

Advanced coating of interior of tanks for rising environmental safety - novel applications of polyurethanes

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ABSTRACT

The aim of this study was to develop urethane elastomers of predefined properties to be used as elastic coating in the cargo tanks of tankers. A method for coating the liquid polyurethane system onto steel and steel-concrete elements, and a way to join polyurethane coating with the aforementioned elements, were elaborated. The technique of injection the reactive liquid polyurethane system onto cold steel elements was used. The method for utilization and recovery of urethane oligomerols from the waste polyurethane coating in chemical recycling by using low molecular weight glycols as glycolysis agents was proposed.

Keywords: polyurethane elastomers, multi-layer constructions, adhesives, recycling

INTRODUCTION

Urethane elastomers are polymeric materials which are used more and more often in industrial applications to solve particularly difficult problems. This is due to the fact that the segmented and domain structures of polyurethanes create a good combination of features such as elasticity, mechanical resistance and hardness. Cast urethane elastomers can be used as construction elements because these polymers are characterized by large modulus of elongation, tear strength, high abrasion resistance, good tensile properties as well as they display better load-carrying capacity than rubber elastomers. Moreover, they are resistant to the factors causing physical ageing (air, ozone) and also to the commonly used solvents, oils and weathering. Glass transition temperature (T_g) of rigid segments usually ranges from 107°C to over 200°C, while for flexible segments it depends on the oligomerol used and most often falls below -30°C. These features predispose polyurethanes to being used in products exposed to temperatures below and above 0°C [1]. The application of polyurethanes as a polymer core in the SPS (Sandwich Plate System) constructions in building of ships or drilling platforms is well known [2]. This particular technology has been approved for ship applications by Lloyd's Register [3] and other recognized classification societies. SPS technology allows the elimination of large number of reinforcement features in steel elements which facilitates their production, reduces the number of welds and at the same time, eliminates the sources of fatigue cracks and corrosion. The other advantages are: a reduction of the construction weight and building costs (shorter time is necessary to produce construction elements); increased precision of production and construction longevity; lower labor consumption including

troublesome welding and painting operations; a reduction of surfaces requiring anticorrosive protection; the facilitation of applying paints; and a significant reduction in the extent, time and costs of maintenance and repairs. An important advantage of sandwich systems is their high resistance to impact energy, capability of damping vibrations, good fire resistance, and thermal and acoustic insulation. The use of polyurethane systems of density more than six-fold lower as compared to steel, to the polymeric core production allows to obtain a light construction that is additionally reinforced within the whole double hull of the ship [1, 3].

Sandwich systems are made from steel sheets interlaminated with a layer of polyurethane. Steel-polyurethane composites have been widely applied in construction industry, e.g. to build bridges, where unusually large steel elements are used. SPS structures are lighter and less time-consuming to build than those made of steel, and they have an in-built fire and vibration resistance.

In the case of a road bridge constructed in Saint Martin de Beauce (Canada), the use of the steel-polyurethane sandwich system resulted in the bridge mass reduction of 60% as compared to the construction built with traditional technology. At present, steel-polyurethane building elements are used for constructing sports facilities, public and industrial buildings, storage facilities, drying houses, commercial cold stores, temporary facilities on the construction sites, containers, stores, freezers as well as office and apartment buildings.

The aim of our work was to develop a polyurethane elastomer of defined properties and the technology for coating it on large-size ship structures, and to obtain a hybrid steel-polyurethane-concrete sandwich system of defined mechanical resistance of joints.

EXPERIMENTAL PART

Materials

The following materials were applied: 4,4'-diphenylmethane diisocyanate (MDI), liquid, filter-purified, manufactured by Borsdochem (Hungary); oligo (oxytetramethylene) diol (PTMG) molecular mass 1000, manufactured by Du Pont (USA); oligo (oxypropylene) diol (ROKOPOL D2002) molecular mass 2000, manufactured by Inter Rokita S.A., Brzeg Dolny (Poland); oligo(ϵ -caprolactone)diol (CAPA 212) molecular mass 1000, manufactured by Solvay (Belgium); oligo (ethylene-butylene adipate) (POLES 55/20) molecular mass 2000, manufactured by Organika - Zachem S.A. (Poland); 1,4-diazabicyclo[2.2.2]octane (DABCO) manufactured by Hondry - Hüls (Germany); butylene glycol (BDO) manufactured by BASF (Germany); 1,6-hexanediol (HDO) manufactured by Du Pont, (USA); 1,3-propanediol, manufactured by POCh (Poland); ethylene glycol (GE), manufactured by POCh (Poland); oligo(oxyethylene)diol (PEG 300) manufactured by Aldrich-Chemie; orthophosphoric acid manufactured by POCh (Poland)

Catalysts: potassium acetate (KAc) manufactured by POCh, sodium hydroxide (NaOH) CIL bonding agents.

Measurements

The viscosity of prepolymers and glycolysates was measured with a Brookfield DV-II viscometer (manufactured by Brookfield Engineering Labs. INC. Stoughton, U.S.A.) equipped with a SP31 spindle.

The measurements were performed at 50, 60, 70 and 80°C for the spindle's rotational speed of 60rpm. The density values for prepolymers and glycolysates were determined picnometrically at 50°C. Density was calculated based on the mass of picnometer with glycolysate, empty picnometer and the picnometer filled with water.

Spectral analysis of prepolymers, glycolysates, urethane elastomers and polyurethanes obtained from glycolysates was performed by means of a Nicolet 8700 FTIR spectrometer (Thermo Electron Co.) by using the Specac Golden Gate single-reflection diamond-heated ATR accessory. Spectra were recorded at 4cm⁻¹ resolution for 64 scans. Thermogravimetric analysis of polymer samples was conducted with a Netzsch TG 209 analyzer. Samples were heated from 20°C to 500°C at the rate of 10°C/min. The analyses were performed in an argon atmosphere. The values of $T_{5\%}$ and $T_{10\%}$ were read from thermograms, while the temperature of the fastest mass loss from the DTG curve. Gaseous products that originate during thermal decomposition of the analyzed samples were analyzed by means of a FTIR spectrometer coupled with the thermobalance. Based on the obtained spectra, the main decomposition products were identified and their emissions in dependence on temperature were compared. Dynamic mechanical thermal analysis was performed by means of a Mk III thermomechanical analyzer (Polymer Laboratory) by using the probe suited for up to 300°C, a temperature range from 25 to 120°C, the rate of temperature change of 4°C/min, and frequency 10 Hz. Samples of the approximate dimensions 10 x 50 x 3 mm were analyzed. Resistance- to- stretch measurements (modulus of rigidity and elongation) were determined according to PN - ISO 37: 1998 with a Zwick Z020 universal tensile machine in samples with the dimensions 80 x 10 x ca. 2mm. For each type of elastomer and polyurethane from recycle, three samples were investigated. Resistance to abrasion was determined by means of a Schopper-Scholbach

apparatus; samples shaped as truncated cones (3 for each material type) were cut with the in-built cutting device. The values of polyurethane density were measured with a Westphal-Mohr balance. Distilled water was used as an immersion fluid.

THE DEVELOPMENT OF URETHANE PREPOLYMERS

Urethane prepolymers were obtained in a reaction between di-isocyanide MDI and different oligomerols. To this end, the pre-calculated amount of an oligomerol was introduced into the heated reactor. Next, after drying and de-gassing of this ingredient at 60°C, liquid MDI devoid dimers and trimers was being added in the amount necessary to obtain - via chemical reaction - prepolymer of defined structure (content of NCO groups from 4 to 9%). After the reaction, prepolymer was stabilized with orthophosphoric acid [4-10]. Prepolymers were characterized by determining variation in the [NCO] group concentration and dynamic viscosity at different temperatures and shear stress values (Brookfield viscometer), and by an FTIR spectral analysis. Prepolymer density was measured picnometrically. Chemical stability determinations of prepolymers with different structures were conducted during 4 weeks.

THE DEVELOPMENT OF SANDWICH SYSTEM MATERIALS

Based on the obtained prepolymers, a technology for producing moulded urethane elastomers by means of the RIM technique was elaborated to suit defined properties of the material. Moulded urethane elastomers for using as elastic protective coating were obtained in this study by means of a two-step method. Step I consisted of prepolymer synthesis, while step II was the prepolymer elongation by means of BDO or GE glycol. The material to be used as urethane coating was obtained for different molar [NCO]:[OH] ratios ranging from 0.95 to 1.20. It has been established that for the ratio of 1.05 the material had the maximum hardness measured after 24h in warm samples. Polyurethane systems of various chemical compositions were also investigated with the aim to develop a way of joining the cross-linked polyurethane layers among themselves and with other materials. In this study a wide spectrum of factors was considered which might influence the joint strength such as polyurethane system temperature, the temperature and time of gelation, surface preparation and adhesive type. Experiments were conducted without an adhesive as well as with the previously selected glues, i.e. epoxy adhesive (patent KTP), Thixon 405 (ICI) and CILBOND (CIL).

RECYCLING OF ELASTIC POLYURETHANE COATING

Recycling of material was applied for the mass ratios of scrap polyurethane to glycol ranging from 2:1 to 10:1 [4-16]. A catalyst was used in the process. The reactor loaded with glycol and catalyst was heated at temperatures from 190 to 240°C. Dosing time varied and depended on the mass ratio of polyurethane to glycol. After the reaction, glycolysates were cooled down. The liquid products were poured into a vessel and left for 24h to allow phase separation. Polyurethanes were obtained from glycolysates by means of prepolymer method and using, as before, di-isocyanide MDI and different extenders [17,18].

RESEARCH RESULTS

PREPOLYMERS

Urethane prepolymers with the viscosity values from 1000 to 55000 mPas were developed in dependence on the [NCO] group concentration, temperature and shear stress. They were used as semi-products in the production of urethane elastomers to be applied as protective coating [10,19]. In Fig. 1 the variations of dynamic viscosity of urethane prepolymers obtained from Rokopol D 2002 and di-isocyanide MDI, in dependence on the rotation speed of the probe and prepolymer temperature, are presented. The FTIR spectra confirmed the time-dependent structural changes in prepolymers. In Fig. 2 the spectra of the 4-week old prepolymers obtained from Rokopol D-2002 and MDI, are shown.

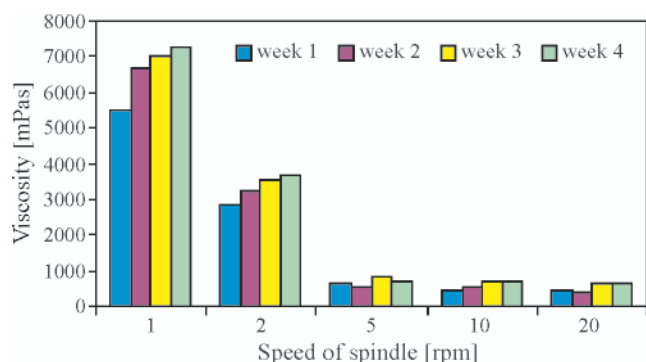


Fig. 1. Relation between the number of revolutions of the spindle and dynamic viscosity of urethane prepolymers investigated over a period of 4 weeks. [NCO] = 6%; measurements performed at 75°C

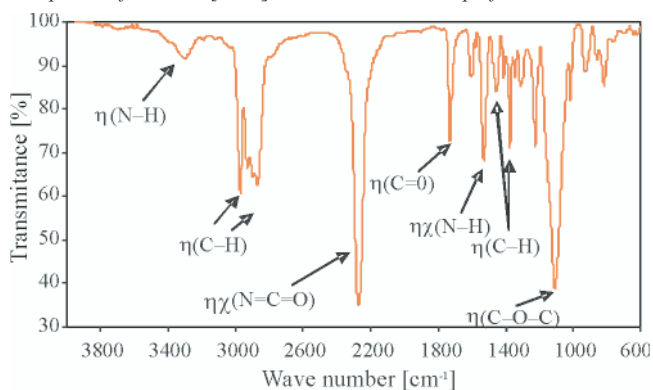


Fig. 2. FTIR spectrum of prepolymer with the [NCO] group concentration of 7% (4 weeks after the synthesis)

The obtained urethane prepolymers absorbed infrared light within the frequency range (600-4000 cm^{-1}). The resulting spectra were very similar and displayed, as predicted, the comparable infrared absorption bands for the identical frequency ranges. It has been observed that over the period of 4 weeks, the intensity of the NCO band at 2273 cm^{-1} was decreasing. This shows that the content of NCO groups in the prepolymer was decreasing, and therefore the prepolymer structure was changing. It has been determined that prepolymers obtained from PTMG were characterized by higher chemical stability as compared with those obtained from MDI and Rokopol D2002 (Fig. 3); the former displayed a small change of ca. 0.2% in the [NCO] group concentration while in the latter such concentration change reached as much as 12%. Prepolymers obtained from oligoestrols, i.e. Poles 55/20 had chemical stability similar to that of the prepolymers obtained from Rokopol D2002.

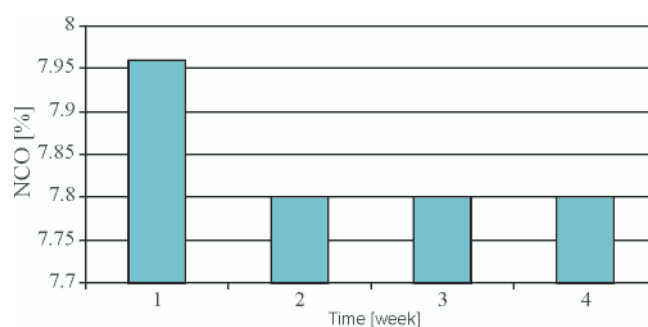


Fig. 3. Variation of the [NCO] group concentration in urethane prepolymer obtained from MDI and PTMG over a period of 4 weeks. Initial [NCO] concentration=8%

ELASTOMERS

Based on the analysis of the tangent of the loss angle in function of time (see Fig. 4), the glass transition temperature (T_g) was determined for the elastomers obtained from the previously developed prepolymers. (T_g) corresponds to the maximum on the $\text{tg } \delta = f(T)$ curve at which the transition between the glassy and rubbery state occurs. The glass transition temperatures measured by the DMTA method in polyurethanes produced with BDP extenders ranged from -2 to 5°C [11-14].

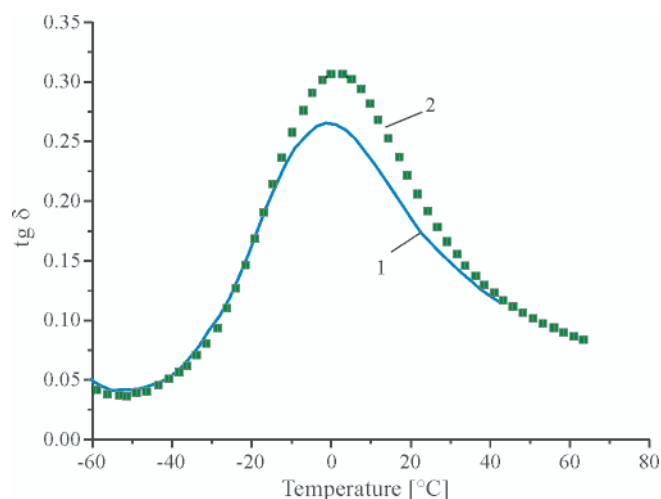


Fig. 4. Temperature dependence of the loss tangent of PU obtained from MDI, PTMG and low molecular weight extender BDO for different molar [NCO]/[OH] ratios. Curve 1 - PU9P-1.00; curve 2 - PU10P-1.05

The strength characteristics of the polyurethane used as elastic coating is shown in Fig. 5. The material was obtained by the RIM technique by means of pouring the polymer into steel moulds without pre-heating and without heat treatment during the gelation and cross-linking steps. The results of strength analysis performed on layered samples with different chemical structures are presented in Tab. 1, while the outcome of a study on the interaction between crude oil and the obtained polyurethane is shown in Tab. 2.

The capacity of the samples to absorb crude oil varied with the structure and properties of specific polyurethanes. For the polyurethane obtained from Poles 55/20 ([NCO] = 9 %; Tab. 2), Capa 212 and Poles 55/20 ([NCO] = 5 %), the capacity values ranged from 0.59 to 1.33 %, from 0.92 to 1.34 % and from 0.78 to 1.12 %, respectively. The absorbance capacity measurements were performed over a period of 364h.

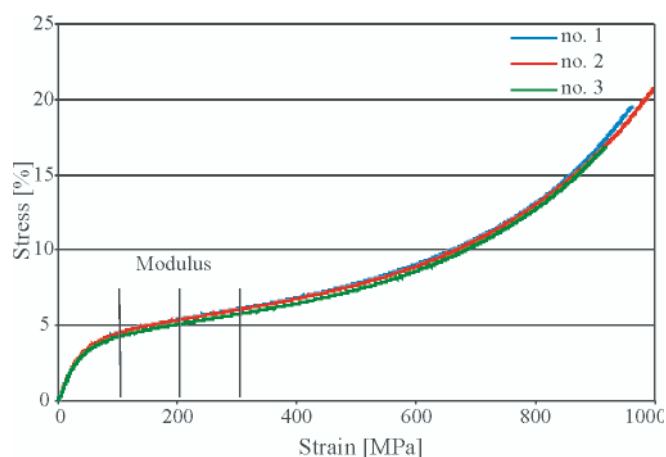


Fig. 5. Stress-strain characteristics of polyurethane used as protective coating (3 samples)

In order to define the conditions for obtaining strong jointing between the various polyurethane types and between polyurethanes and other materials, a number of layered samples were prepared that differed in the layer thickness and properties. Varied conditions were used to obtain the dual-layer samples, i.e. different temperatures of mould as well as of system, different levels of cross-linking of polymer before pouring onto it or jointing it with the second layer, and varying polymeric surface conditions.

Tab. 1. Strength properties of polyurethane dual-layer samples with different structures. Prepolymer obtained from MDI + Poles 55/20 (samples PU1PC – PU6PC), and from MDI + Capa 212 (other samples). The NCO group concentration in polyurethane prepolymer ca. 9%

Symbol of dual-layer sample	Modulus 100 [MPa]	Modulus 200 [MPa]	Modulus 300 [MPa]	Tensile strength [MPa]	Tensile elongation [%]	Permanent elongation [%]
PU1PC	11.0	14.7	17.6	20.3	520	36
PU2PC	11.0	14.3	16.6	25.1	544	41
PU3PC	11.2	12.8	14.4	15.0	340	32
PU4PC	12.3	15.2	18.3	23.8	400	40
PU5PC	11.1	14.0	16.9	20.0	421	30
PU6PC	11.0	12.6	14.4	22.7	448	36
PU7PC	10.1	12.6	14.9	18.4	336	22
PU8PC	13.2	14.5	17.7	19.1	387	28
PU9PC	12.6	13.1	14.3	15.2	416	28
PU10PC	10.0	11.7	12.9	17.9	440	36
PU11PC	10.5	11.6	11.8	12.4	320	22
PU12PC	11.3	12.8	13.3	13.6	360	27

Tab. 2. Measurements of capacity for absorbing crude oil by single-layer polyurethanes obtained from MDI, Poles 55/20 and BDO. The NCO group concentration in polyurethane prepolymer ca. 9%

Sample symbol	Initial mass of dry sample [g]	Capacity for absorbing crude oil [%]									
		24h	48h	72h	96h	168h	192h	216h	250h	274h	346h
PU1P9	2.0008	0.23	0.27	0.35	0.39	0.52	0.56	0.59	0.59	—	—
PU2P9	1.9993	0.43	0.63	0.73	0.80	1.02	1.07	1.12	1.19	1.20	—
PU3P9	1.9990	0.33	0.47	0.56	0.62	0.79	0.89	0.93	0.98	1.02	1.05
PU4P9	2.0012	0.59	0.75	0.92	1.01	1.25	1.29	1.29	—	—	—
PU5P9	2.0003	0.58	0.73	0.89	1.01	1.26	1.29	1.29	—	—	—
PU6P9	2.0017	0.67	0.84	0.98	1.08	1.33	1.40	1.42	1.42	—	—
PU7P9	2.0011	0.63	0.81	0.93	1.01	1.21	1.28	1.32	1.33	—	—

Based on the obtained results, it has been established that the surface treatment of steel elements by grit blasting definitely improved the adhesion of polyurethanes to steel. The use of adhesives mostly increased the strength however in the case of large-size products the problem of applying the adhesive quickly enough had become apparent.

It was also determined that the production process of layered samples did influence the strength of polyurethane-steel joints [15, 16]. Samples obtained by pouring the urethane system between the metal elements were characterized by a higher strength than those obtained by gluing the cross-linked polyurethanes to steel sheets. This latter finding resulted in the choice of the RIM technique for applying polyurethane coating onto steel and steel-concrete constructions during our study.

HYBRID POLYURETHANE-STEEL-CONCRETE ELEMENTS

In this study the elastic polyurethane coating was applied into the fuel tanks in the form of liquid polyurethane system that was being dispensed onto the light ceramic material filling the steel construction. Preliminary experiments to verify this method were conducted by coating large-size steel samples covered with ceramic material of varying surface characteristics and water content. The polyurethane system was poured onto steel-concrete samples by using a EC305 machinery (Secmer, France). In the technology developed by us, the protective

polyurethane layer was applied to the ceramic surface without adhesives; the high surface roughness was used as the only feature.

It has been determined that priming the ceramic material with resin improves the quality of coating. Increasing the polyurethane gelation time is also advantageous because it creates conditions for better de-gassing of the ceramic material. This results in a more homogenous surface that secures the proper tightness of the construction [2-6 and 17-21]. It has been determined that the technology of pouring a reactive polyurethane system is useful for producing the elastic polyurethane coating on metal as well as ceramic (concrete) surfaces.

The moisture content of a ceramic mass influences the quality of polymeric coating. Application of the coating in a dual-layer form is optimal because it improves the quality of the polymer's surface. This is due to the reduction in pore number on the ceramic surface and the increased strength of the elastic polyurethane coating.

RECYCLING

All polyurethanes obtained from glycolysates had similar tensile characteristics ranging from 13 to 15.5 MPa (Tab. 3). The polyurethane coded PU2 had lower elongation at break and slightly smaller permanent elongation as compared to polyurethane PU1, which can be attributed to the higher content of cross-linking via allophanic and biuret bonds. The results of the TG analysis are presented in Fig. 6. Polyurethane displayed the temperature of the maximum mass loss T_{max} similar to that of glycolysates T_{max2} . The mass loss at this specific temperature most likely resulted from the degradation of the chains forming flexible segments. In Fig. 7 the FTIR spectra of the gaseous decomposition products of polyurethane at different temperatures, are shown. In the case of elastomer the carbonyl band has couple peaks at ca. 1730, 1745 i 1755 cm^{-1} , which indicates high complexity of the mix of compounds. Similarly to glycolysates, the intense band at 1107 cm^{-1} corresponding to the ν_{C-O-C} vibration indicates the presence of decomposition products of flexible polyether segments [20, 21].

Tab. 3. Tensile strength and relative elongation of polyurethanes obtained from glycolysates

Sample	Extender	P _{NCO} [%]	Tensile strength [MPa]	Elongation at break [%]	Permanent elongation [%]
PU1	BDO	9.2	14.9	122.9	16.0
PU2	BDO	10.7	13.4	59.3	15.7
PU3	EG	10.0	15.6	61.3	14.9
PU4	BDO	10.0	14.9	62.2	15.4
PU5	HDO	10.0	14.8	71.6	17.6

The bands at 1612 cm^{-1} and 1513 cm^{-1} most likely correspond to a valent vibration of the $\nu_{C=C}$ aromatic ring. The characterization of the band marked in Fig. 7 has been presented in Tab. 4.

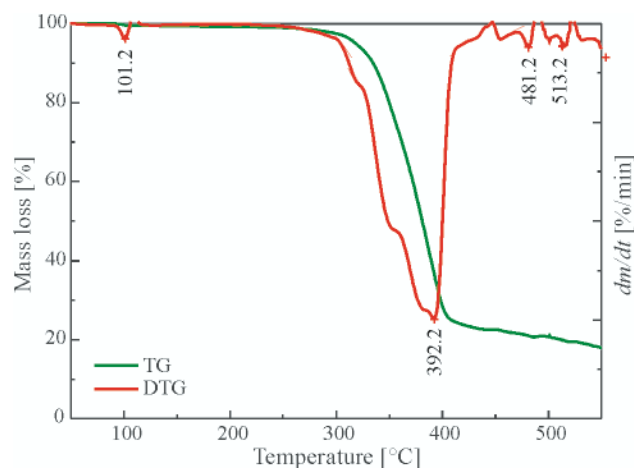


Fig. 6. TG and DTG curves obtained for PU1

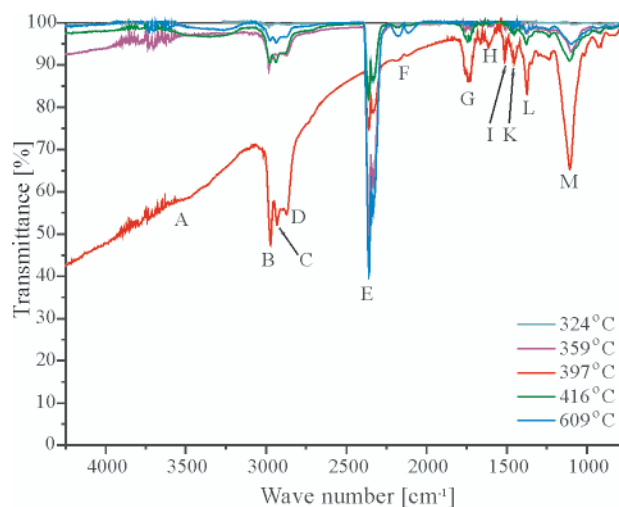


Fig. 7. FTIR spectra of gaseous decomposition products of polyurethane obtained from glycolysate

Tab. 4. Description of the main absorption bands of gaseous decomposition products of polyurethane

Symbol	Wave-number ν [cm^{-1}]	Vibration type or compound
A	3590	ν_{OH}
B	2970	$\nu_{CH_3,as}$
C	2923	$\nu_{CH_2,as}$
D	2871	$\nu_{CH_3,sym}$
E	2360	CO_2
	2320	
F	2183	CO
	2117	
G	1745	$\nu_{C=O}$
H	1612	$\nu_{C=C}$
I	1513	
K	1452	$\delta_{CH_3,as}$
L	1375	$\delta_{CH_3,sym}$
M	1107	ν_{C-O-C}

SUMMARY

The composition and methods for obtaining a prepolymer as well as its further processing by the RIM technique by using small molecule glycol extender, were elaborated. The used technique allows the production of durable polyurethane coating by applying the technology that does not require pre-heating of the steel elements and additional heating of polyurethane dispensed onto different surfaces. The conditions for obtaining coatings of the hybrid polyurethane-steel-ceramic type were defined. The recycling procedure was proposed for the waste polyurethane coating that comes from ship breaking or future pre-planned repair operations on the vessels. It will allow to obtain recycled semi-products, the so-called urethane oligomers, that have the properties and structures suitable for using them to manufacture new polyurethane products.

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