UDC 687.021

S.V. PETEHERYCH
Khmelnytsky National University

THE EVALUATION OF CHANGES IN SANITARY AND CHEMICAL PROPERTIES OF ARTIFICIAL LEATHER DURING THEIR STABILIZATION BY COMPOSITE MATERIALS BASED ON POLYETHYLENETEREPHTALATE WASTE

The article presents the cycle of sanitary and chemical investigations of various artificial leathers and the polymer composition on the basis of polyethyleneterephtalate waste. The possibility of conducting direct stabilization of artificial leathers by the polymer composition on the basis of polyethyleneterephtalate waste without worsening hygienic properties, has been proved.

Keywords: a harmful substance, artificial leather, polymer composition, the waste, the concentration of chemical substances, hygienic assessment.

С.В. ПЕТЕГЕРИЧ
Хмельницький національний університет

ОЦІНКА ЗМІН САНІТАРНО-ХІМІЧНИХ ВЛАСТИВОСТЕЙ ШТУЧНИХ ШКІР ПРИ ЇХ СТАБІЛІЗАЦІЇ КОМПОЗИЦІЙНИМИ МАТЕРІАЛАМИ НА ОСНОВІ ВІДХОДІВ ПОЛІЕТИЛЕНТЕРЕФТАЛАТУ

В статті представлено цикл санітарно-хімічних досліджень різних штучних шкір та полімерної композиції на основі відходів поліетилентерефталату. Доведена можливість проведення прямої стабілізації штучних шкір полімерною композицією на основі відходів поліетилентерефталату без погіршення гігієнічних властивостей. Автором проведено ряд фізико-хімічних випробувань на визначення вмісту та значень гранично допустимих концентрацій шкідливих хімічних речовин в різних матеріалах та сферах довкілля.

Ключові слова: шкідлива речовина, штучна шкіра, полімерна композиція, відходи, концентрація хімічних речовин, гігієнічна оцінка.

Introduction

The application of artificial leathers (AL) for clothing production is impossible without rendering necessary shape stability to separate clothing parts. The experimental and theoretical investigations demonstrate that it is possible to improve the shape stability of the parts from AL with the minimal change of their thickness [1-3]. This improvement can be achieved with the help of direct stabilization by polymer compositions based on polyethyleneterephtalate waste.

However, the requirements are imposed on AL for clothing which are connected with the peculiarities of their performance. First of all, they include hygienic requirements. It is necessary to observe the national sanitary norms and rules "Polymers and polymer-containing materials, goods and structures used in construction and furniture production. Hygienic requirements". At present these sanitary norms most fully meet the requirements to clothing made from artificial leathers. The hygienic evaluation of polymers and polymer-containing materials is a complex of investigations (sanitary and chemical, toxicological, physical and hygienic, etc.) which are conducted in the modeled and natural conditions, experimental premises, chambers. The aim of these investigations is to determine their use which is safe for human health.

Setting the tasks

In order to evaluate how promising is the improvement of quality of the clothing from AL after its direct stabilization by polymer compositions based on polyethyleneterephtalate waste, we set the task to assess the degree of change in their hygienic properties with the help of sanitary-chemical investigations.

The artificial leathers with knitwear basis covered with polyurethane were selected for this investigation. Such materials are most often used in the production of domestic clothing [4]. Also, for comparison we chose AL with vinyl chloride coating. The characteristics of these leathers are presented in Table 1. The fourth material used in the investigation is the polymer composition based on polyethyleneterephtalate waste which is a complex thermoplastic polyester of terephtalic acid and ethylene glycol [5].

Table 1

Characteristics of artificial leathers

Name designation	Producer	Characteristics of the basis	Coating
SS 105	Indonesia	Knitwear	polyurethane
FW 208	Turkey	Knitwear	polyurethane
Vinyl leather (for nonwoven basis)	Joint-stock "Iskozh plant", Russia	Nonwoven fabric	polyvinylchloride

Main content

Different materials and chemical substances are used in the manufacture of modern light industry goods.

As a result, their different components can migrate in the air of the underclothing space. The migrants can cause skin irritation and local allergic action. The skin irritating action depends on the area of contact of clothing with human skin and can be more prominent because of high permeability of skin layer. Chemical substances can penetrate into the organism by oral way, and the use of textile auxiliary substances in high concentration can provoke the inhaling penetration of migrants in the organism. Therefore, sanitary-chemical investigations of hygienic properties are extremely significant in evaluation of the safety of new materials for light industry [6].

The aims of sanitary-chemical investigations are: 1) to reveal the possible evolution of harmful substances from materials and footwear into the contacting environment; 2) to study the intensity and dynamics of their migration; 3) to forecast the degree of their unfavorable effect on the organism.

The extraction and identification of chemical substances from polymer materials are carried out by two ways.

In order to determine the migration of substances in the air environment, the investigated specimens are placed into the hermetically closes vessels-exsiccators, from which, after certain exposition, samples are extracted with the help of electrical aspiration device with 6-10 – fold air exchange capacity. The time of exposition is predetermined by the time of maximal accumulation of harmful substances; as a rule, it's 3 days.

During the analysis for migration of toxic substances in the air environment the specimens are put in exsiccators or chambers:

- for the materials with the weight of up to 500 grammes - the ratio of specimen mass to the volume of air must 1:1,000; or to the volume of area – 1:1;
- for the materials with the weight of over 500 grammes the ratio of specimen mass to the air volume is 1:1.

In orders to reveal the toxic substances that migrate into a liquid model environment, the materials or the given specimens are wetted in the distilled water in the mass ratio 1:10.

The test specimens (artificial leathers and the samples of the composite materials on the basis of polycthyleneterephtalate (PETP) waste are divided into pieces 1cmx1cm, kept during 24 hours in a liquid environment (water) at room temperature, or at 37^{o}C during 6 hours. Depending on the material type the list of toxic substances whose concentration was determined will be different.

According to the regulations [7-10], acting on the territory of Ukraine, synthetic artificial leathers are examined on the content of formaldehyde, dibutyl phthalate (DBP), dioctyl phthalate (DOP), pH, ethylene glycol, toluol, vinyl chloride, acetaldehyde, salts of heavy metals.

The research on the detection of formaldehyde was carried out by MB 1849-78 [7]. Formaldehyde leads to mutagenic carcinogenic and toxic effects on warm-blooded beings and the human body. Formaldehyde is highly reactive chemical compound.

The principle of the method is in the interaction of formaldehyde with formaldimedon in the organic solvents – model environments, followed by chromatography on "Sylufol" plates.

The research on the content of solvents, alcohols and salts of heavy metals is conducted on the gas chromatograph "Kristall-400."

The preparation of samples we perform similarly to all research in a liquid medium. In contrast to studies in a thin layer of sorbent or by using photoelectric (photoelectriccolormeter), the researches on chromatography are performed several times faster [8].

The salts of heavy metals are determined in accordance with MB 4096-86 [9]. The method is based on extracts mineralization in sealed or less open containers by concentrated nitric acid and perhydrol, putting them in a propane-butane-air flame and determination of the concentration of elements by measuring the optical density at the resonant lines of certain elements.

In determining its solvents the extraction of explored solution is carried out by heating in a tightly sealed container or when selecting the sample vapor air mixture over the solution and its subsequent chromatography on the gas chromatography by flame ionization detector.

The hydrogen parameter (pH) in a liquid model medium is important because requirements to natural and synthetic materials on conformity to norms of acidity and alkalinity have been increased recently. The extract of pieces of material is prepared by extraction in the distilled water. Measurements are carried out on a device "Ionomer I-160MI". The acidity of the solution-extraction should not exceed 7.5 units of pH.

Dibutyl phtalate (DBP) and dioctyl phthalate (DOP) were determined according to the instructions 4259-87 (10). The method is based on extraction of phthalates by organic solvents of liquid model medium, followed by chromatography in a thin layer of sorbent.

To determine the toxicological properties of recyclat PETP and artificial leather with polyurethane and vinyl chloride coated, according to the above methods, a number of physical and chemical tests to determine the content of harmful chemicals were held. The research results are presented in Table 2.

Investigated synthetic leather SS 105 and FW 208 brands have approximately the same content of standardized components and the test sample – soft artificial leather HT, under extracting in liquid model medium, showed slightly increased concentration of dioctyl phthalate that may cause allergic reactions after the contact with human skin. As for recyclat based on PETP, the concentration of harmful substances in them is from 0.35 to 0.0033 boundary admissible concentration (BAC) particles that testifies to low level of toxicity.

Table 2

The concentration of harmful substances in materials

The name of harmful substances	Vinyl leather HT	Artificial leather SS 105	Artificial leather FW 208	Recyclat on the basis of waste PETP
Liquid model environment*				
dioctyl phthalate	0,051	-		-
dibutyl phthalate	0,18	-		-
formaldehyde	0,0012	0,0003	0,0001	0,001
pH	7,18	7,3	7,3	7,3
styrol	-	-	-	-
lead	0,004	0,0037	0,003	-
cadmium	0,00012	0,0003	0,0024	-
zinc	0,0003	0,0004	0,0003	-
copper	0,0015	0,0011	0,0009	-
ethyl acetate	-	0,004	0,003	-
methanol	-	0.007	0,0075	-
butyl spirit	-	0,0044	0,0032	-
isobutyl spirit	-	0,0058	0,005	-
propyl spirit	-	0,0063	0,0072	-
isopropyl spirit	-	0,0023	0,0025	-
Air modeling environment**				
vinyl chloride	0,02	-	-	-
ethylene glycol	1,9	-	-	2,0
acetaldehyde	0,0001	-	-	-
toluol	0,067	-	-	0,02
xylol	-	-	-	0,007
benzol	-	-	-	0,05

*mg/dm^3
**mg/m^3

In the subsequent phase of work the task was set to compare the experimental results for the test objects with the help of physical-chemical methods. The concentrations of hazardous components of materials resulted in a single dimensionless parameter to gain that aim.

For determining the criteria of evaluation of the admissible number of ecotoxicants in the light industry materials it is necessary to establish which ecotoxicants, those referred in the standard, it is necessary to consider and take into account (except the basic condition – no content excess items (bi) to established standards (BAC), i.e. $b_i \le BAC_i$ ..) the aggregate effect of chemicals, for instance, due to the so-called "toxicity index" [11]:

$$IT_i = \sum_1^n \frac{b_i}{ГДК_i} \le 1, \quad (1)$$

Where b_i – is concentration of chemical-toxicant, mg/m^3 or mg/dm^3;

BAC_i ($ГДК_i$) – the boundary admissible concentration;

i – studied material.

The value, of the boundary admissible concentrations of harmful substances in different areas of the environment according to [12] are shown in Table 3.

Table 3

The value of the maximum permissible concentration (ГДК) of harmful substances in different areas of the environment

The name of the chemical compound	BAC, mg/m3	Measurement errors
Liquid model environment		
formaldehyde	0,003	10%
pH	4,5-7,5	0,1 un.pH
styrol	0,04	0.40%
dioctyl phthalate	2	error is not standardized
dibutyl phthalate	0,2	error is not standardized
ethyl acetate	0.01	10%
methanol	0,2	10%
butyl spirit	0,5	10%
isobutyl spirit	0,5	10%
propyl spirit	0,1	10%
isopropyl spirit	0,1	10%
lead	0,03	18%
cadmium	0,001	12%
zinc	0,03	12%
copper	1,0	12%
air modeling environment		
vinyl chloride	0,1	error is not standardized
ethylene glycol	5,0	20%
acetaldehyde	0,001	25%
toluol	0,6	14%
xylol	0,2	25%
benzol	1,5	10 %

According: to the formula (1) we determine the index of toxicity (IT) for investigated material:

$$IT_{recyclat} = \frac{0,001}{0,003} + \frac{2,0}{5,0} + \frac{0,01}{0,04} + \frac{0,02}{0,6} + \frac{0,05}{1,5} + \frac{0,007}{0,2} = 1,085;$$

$$IT_{vinyl\ leather} = \frac{0,0012}{0,003} + \frac{0,05}{2} + \frac{0,18}{0,2} + \frac{1,9}{5,0} + \frac{0,0067}{0,6} + \frac{0,02}{0,1} + \frac{0,0001}{0,001} + \frac{0,004}{0,03} + \frac{0,00012}{0,001} + \frac{0,0003}{0,03} + \frac{0,0015}{1} = 2,28;$$

$$IT_{SS\,105} = \frac{0,0003}{0,003} + \frac{0,004}{0,01} + \frac{0,007}{0,2} + \frac{0,0044}{0,5} + \frac{0,0058}{0,5} + \frac{0,0063}{0,1} + \frac{0,0023}{0,1} + \frac{0,0037}{0,03} + \frac{0,0003}{0,001} + \frac{0,0004}{0,03} + \frac{0,0011}{1} = 1,1;$$

$$IT_{FW\,208} = \frac{0,0001}{0,003} + \frac{0,003}{0,01} + \frac{0,0075}{0,2} + \frac{0,0032}{0,5} + \frac{0,005}{0,5} + \frac{0,0072}{0,1} + \frac{0,0025}{0,1} + \frac{0,003}{0,03} + \frac{0,00024}{0,001} + \frac{0,0003}{0,03} + \frac{0,0009}{1} = 0,9.$$

As we can see, for all material types the content of formaldehyde is over 0,1 part of boundary concentration, and in the vinyl leather this part is the biggest. A high toxicity of the vinyl leather is conditioned by the presence of dibutylphtalate in it. A considerable part of ethylene glycol, in the limits of boundary concentration, is characteristic of the vinyl leather and the recyclat. Therefore, the main substances which considerably contribute to the toxicity of material, according to the index of toxicity are dibutyl phthalate, formaldehyde and ethylene glycol, and cadmium – for polyurethane material. All values of the mentioned concentrations in the materials are in the limits of boundary concentration.

Conclusion

The analysis of values of the index of toxicity demonstrates that the use of polymer composition on the basis of polyethyleneterephtalate waste for direct stabilization of artificial leathers will not cause the worsening of hygienic properties of clothing.

References

1. Bereznenko M.P. Marketynhovi doslidzhennia vykorystannia shtuchnykh shkir na shveinykh

pidpryiemstvakh Ukrainy / M.P. Bereznenko, S.V. Kovalchuk, S.V. Peteherych // Visnyk KNUTD. – 2010. – # 5. – T. 1. – S. 15–19.

2. Peteherych S.V. Khimichni metody nadannia formostiikosti detaliam shveinykh vyrobiv iz shtuchnoi shkiry / S.V. Peteherych, T.V. Ivanishyna, M.P. Bereznenko // VisnykKhNU. – 2011. – # 2. – S. 62–67.

3. Petegerych S.V., Misiats V.P., Bereznenko N.P., Paraska G.B. Theoretical researches of process causing polymeric coverage are on fabrics : monograph: Engineering and methodology of modern technology. Khmelnytsky. 2012. P. 119–133.

4. Zhuk O.V. Porivnialna kharakterystyka viazkopruzhnykh vlastyvostei shtuchnykh shkir ta paketiv na yikh osnovi / O.V. Zhuk, S.M. Bereznenko // Visnyk KNUTD. – 2010. – # 4. – S. 251–256.

5. Peteherych S.V. Khimichni metody nadannia formostiikosti detaliam shveinykh vyrobiv iz shtuchnoi shkiry / S.V. Peteherych, T.V. Ivanishyna, M.P. Bereznenko // Visnyk Khmelnytskoho natsionalnoho universytetu. – 2011. – # 2. – S. 62–67.

6. Onyshchenko H.H. Khymycheskaia bezopasnost kak vedomstvennaia problema. Rol hossanэpydsluzhbы Rossyy v obespechenyy khymycheskoi bezopasnosty naselenyia / H.H. Onyshchenko // Toksykolohycheskyi vestnyk. – 2002. – # 1. – S. 2–8.

7. Metodycheskye rekomendatsyy po opredelenyiu formaldehyda v vodnыkh vыtiazhkakh y modelnыkh sredakh : MV1849-87. – [Deistvuet s 1979-01-01]. – M., 1978. – 11 s.

8. Metodycheskye ukazanyia po opredelenyiu rastvorytelei v vodnykh seredakh : MV 4149-86. – [Deistvuet s 1986-01-01]. – M., 1985. – 11 s.

9. Metodycheskye ukazanyia po opredelenyiu po opredelenyiu solei tiazhelыkh metalov v vodnykh seredakh : MV 4096-86. – [Deistvuet s 1987-01-01]. – M., 1986. – 14 s.

10. Hihiienichna otsinka materialiv, do skladu yakykh vkhodiat humy : Ynstr. 4259-87. – [Deistvuet s 1988-01-01]. – M., 1987. – 14 s.

11. Olshanskaia O.M. Kryteryy otsenky эkolohycheskoi chystotы lnianoi tekstylnoi produktsyy / O.M. Olshanskaia, V.V.Kotyn, A.V. Artёmov // Zhurnal Rossyiskoho khymycheskoho obshchestva ym. D.Y. Mendeleeva. – 2002 . – T. XLVI. – # 2. – S. 66–76.

12. Bespamiatnov H.P. Predelno dopustymыe kontsentratsyy khymycheskykh veshchestv v okruzhaiushchei brede : spravochnyk / H.P. Bespamiatnov, Yu.A. Krotov. – L. : Khymyia, 1985. – 528 s.

Література

1. Березненко М.П. Маркетингові дослідження використання штучних шкір на швейних підприємствах України / М.П. Березненко, С.В. Ковальчук, С.В. Петегерич // Вісник КНУТД. – 2010. – № 5. – Т. 1. – С. 15–19.

2. Петегерич С.В. Хімічні методи надання формостійкості деталям швейних виробів із штучної шкіри / С.В. Петегерич, Т.В. Іванішина, М.П. Березненко // ВісникХНУ. – 2011. – № 2. – С. 62–67.

3. Petegerych S.V., Misiats V.P., Bereznenko N.P., Paraska G.B. Theoretical researches of process causing polymeric coverage are on fabrics : monograph: Engineering and methodology of modern technology. Khmelnytsky. 2012. P. 119–133.

4. Жук О.В. Порівняльна характеристика в'язкопружних властивостей штучних шкір та пакетів на їх основі / О.В. Жук, С.М. Березненко // Вісник КНУТД. – 2010. – № 4. – С. 251–256.

5. Петегерич С.В. Хімічні методи надання формостійкості деталям швейних виробів із штучної шкіри / С.В. Петегерич, Т.В. Іванішина, М.П. Березненко // Вісник Хмельницького національного університету. – 2011. – № 2. – С. 62–67.

6. Онищенко Г.Г. Химическая безопасность как ведомственная проблема. Роль госсанэпидслужбы России в обеспечении химической безопасности населения / Г.Г. Онищенко // Токсикологический вестник. – 2002. – № 1. – С. 2–8.

7. Методические рекомендации по определению формальдегида в водных вытяжках и модельных средах : МВ1849-87. – [Действует с 1979-01-01]. – М., 1978. – 11 с.

8. Методические указания по определению растворителей в водних середах : МВ 4149-86. – [Действует с 1986-01-01]. – М., 1985. – 11 с.

9. Методические указания по определению по определению солей тяжелых металов в водних середах : МВ 4096-86. – [Действует с 1987-01-01]. – М., 1986. – 14 с.

10. Гігієнічна оцінка матеріалів, до складу яких входять гуми : Инстр. 4259-87. – [Действует с 1988-01-01]. – М., 1987. – 14 с.

11. Ольшанская О.М. Критерии оценки экологической чистоты льняной текстильной продукции / О.М. Ольшанская, В.В.Котин, А.В. Артёмов // Журнал Российского химического общества им. Д.И. Менделеева. – 2002 . – Т. XLVI. – № 2. – С. 66–76.

12. Беспамятнов Г.П. Предельно допустимые концентрации химических веществ в окружающей бреде : справочник / Г.П. Беспамятнов, Ю.А. Кротов. – Л. : Химия, 1985. – 528 с.

Рецензія/Peer review : 19.1.2014 р. Надрукована/Printed :7.2.2014 р.
Рецензент: д.т.н. Параска Г.Б.