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TOXICOLOGICAL PATTERNS OF MULTICOMPONENT POLYMER SYSTEMS

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ABSTRACT

Development of new polymer systems (PS) based on thermo-active resins is important not only from a chemical viewpoint but also because of the opportunity for programmable changing their properties and subsequent application in clinical practice. Some chemical features of a new composition for a multicomponent polymer system (MPS) based on hydrophilized unsaturated polyester resin (HUPR) are presented. Strength parameters of several resins of different compositions are examined. The analysis of the acute oral toxicity of these resins in white Wistar rats proves that they are low toxic. These PS do not demonstrate any harmful effects on human skin after the predicting irritation and sensitization tests using epicutaneous samples. Their main advantages include preliminary water-solubility and capacity to incorporate water, good dilution into water and resin water dispersions, porosity, low relative mass, high strength indices, improved ecological features, thin-founding capacity, good relief impressions in combination with high adhesion ability towards wet surfaces. A wide MPS usage in the manufacture of orthopedic plaster dressings, prostheses, splints, insoles, positive-sample dental imprints, and casts is recommended.

Key words: hydrophilized unsaturated polyester resin, chemical composition, physico-chemical properties, skin toxicology

INTRODUCTION

The wide introduction of unsaturated polyester resins (UPR) and cements in modern industry has lead to a variety of occupational skin diseases. There is increasing evidence of the hazardous effects of components of PR such as methyl ethyl ketone peroxide (23), N-benzyl-N, N-dimethylamine (5), polyamide polyesters (11) and polyester fibers (20). Recently, a series of publications occurred dealing with occupational dermatoses among workers in fibreglass-reinforced plastics factories (15,16,21), skin allergy (22), and allergic contact dermatitis in car repair work (18,21) and painting (12). Contact sensitivity to UPR was reported with limb prosthesis (13). The most common chemicals causing allergic contact dermatitis are diethyleneglycol maleate (18,21), methyltetrahydrophthalic anhydride, and methylhexahydrophthalic anhydride (14,22). Some components of the UPR such as maleic anhydride, phthalic anhydride, ethylene glycol and dicyclopentadiene have caused allergic contact dermatitis probably because of the specific composition features of the blends (14). The challenges of timely and correct diagnosis of sensitivity to chemicals are successfully answered by the creation and further improvement of the thin layer rapid use epicutaneous (TRUE) test (6,7,9,10), presenting a test system with documented stability and allergen content and a significant step towards higher reliability of patch testing.

Polymer systems (PS) composed by two polymers have been used for a long time for preparation of materials combining the properties of these polymers blended. The clarification of the structure and properties of blends of thermo-active resins is challenged by the complex formation of the network of chemical bonds in compound resins and the different chemical properties of thermo-active materials. Therefore, it looks crucial to establish the compatibility between cross-linking materials thus enabling their mutual solubility and understanding their parameters. Development of new PS based on thermo-active resins is topical not only from a chemical point of view but also because of the opportunity for programmable changing their properties in order to satisfy some specific requirements in the field of medicine and dentistry.

The purpose of this communication is to demonstrate the chemical and toxicological patterns as well as some promising features of the hydrophilized MPS.

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MATERIAL AND METHODS

Preparation of the multicomponent polymer system (MPS)

Previously, a HUPR' was obtained through hydrophilization of UPR with 25% ammonia water (4). Recently, a HUPR" was obtained through hydrophilization of UPR with alkaline-acting blend of equivalent quantities of calcium hypochlorite and calcium dichloride as a hydrophilizing component (HC). After its modification, HUPR" could be diluted with water and, at the end of the process, supplemented by another chemically different resin, e. g., the water-soluble carbamide formaldehyde resin (CFR). The co-polyester of propylene glycol, maleic anhydride, and phthalic anhydride in styrene solution was used to examine the UPR. Cyclohexanone peroxide (CHP) served as an initiator of UPR hardening but cobalt naphthenate (CN) as an accelerator. As a result of UPR co-polymerization in the presence of HC with a redox system of CHP/CH some hardened HUPR" samples were prepared (3) along with hardened HUPR' ones for comparison. This redox system was preliminarily used to obtain a non-modified HUPR, too. The chemical changes in the polyester chains allowed a compatibility with other polymer emulsions such as CFR. During the mutual solution of their components some one-phase polymer blends were obtained that, after spatial cross-linking, fixed certain structures with interpenetrating polymer networks (IPN). Infrared spectroscopy proves that blending of HUPR with resins of different chemical nature such as amino formaldehyde does not change their differential infrared spectra (8). Therefore, the process of compatible hardening is accompanied only by physical but not by chemical reactions between binding resin components, i. e. it does not induce any obtaining of copolymers but a formation of polymer blends or IPN (8). The optimal ratio between these components and the correct prescriptive preparation of MPS itself was favoured to IPN formation. That was why the end products based on IPN possessed improved ecological parameters.

Along with the preparation of its composition, HUPR" was diluted with distilled water for the preparation of hardened samples of HUPR"/H2O composition in a ratio of 75/25 mass parts.

CFR was obtained by polycondensation of carbamide and formaldehyde and cross-linked in the presence of phosphoric acid (PA). The CFR was applied during the development of a two-component PS based on HUPR" as HUPR"/CFR system was used in different proportions. The latter was hardened under joint cross-linking of both resins after consecutive adding of their selective hardeners in the following order: CN, CHP, and PA.

In order to forecast the time-related changes of the mechanical properties, the alterations in the relaxation spectra of polyester resins and compounds were studied. Temperature correlates of the velocity of small deformations or velocity spectrum were used to define the relaxation transitions. The comparison of the spectra of different compounds enabled to prognosticate the degree of change of strength patterns in various areas of relaxation as well as to establish the most critical temperature interval (17). The kinetics of hardening of UPR at low temperatures and high humidity was assessed. Some new hardening-initializing systems containing sodium formaldehyde sulphoxylate, dimethylalanine, and rongalite as co-accelerators were applied (19). The mechanical tests were done by means of TIRA TEST 2300 machine linked with plotter for drawing-up the strength-shifting relationship (19).

Strength parameters of the single resins such as UPR and CFR, HUPR without and with diluting water (0-30%), and HUPR/CFR at different proportions were examined according to the Bulgarian National Standard 12602-81. The materials obtained were new and not standardized yet. The mechanical tests were done according to ASTMD 695 and 790.

Toxicological characteristics

Acute oral toxicity of these resins was examined in 36 white Wistar rats of both sexes weighing 180-200g. Animals were raised under standard vivarium conditions such as air temperature of 20-24°C, relative air humidity of 65-85%, at natural ventilation and lighting as well as without any abnormally elevated ammonia concentrations. They were fed a routine briquette food. The rats were introduced 20% suspensions of the resins on an empty stomach per straight metal probe, 2mm in diameter and 10cm in length. After the peroral administration of the resins, the animals were observed every hour until the 6th hour and then daily for 14 days. The animals were divided into 3 groups of each gender and given one and the same dose. Three different dosages of the resins such as of 6000, 8000, and 10000mg/kg b. m. were applied. The experiments were carried out in accordance with the requirements of the EU and of the Bulgarian State Standard (No. 15049-80).

The predicting irritancy test was carried out in 20 healthy volunteers aged 21-28 years (13 males and 7 females) by the method of single epicutaneous samples with the MPS (1,2). The data were read after 48 hours. The predicting skin sensitization test was performed with 35 healthy volunteers aged 20-32 years (27 males and 8 females) using fivefold epicutaneous samples with these systems. The results were read after 48 and 72h.

Table 1. Quantitative contents of components designed for different hardened HUPR" (mass %)

UPR	HC [$Ca(OCl)_2$ and $CaCl_2$]	Solvent (H_2O)	CN	CHP
94	-	-	2,3	3,7
90	4,5	-	2,0	3,5
85,5	4,3	5	1,9	3,3
76,5	3,8	15	1,7	3,0
67,5	3,4	25	1,5	2,6

RESULTS AND DISCUSSION

Some compositions of a hardened hydrophilized and/or water-diluted resin are shown on Table 1. This table can considerably be expanded when including the other HC types that, on their side, can be used in different quantities (3).

Table 2. Compositions of polymer blends based on HUPR" and CFR (mass %)

UPR	HC	CFR	CN	CHP	PA	Total	
						HUPR"+CN+CHP	CFR + PA
94	-	-	2,3	3,7	-	100 (UPR)	-
90	4,5	-	2,0	3,5	-	100	-
81	4,0	9,9	1,8	3,2	0,1	90	10
63	3,0	29,8	1,4	2,6	0,2	70	30
36	1,8	59,7	0,8	1,4	0,3	40	60

Table 3. Strength characteristics of PS

Polymer system	Compressive strength in *kN*	Flexural strength in kN/m^2
UPR	9,3 ±0,5	8,4 ±0,4
HUPR'	6,0 ±0,3	5,3 ±0,2
HUPR"/H2O = 75/25	4,2 ±0,2	4,5 ±0,2
HUPR"	5,5 ±0,3	7,3 ±0,4

Some compositions of PS based on HUPR"/CFR are shown on Table 2. Every row with the substances composing the HUPR"/CFR at different proportions precisely follows their prescriptive preparation sequence. The HUPR" surpasses the HUPR' in its strength features (Table 3).

Table 4. Predicting sensibilization and irritancy tests

Polymer system	subjects	moderate sensibilization	slight sensibilization	Subjects	slight irritancy
UPR	35	0	2	20	2
HUPR'	35	0	1	20	1
HUPR"	35	0	0	20	0
HUPR"/H_2O = 75/25	35	0	1	20	1
HUPR"/CFR 90/10	35	0	1	20	0
HUPR"/CFR 70/30	35	1	2	20	1

Recent studies dealing with its filling with powdered and fibrous fillers are strongly promising when compared with the UPR polymer matrix under the same conditions.

The dynamic following-up the appearance and behaviour of the rats does not indicate any alterations at all.

There are no deaths among the animals perorally treated with the aforementioned dosages. That is why we have failed to estimate the quantitative parameters of the acute oral toxicity of these resins at all. Therefore, DL_0 seems to be higher than 10000mg/kg b. m. According to the oral DL_{50}, the examined PSs belong to class IV of the classification of the chemical compounds after their toxicity (Bulgarian State Standard No 15049-80). Thus they are low toxic and low dangerous as well and are allowed for wide application.

Table 4 summarizes the comparative characteristics of the predicting irritation and sensitization tests. The negative allergic reactions clearly demonstrate the good compatibility of these systems with human skin.

The newly created composition for a MPS based on HUPR (3) is designed for application as resin plaster in building, architecture, medicine, and dentistry as well.

The chemically modified UPR underlies several main advantages of HUPR" after hardening. They are the following: preliminary water-solubility and capacity to incorpo-

rate water (up to 50% towards its own mass); good dilution into water and resin water dispersions; porosity; low relative mass; high strength indices; improved ecological features; thin-founding capacity; good relief impressions in combination with high adhesion ability towards wet surfaces. The end products of MPS look like plaster. Their density is low and appearance is good.

The very favourable results concerning the skin compatibility not only of the HUPR" and HUPR"/H2O=75/25 one-component but also of the HUPR"/CFR=90/10 and HUPR"/CFR=70/30 two-component systems should be emphasized. The newly prepared compositions reliably avoid the aforementioned sensitizing and irritating effects in rats and humans as well. This circumstance suggests the opportunity for their future clinical application. Therefore, they could successfully be applied in the manufacture of individual orthopedic plaster dressings designed for patient's use after plaster removal during reconvalescence as well as in the production of prefabricated orthopedic prostheses, splints, insoles, backs for wheel-chairs, positive-sample dental imprints, dental casts, etc.

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