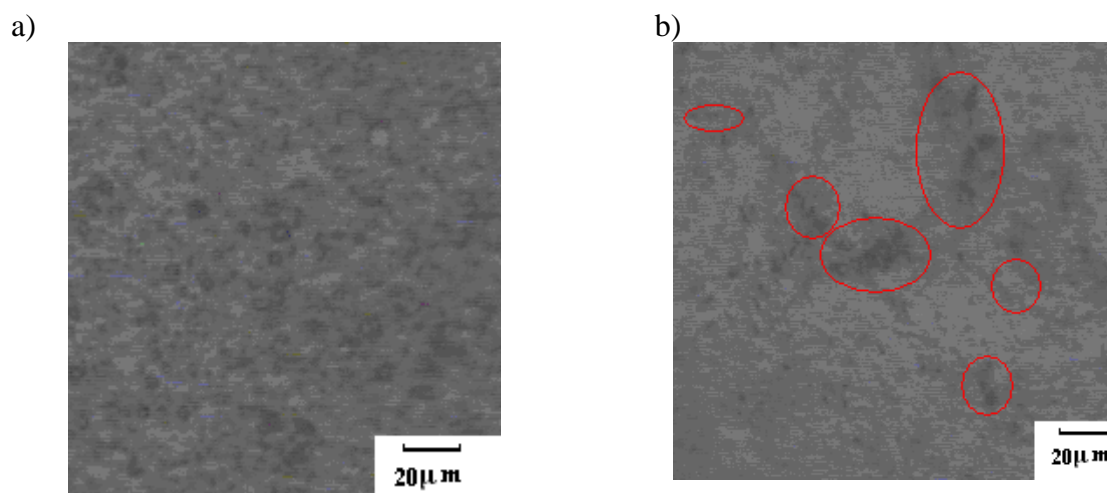


Fig. 1. Optical microscopy examination of PEEUR 3,0:1 coating surface - without biocides; a) coating surface before sea water exposure, b) coating surface after exposure to the sea water

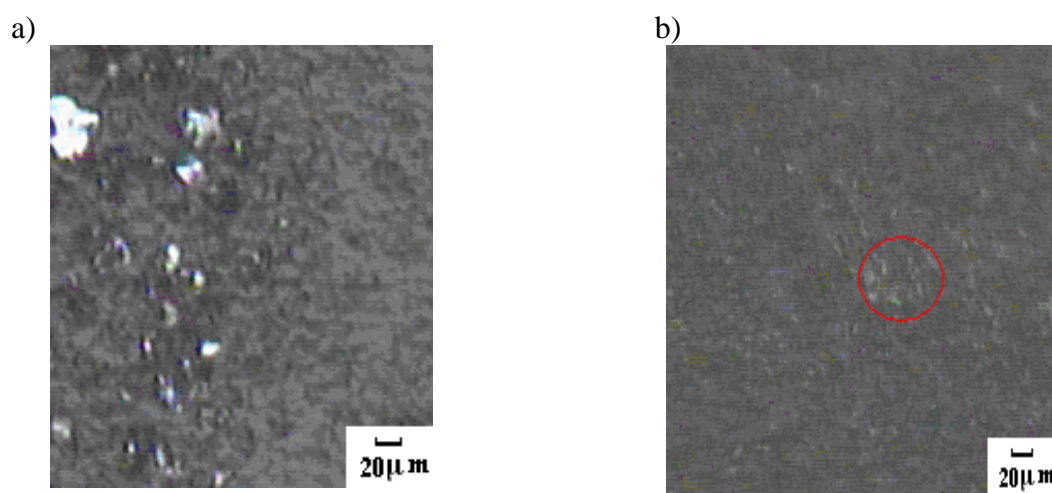


Fig. 2. Optical microscopy examination of PEEUR 3,0:1 coating surface - with biocides a) coating surface before seawater exposure, b) coating surface after exposure to the seawater

Analysis of presented optical microscope images of PEEUR coatings without organic biocide and copper monoxide (I) showed that these coatings do not have antifouling properties. The overgrowth percent of studied surface was in the range of 10-35%. The surface observations of PEEUR filled with biocide showed that formed cover was homogenous, without agglomerates of biocide fillers on its surface. Obtained matrices with biocides were found to be resistant to sea water interactions. Optical microscope evaluation didn't show any micro- or macrofractures.

CONCLUSIONS

In this paper was described the synthesis of novel poly(ester-ether urethane)s (PEEUR) for antifouling coatings. PEEUR were obtained from unsaturated oligo(alkyleneester-ether)diols (OAEE) and 4,4'-methylenebis(phenyl isocyanate) (MDI), with or without biocide. Obtained

polyurethanes were subjected to the crosslinking with styrene. Hardened coatings were examined for their physicochemical and mechanical properties to evaluate their ability for further applications.

Poly(ester-ether urethane) samples, without biocides, have tensile strength, estimated in the range of 16-29 MPa, wherein T_{SB} parameter depend on NCO/OH ratio. Hardness of obtained PEEURs were in the range of 92°ShA - 97°ShA for sample NCO/OH 1,5/1 and NCO/OH 3,0:1 respectively. Glass transition temperature was from 59,4°C to 73,8°C. Obtained antifouling PEEUR coatings (containing biocide) have decreased tensile strength (6,8-8,5 MPa), but hardness (82-92°ShA) and glass transition temperature (57,4-72,7°C) stays in the range of measured values for PEEUR without biocides. Mass loss of PEEUR containing 0,5% of organic biocide and 5% of inorganic biocide after 6 month exposure to the sea water is higher than that measured for PEEUR samples without biocides. Optical microscope images of PEEUR coatings without biocide showed that these coatings do not have antifouling properties. The overgrowth percent of studied surface was in the range of 10-35%. The surface observations of PEEUR filled with biocide showed that formed cover was homogenous, without agglomerates of biocide fillers on its surface. Optical microscope evaluation didn't show any micro-or macrofractures. Obtained coatings were found as resistant to sea water and their mass loss didn't excess 0,4%, independently to the hard segment content. PEEUR exposure to the sea water for the 6 month period showed that obtained antifouling coatings do not undergo degradation in seawater and constitute perfect antifouling protection.

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