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Development of environmentally friendly polymeric materials

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Abstract

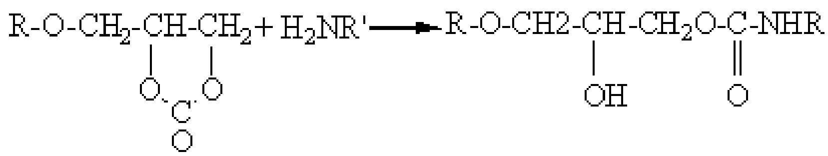
The paper is devoted to advanced chemical and UV-resistant coatings for industrial application based on reaction of cyclocarbonates primary amines and epoxy resins. We present results of investigations of advanced fire resistant and flame-retardant coatings on the base of sodium silicate, aluminum hydroxide, sodium oxalate, and pigments and results of investigations of biodegradable ecopolymer compositions applied as coating for various hydrophilic substrates.

One of the main methods of decreasing environmental hazards is applying environmentally friendly materials [1]. We would like to describe a few of them.

1 Nonisocyanate polyurethane coatings

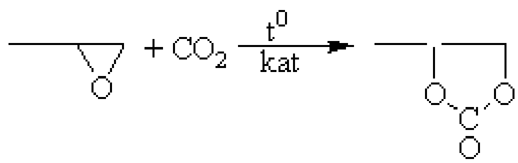
Network nonisocyanate polyurethanes are formed as a result of the reaction between cyclocarbonate olygomers and primary amine oligomers [2].

This reaction forms an intra-molecular hydrogen bond through the hydroxy group at the ß-carbon atom of the polyurethane chain as illustrated below:



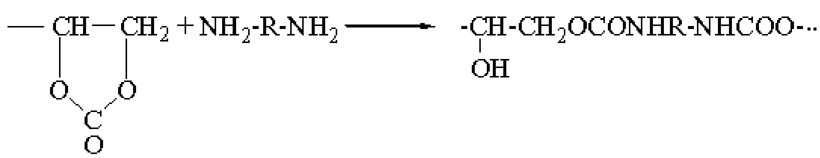
(1)

Cyclocarbonate oligomers are synthesized by a new method from epoxy oligomers and CO_2:



(2)

The technology is safe and easy. The process is characterized by temperature 120-150^{0}C, pressure 0.5-10 Bar, and duration 0.5-2hrs. It is possible to use a continuous method. **Adducts** of cyclocarbonates and amino-containing oligomer are synthesized as a curing agent:



, (3)

where: R might be alkyl, isophorone, xylelene, etc.

Advantages of chemical resistant hybrid nonisocyanate polyurethane (HNIPU):

- high solidity;
- hardness of a paint film;
- high chemical resistance;
- good mechanical properties, abrasion resistance;
- simplicity of production and using technology compared to that without isocyanates (insensitivity to moisture);
- suitability for primers, flooring, chemical resistant coatings;
- possibility of using instead of epoxy chemical resistant binder.

HNIPU materials are the next generation of polyurethanes with high chemical resistance and increased mechanical properties. They are environmentally friendly and do not consist any dangerous components.

Hybrid nonisocyanate chemical resistant epoxyurethane network polymers are formed as a result of the reaction between olygomeric amino-urethane adducts and aromatic amines (adducts) with epoxy resins.

HNIPU display the same chemical resistant properties as conventional epoxy resins yet their mechanical properties are superior. Hybrid nonisocyanate UV-stable network polymers are formed as a result of the reaction between oligomeric amino-urethane adducts with cycloaliphatic epoxy resins or acrylic cyclocarbonate olygomers with amino containing compounds.

UV-stable HNIPU aliphatic and acrylic are recommended as a top coating instead of conventional polyurethane coatings.

Our investigations show that HNIPU coatings have no sensitizing effect and are harmless; for example, the toxic factor of methaxylelenediamine (MXDA) using for HNIPU is 50 times less than that of methylene-di-isocyanate (MDI) used for common polyurethanes [5].

2 Water-born compositions for fire-resistant coatings

Fire-protection coatings of wood, metals and plastics can be applied for shipbuilding, building, and automotive industries.

The coating material represents a combination of inorganic and organic particles that expand at heating and release endothermically a steam-gas mixture at the temperature of inflammation, inorganic water glass, and a water dispersion of chloro-sulfonated polyethylene (Table 1) [3, 6].

Physical properties	**Units**	**Method**
Color	White	
Density, as supplied	1.82 g/ml	
pH	10.5–11.5	
Viscosity	100 s	ASTM D4212-93 (nozzle 4 mm)
Viscosity	1500 cPs	ASTM D2196-86 (Brookfield, 20^0C, Spindle N2, speed 3.0 rpm)
Freezing point	-30^0C	

Table 1: Properties of the material as supplied.

Water glass on heating endothermically releases water and forms a foam-like vitrificated barrier coating that protects substrates from the oxygen supply.

Chloro-sulfonated polyethylene (CSPE) forms at burning a protective carbonated layer. This layer, together with a vitrificated layer, increases the barrier effect of a fire protection and, at the same time, imparts to the coating water-resistance and resistance to atmospheric carbon dioxide. Main properties of dried coatings are shown in Table 2.

Property	**Unit**
Density	2.8 g.cm^3
Application	1-4 layers
Coverage thickness	0.12–0.4 mm
Weight loss after 2 min exposure at 200^{0}C	$< 4\%$
Fire resistance after exposure to flame > 800 kW/m^2	950^{0}C $>$ 15 min
Adhesion to asbestos - cement plates	3.1 Mpa
Flame spread index (according to ASTM E84)	10–20 (Class A)
Smoke developed index (according to ASTM E84)	15

Table 2: Properties of dry fire-resistant coatings.

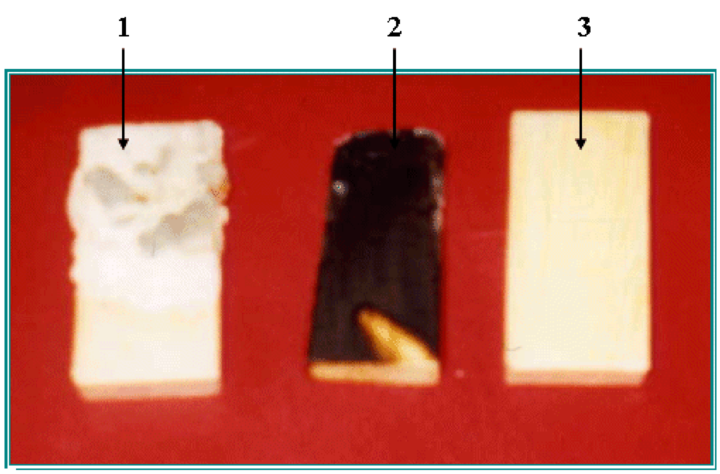


Figure 1: Testing of wood samples. 1: Dry coated wood sample after flame – no ignition takes place. 2: Dry non-coated wood sample – ignites in a few seconds after exposure. 3: Fully coated sample before exposure.

Wood samples sized 150x30x10 mm, covered from all sides by fire-protecting coating, were tested under open flame during one hour; the weight loss was 10%. Control non-coated wood samples were burned after 3-4 min fire test; the weight loss was 35% after 5 min (Fig. 1).

Steel samples 60 x 60x 2 mm, were tested in a special heat-insulated cell in the gas burner flame, which imitated the fire flame at the steel critical temperature 500^{o}C. The time was 60 and 100 min for coated samples (see curves below), while for control samples without coating (upper curve) this temperature was about 5-7 min (Fig. 2).

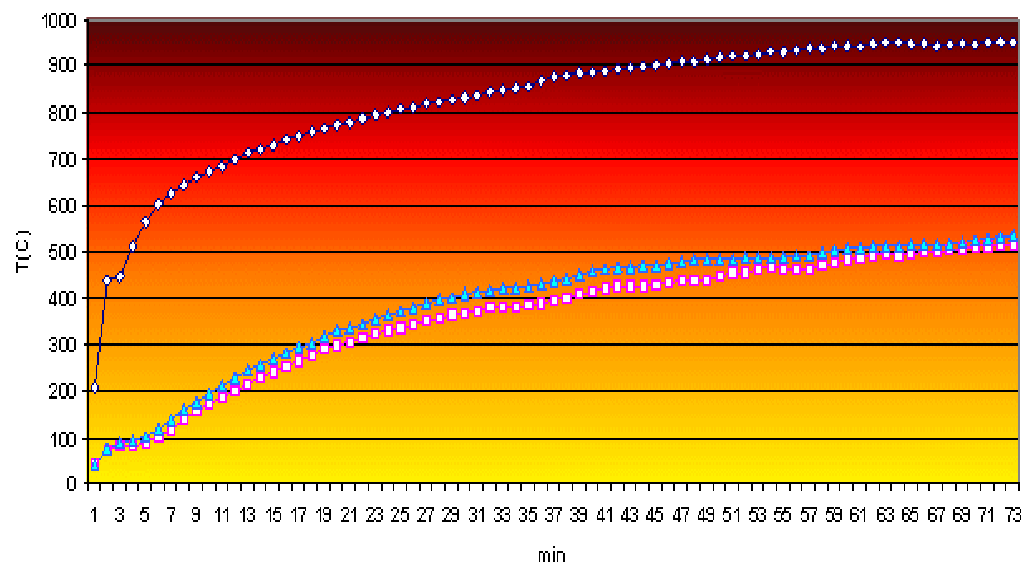


Figure 2: Testing of steel samples.

3 Advanced biodegradable water-born coatings

We have developed advanced water-born and environmentally friendly ecopolymer dispersions applied as multifunctional protected coatings for various hydrophilic substrates [4]. A special biodegradable aliphatic polyester was used as such ecopolymer. The ecopolymer was synthesized by the method of emulsion polymerization in water medium. The reaction system contained monomers, emulsifiers, stabilizers, catalysts and water. The product of the synthesis was of 40-50% aqueous dispersion.

Latex compositions can contain also modifying additives: surfactants, stabilizers, lubricants, hydrophobizators, anti-blocking and cross-linking agents, pigments, and some other components. The composition is ready for using.

Main application fields of developed dispersions are:

- producing of various paper and paperboard packaging with protective layers;
- protective coating for wood;
- protective coating for building materials;
- protective coating for other substrates.

Biodegradable cellulose substrate is coated with the modified latex by means of a coater and then dried. As result, the final product - the coated substrate (cellulose-ecoplastic) - can be manufactured (see Figs. 3 and 4).

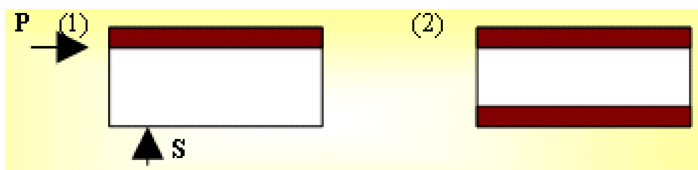


Figure 3: Scheme of coated substrates.

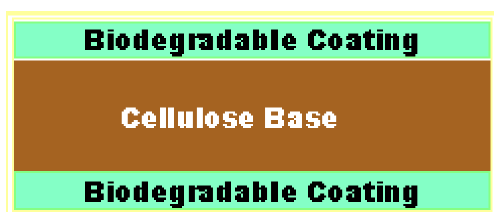


Figure 4: Biodegradable coating.

The cellulose-ecoplastic called Rapid Biodegradable Hydrophobic Material (RBHM) can have the “Bread-Butter” (1) or the “Sandwich” (2) structural type. These materials contain a thin (5-10 microns) layer of biodegradable polymer (P) and a thick (0.2-0.5 mm) substrate sheet (S). The layer “P” is barrier and the sheet “S” imparts strength to coated substrate.

The one-side coated substrate (P-S) is simple and cheap. Uncoated side of the material “Bread-Butter” can be used for printing. The two-side coated substrate (P-S-P) is more expensive but has excellent barrier properties.

Barrier properties of the cellulose-ecoplastic depend on composition of the layer “P” of Fig. 3. We have developed four types of the RBHM-materials. The "G"- type is a grease-stable material. The "W"- type is stable against water penetration. The “G-W”-type is intended against both grease and water penetration. The universal material of the "U"-type has excellent barrier against penetration greases, water and some organic solvents, as well as moisture, oxygen and other gases. Color of the coated cellulose substrates can be different and depend on the pigment type in coating compositions.

RBHM can be used for producing bags, sacks, boxes, containers, plates, cups, flowerpots, tablecloths, and other articles. Main properties of the cellulose-ecoplastics are shown in Table 3.

Type	3M Kit No	$Cobb_{30}$ g/m^2	MVTR g/day m^2	$T(O_2)$	P MPa
G	10-12	20-25	180-200	12	40-60
W	6-8	10-12	50-70	9	40-60
G-W	10-12	15-17	130-150	10	40-60
U	10-12	0.5-1	3-5	7	40-60

Table 3: Properties of the cellulose-ecoplastics (RBHM).

Description of the parameters shown in Table 3:

3MKit No is a parameter of grease resistance of the material; the maximal Kit No=12 is related to the plastic that is fully impenetrable for greases, while the minimal Kit No=0 is related to the material that is easy penetrable for greases.

$Cobb_{30}$ is a parameter of water absorption for 30 min; it is the amount of water in grams that is absorbed by one square meter of the plastic sheet for 30 min.

MVTR is a moisture vapor transmission; it is the amount of water vapor in grams that permeates through one square meter of the plastic sheet at 25^oC and RH = 85% for 24 h.

$T(O_2)$ is an oxygen transmission, $(cm^3\ cm)/(m^2 day\ atm)$; it is the amount of oxygen in cm^3 that permeates through one square meter of the plastic sheet at 25^oC and pressure 1 atm for 24 h.

P is a tensile strength of the ecoplastic.

Mechanical (P) and barrier properties (Kit No, Cobb, $T(O_2)$ and MVTR) of the cellulose-ecoplastics are better than those of existing ecoplastics based, for example, on Polycaprolactone. Barrier properties of the "U"-type of RBHM are similar to the properties of polyethylene. Therefore, this biodegradable ecoplastic can serve as a replacement of a biostable synthetic polymer material.

There are two options for liquidation of wastes of ecoplastics and their articles.

- The first option is repulping of the material wastes together with paper and board wastes for pulp using in the paper industry;

- The second option is decomposition of the biodegradable wastes by composting.

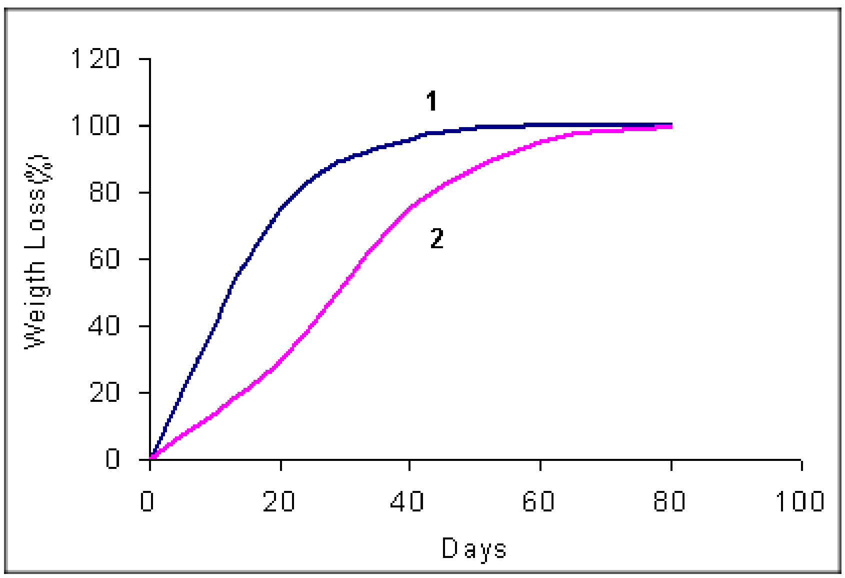


Figure 5: Weight loss (%) of the polymer materials under composting in a wet soil. 1-cellulose substrate (the upper curve); 2- RBHM: cellulose substrate coated with GW barrier layer (the lower curve).

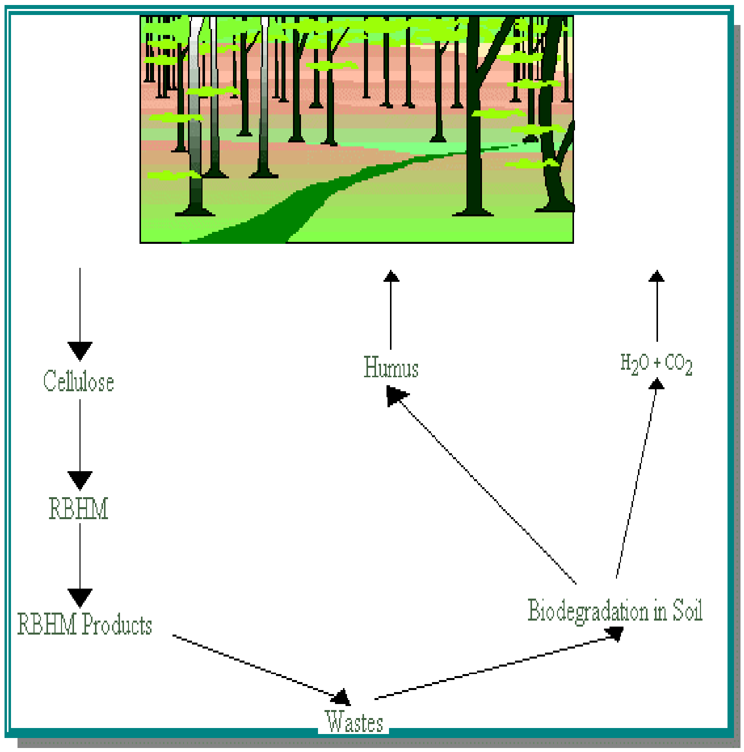


Figure 6: Forming of environmentally friendly substances at biodegradation process of the cellulose-ecoplastic: RBHM.

Decomposition process of the novel cellulose-ecoplastics in wet soil occurs rapidly, during 2-4 months (Fig. 5). The natural-based cellulose-ecoplastics are manufactured from trees and other plants as it is shown in Fig. 6. As a result of decomposition of the eco-plastic in aerobic conditions, only the environmentally friendly substances, i.e. water, carbon dioxide and humus, are formed. These substances return to the environment and are utilized by plants in their growing process (Fig. 6).

4 Conclusions

HNIPU materials are the next generation of polyurethanes with high chemical resistance and increased mechanical properties. They are environmentally friendly and do not consist any dangerous components. Hybrid non-isocyanate chemical resistant epoxy-urethane network polymers are formed as a result of the reaction between oligomer amino-urethane adducts and aromatic amines (adducts) with epoxy resins.

Environmentally friendly fire resistant and flame retardant coatings on the base of sodium silicate, aluminum hydroxide, sodium oxalate, and pigments have been investigated. Fire resistance of wood has been increased 3 to 3.5 times (0.5-1 hour).

Environmentally friendly biodegradable ecopolymer composites were investigated as protective coatings. Barrier properties of the coatings are similar to the properties of common synthetic polymers. The compositions may be applied as multifunctional protective coatings for various hydrophilic substrates.

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