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ULTRAVIOLET PROTECTION AND DAMPING ABILITY OF TRANS-PARENT POLYURETHANE MATRICES WITH THE COMPONENTS OF DIFFERENT CHEMICAL NATURE

This article is devoted to the study of the influence of the chemical nature of the components of polyurethane matrices (PU) on their optical and viscoelastic properties in order to obtain polymer materials that combine several different functional properties: high transparency, effective UV protection and high damping ability. PU matrices with different chemical structures of diisocyanate (aliphatic (hexamethylene diisocyanate) or aromatic (toluylene diisocyanate)) and oligodiol (oligoether (oligooxypropylene glycol) or oligoester (oligodiethylene glycol adipate)) were synthesized. PU matrices with different molecular weights of ester (800 and 1500) were synthesized too. It was established that all PU matrices have a fairly high (~90 %) transmission coefficient in the range of visible wavelengths and UV blocking. However, the range of UV absorption significantly depends on the PU components. Matrices based on aliphatic diisocyanate absorb UV up to 250–280 nm. The UV absorption of PU matrices based on aromatic diisocyanate, regardless of the nature of their oligoester component

and its molecular weight, undergoes a shift to the long-wavelength region – up to 300–400 nm, which is due to the presence of aromatic rings. For PUs with an aromatic component, the highest absorption in the UV region is observed for PUs based on oligoesters, which is explained by the greater absorption ability of ester groups relative to ether ones. It was found that PU matrix based on oligoester has better elastic properties, but the PU matrix based on oligoether is characterized by a wider temperature range of effective damping. The replacement of aliphatic diisocyanate with an aromatic one shifts the area of effective damping of PU material towards positive temperatures. Therefore, by changing the nature of PU components, as well as the molecular weight of the PU oligoester component, it is possible to obtain transparent materials with a wide temperature range of effective damping in combination with high protection against UV radiation.

Key words: *polyurethane, ultraviolet protection, damping ability, viscoelastic properties, transparency.*

Introduction

The development of modern technologies requires the creation of new polymeric materials that combine several different functional properties. In particular, the development of transparent polymer coatings with effective UV protection and high damping ability is relevant to expand the scope of their application and to increase commercial attractiveness.

The basis for such materials can be polyurethanes (PU) – an important class of thermoplastics and thermosetting polymers [1], the properties of which can be adapted to different needs by the interaction of various polyols and polyisocyanates [2, 3].

It is known that, due to the peculiarities of chemical structure, PUs have effective damping properties, so they are widely used as coatings in mechanical structures to reduce or completely dampen harmful vibrations [3–6]. Another negative factor that can dramatically accelerate the aging of many materials and cause harmful effects on humans is ultraviolet (UV) radiation as part of sunlight, and this situation is exacerbated over the years due to ozone depletion [7, 8]. Also, in addition to solar, there are many artificial sources of UV radiation, which are widely used in some professional, medical and recreational areas – incandescent lamps, fluorescent lamps, and electric welding arcs.

Therefore, the creation of materials with effective blocking of UV radiation and transparent in the wavelength range of visible light [9, 10] is an interesting field of scientific research today. Based on PU matrices it is possible to obtain polymer nanocomposites with effective UV radiation protection, which are recommended for use as UV-protective coatings in various fields [11–14]. Widespread use of PU is due to the ease of their synthesis, which can be performed in "mild" conditions, and the possibility of varying components of different nature (polyols and polyisocyanates), which allows to obtain PU with different properties.

Due to the fact that UV radiation is conditionally classified into 3 bands in the order of increasing energy: UV-A (320–400 nm), UV-B (280–320 nm), and UV-C (100–280 nm) [15], and the range of UV absorption depends on the absorption capacity of structural units of the substance, it is assumed that you can adjust the selectivity of UV absorption of PU matrices by varying the chemical nature of PU components.

The aim of this work is to establish the influence of the chemical nature of oligodiol component (oligoether or oligoester) and its molecular weight, and the nature of isocyanate component (aliphatic or aromatic) on the ability of PU matrices to UV protection and damping.

Experimental section

Materials

Oligodiethylene glycol adipates with MM 800 (ODA-800) and MM 1500 (ODA-1500) (commercial firms), oligooxypropylene glycol with MM 1000 (OPG-1000) (Aldrich) were dried at temperature of 75 °C and pressure of 1–4 mm Hg for 6 hours.

Hexamethylene diisocyanate (HMDI) (Merck), 2,4-toluylene diisocyanate (TDI) (Merck) were used without further purification.

Trimethylolpropane (TMP) (Merck) was dried at temperature of 50 °C and pressure of 2–4 mm Hg for 60 hours.

Synthesis of cross-linked polyurethanes

Cross-linked polyurethanes (PU) were prepared through the prepolymer step. The prepolymers were prepared by reacting diisocyanates (HMDI or TDI) with various oligodiols (ODA-800, ODA-1500, and OPG-1000) at 70 °C. NCO/OH ratio of

Table 1. **The composition of PU matrices**

Sample	PU composition
PU-1	ODA-1500, HMDI, TMP
PU-2	ODA-800, HMDI, TMP
PU-3	ODA-1500, TDI, TMP
PU-4	ODA-800, TDI, TMP
PU-5	OPG-1000, TDI, TMP

2 : 1 was employed. The reaction mixtures were stirred intensively until the theoretical value of the NCO-groups was reached, which was determined by back-titration by the Stagg method [16]. In the second stage, an equimolar amount of crosslinker (TMP) was added to the prepolymer at 70 °C. The reaction mixture was stirred intensively and then evacuated to remove air bubbles. The films were cured on glass substrates at 60 °C until complete conversion of NCO-groups (7–8 hours). The composition of the studied PU is shown in table 1.

Methods

The optical properties of the synthesized polyurethanes were investigated by spectrophotometry. Transmission spectra were recorded on a Shimadzu UV–2401PC spectrophotometer with ISR-240A device in the frequency range from 800 to 200 nm with a slit thickness of 5 nm. Hand-pressed $BaSO_4$ was used as the white standard.

The transparency of PU films was qualitatively evaluated by images in photographs obtained with a Sony Alpha A7 III camera using a Tamron AF 28-75mm f/2.8 Di III RXD lens.

The viscoelastic properties of PU matrices were investigated by dynamic mechanical analysis (DMA) using the DMA Q800 (TA Instruments, USA) in the Cantilever mode at a frequency of 10

Table 2. **Structural formulas of the PU matrices**

Fig. 1. Transmission spectra for PU-1 (*1*), PU-2 (*2*), PU-3 (*3*), PU-4 (*4*) and PU-5 (*5*)

Hz. Viscoelastic characteristics, i.e. mechanical loss factor (tan δ) and storage modulus (*E'*) of film samples (20.0×5.0×1.5 mm) were determined in the temperature range from –70 to 120 °C with the heating rate of 3 °/min. The glass transition temperature (T_g) was assumed as the position of the maximum of the loss factor (tan δ$_{max}$).

Results and discussion

The synthesized PUs differ in the nature of the flexible oligodiol block (oligoether – OPG and oligoester – ODA), rigid diisocyanate component (aliphatic HMDI and aromatic TDI), and molecular weight of the flexible block (800 and 1500 for ODA, 1000 for OPG) (table 2).

The electronic transmission spectra in the UV and visible light range for the PUs are shown in Fig. 1.

All samples of PU matrices show both a fairly high (~ 90 %) transmittance in the range of visible wavelengths, and blocking UV radiation in a certain range. Fig. 1 shows that, the absorption region in the UV range differs significantly, depending on the components of the PU. It is expedient to investigate this difference. Thus, PU matrices based on aliphatic diisocyanate absorb UV radiation up to 250 nm (PU-1) and 280 nm (PU-2).

For PU matrices based on aromatic diisocyanate, regardless of the nature of their oligoester component and its molecular weight, there is a bathochromic shift of the transmission spectra, which is due to the presence of benzene rings in

their composition, and the UV absorption of these matrices is up to 300 nm (PU-5), 350 nm (PU-3) and 400 nm (PU-4). It is known [17] that in the electronic spectrum of benzene there are three absorption bands with positions of maxima at wavelengths: 184 nm; 204 nm and 255 nm. As the number of condensed cycles increases, as well as in the presence of hydroxyl and carbonyl groups, the absorption bands shift to the long-wavelength region and become more intensive.

However, for PU with an aromatic component (PU-3, PU-4, and PU-5) the greatest absorption in the UV region is observed for PU based on oligoesters (PU-3, PU-4) which is due to the presence of ester groups in their composition [18]. Similar behavior in the absorption spectra of PU based on ethers and esters was observed in work [19].

To explain the different absorption capacity of PUs, it is necessary to take into account the number of all functional groups that affect the absorption (ether, ester, urethane, benzene rings). In our case, increasing the molecular weight of the flexible component reduces the part of urethane groups in PU-1 and PU-3 compared to PU-2 and PU-4, respectively. The part of benzene rings increases in PU-4 relative to PU-3 because the oligodiol component in PU-4 is twice less than in PU-3. As a result, when analyzing the influence of the molecular weight of the oligoester block on the absorption of PU in the UV range (PU-1 – PU-2 and PU-3 – PU-4) (Fig. 1), an increase in PU absorption is observed with a decrease in the molecular weight of the oligoester block (PU-2 and PU-4), although the number of ester groups in this PUs is less than in PU-1 and PU-3.

The relationship between the absorption capacity of different functional groups and their polarity was shown in work [17]. We can assume that in our case, more polar urethane groups and their number, as well as a larger part of aromatic rings, will contribute to greater absorption of UV radiation. The predominant role belongs to the latter, and in the studied series of PU the greatest protection against UV rays will provide PU-4.

The high transparency of all the obtained PU matrices is evidenced by the photos of the films placed on the same background (Fig. 2). Due to the absorption in the range up to 400 nm (violet-blue region), the film PU-4 according to the theory of chromaticity [20] acquires a yellowish hue, but
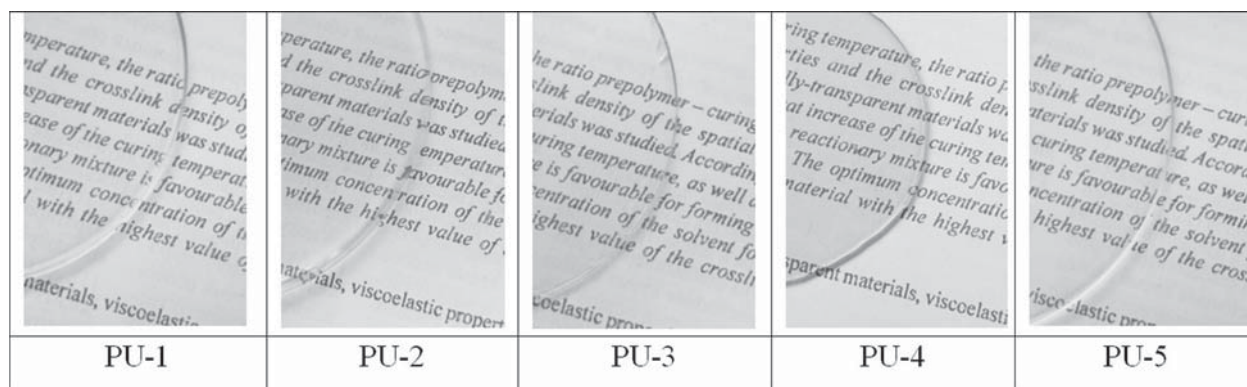
| PU-1 | PU-2 | PU-3 | PU-4 | PU-5 |

Fig. 2. Images of the PU films

this does not significantly affect the transparency, as in the range of 400 nm PU-4 has quite high (up to 90 %) transmittance (Fig. 2). Blocking high-energy violet and blue radiation in the visible range from fluorescent and LED lamps, smartphone screens, etc. and transparency keeping is important for some applications, such as protective screens [21, 22].

It is known that due to the viscoelastic nature, polymers have a unique ability to absorb mechanical energy and convert it into heat under cyclic loading [23, 24]. The damping efficiency of the material is estimated as the energy dissipated during mechanical vibration and is determined by the parameter of mechanical losses. Polymers have the maximum values of tan δ in the region of the relaxation transition, i.e. near the glass transition temperature.

As a rule, for practical application, the damping material must have not only high values of tan δ, but also a wider temperature range in which it has effective vibration-absorbing properties. Usually, it is considered that polymeric materials with mechanical losses at the level of 0.3 (tan $\delta \geq$ 0.3) are effective dampers [25–27]. An important characteristic of the polymer material is also its elastic properties, which are determined by the level of intermolecular and chemical interactions in the polymer system and are denoted by the quantitative value of E'.

Therefore, the damping efficiency of the synthesized PU matrices was evaluated from studies of their viscoelastic characteristics. Based on the temperature dependences of mechanical losses and the parameters of the relaxation maximum, glass temperature, maximum intensity

of mechanical losses (tanδ_{max}) and the range of effective damping temperatures (ΔT), in which tan $\delta \geq$ 0.3, were determined for the studied materials. Based on the comparative analysis of the dependences tan $\delta(T)$ and $E'(T)$, the influence of both the nature of the diisocyanate and oligoether components of PU and the value of oligoether MM on the damping efficiency of the material was studied.

Fig. 3 shows that for PU matrices with oligoester component (ODA) the temperature region of the relaxation transition and its intensity significantly depend on both the molecular weight of ODA and the chemical nature of diisocyanate. It is known that the molecular weight of the oligodiol component is an important regulator of intermolecular interactions in PU. Decreasing the
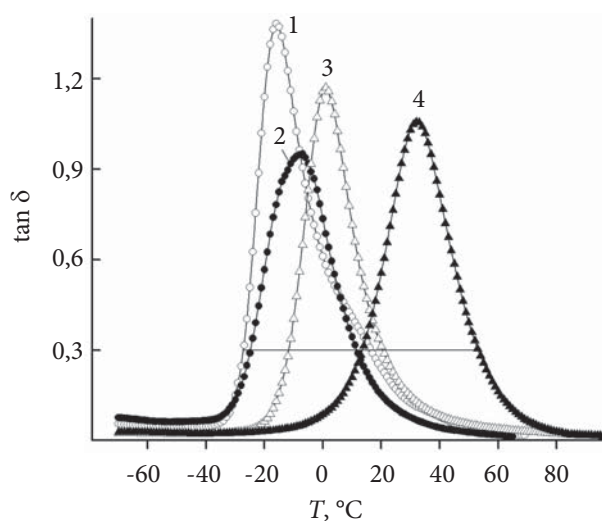

Fig. 3. Temperature dependences of tan δ for PU-1 (*1*), PU-2 (*2*), PU-3 (*3*) and PU-4 (*4*)

Table 3. **Viscoelastic characteristics of the PU matrices**

PU	Oligodiol	Diisocyanate	T_g, °C	$\tan\delta_{max}$	$E'_{20°C}$, MPa	M_c	Range of effective damping from T_1 to T_2 (ΔT) at $\tan\delta \geq 0,3$
PU-1	ODA-1500	HMDI	−16	1,365	1,63	4500	from −27 to 17 (44)
PU-2	ODA-800	HMDI	−8	0,953	4,46	2030	from −24 to 12 (36)
PU-3	ODA-1500	TDI	1	1,167	7,02	1650	from −11 to 21 (32)
PU-4	ODA-800	TDI	33	1,052	500,3	1270	from 12 to 54 (42)
PU-5	OPG -1000	TDI	17	1,032	30,5	2800	from −3 to 53 (56)

molecular weight of oligodiol leads to an increase in the concentration of urethane groups, and at the same time to an increase in the number of strong physical bonds [28].

For the studied PUs, there is also a general tendency of increasing T_g, decreasing $\tan\delta_{max}$ and increasing E' with decreasing MM of oligoester regardless of the nature of the diisocyanate component (table 3). This indicates limited segmental mobility and increased intermolecular interaction in the system with increasing urethane group concentration. The increase in T_g also indicates an increase in the compatibility between the flexible and hard phases in the PU with a decrease in the molecular weight of the oligodiol component [29].

However, the level of change in T_g, $\tan\delta_{max}$ and E' is not the same for PU matrices with chemically different diisocyanate components. Thus, for PU matrices based on aliphatic diisocyanate (HMDI) reduction of MM of ODA from 1500 to 800 leads to an increase in T_g by 8 degrees (PU-1 and PU-2), and for PU matrices based on aromatic diisocyanate (TDI) a similar decrease of MM of the oligoester component leads to an increase in T_g by 32 degrees (PU-3 and PU-4).

The same tendency of the influence of the chemical nature of the isocyanate component on the value of T_g was observed by the authors [29, 30]. They explained this by the fact that the degree of compatibility of flexible and hard phases in PU based on aromatic diisocyanate is higher than for PU based on aliphatic diisocyanate. This conclusion is also confirmed by our studies when comparing the values of T_g for PU samples that have the same molecular weight of the oligoester, but differ in the chemical nature of the isocyanate component.

It is shown that the replacement of HMDI by TDI leads to an increase in the value of T_g for PU based on ODA-1500 (PU-1 and PU-3) and for PU based on ODA-800 (PU-2 and PU-4), but for PU samples based on oligoester with MM = 800, the difference in the values of T_g is almost twice as large as for PU samples based on oligoester with MM = 1500 (table 3). Thus, an increase in the compatibility between the flexible and hard phases in the PU can be achieved both by reducing the MM of oligoester and by replacing the aliphatic diisocyanate with aromatic diisocyanate. The synergistic effect of these factors is observed for the sample PU-4 based on oligoester with the lowest value of MM (ODA-800) and aromatic diisocyanate (TDI), which has the highest value of T_g (table 3).

Thus, it is shown that the chemical nature of isocyanate and MM of the oligoester component determine the phase structure of the PU matrix and its viscoelastic properties, which obviously should affect their damping capacity. The temperature dependences of $\tan\delta$ demonstrate that all PU matrices have a high and wide relaxation transition (Fig. 3), i.e. they are effective damping materials. But at the same time, the temperature range of effective damping depends on the MM oligoester component of PU and the chemical nature of the isocyanate.

It was found that PU matrices based on ODA and HMDI (PU-1 and PU-2) have effective damping in the temperature range below $T = 20$ °C, i.e. below the temperature of normal conditions of material use (table 3). Decreasing the MM of ODA leads to a decrease in the value of ΔT, while the limits of this temperature range are narrowed, but not shifted. It is shown that the replacement of aliphatic diisocyanate with aromatic diisocyanate shifts the range of effective damping towards positive temperatures and the reduction of oligoester MM for PU based on TDI (PU-3 and PU-4) also significantly expands the
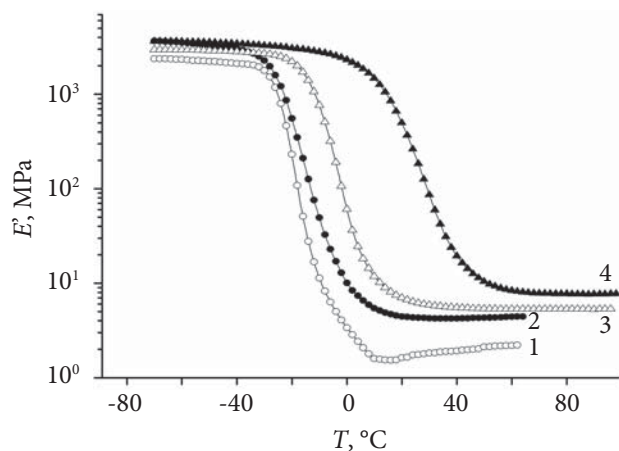
Fig. 4. Temperature dependences of *E'* for PU-1 (*1*), PU-2 (*2*), PU-3 (*3*) and PU-4 (*4*)

Fig. 5. Temperature dependences of tan δ for PU-4 (*1*) and PU-5 (*2*)

range of effective damping, (Δ*T* increases by 10 °C). The effective damping range for PU-4 extends from 12 to 54 °C, which allows the use of such PU matrix as an effective damping material under normal operating conditions.

The dependences *E'*(*T*) also indicate that the temperature region of the relaxation transition of the studied PU matrices is determined by the chemical nature of isocyanate and by MM of oligoester (Fig. 4). Analysis of *E'* values at *T* = 20 °C shows that the reduction of MM of ODA from 1500 to 800 leads to an increase in the modulus of elasticity for PU matrices based on HMDI by almost 3 times (PU-1 and PU-2), and for matrices based on TDI (PU-3 and PU-4) the value of *E'* increases more than 70 times (table 3).

The increase in the values of *E'* in the polymer system with increasing concentration of urethane groups with a decrease in the MM of the oligoester is primarily associated with an increase of the intermolecular interaction. The corresponding enhancement occurs due to the formation of hydrogen bonds both between urethane groups and between N–H groups of the urethane group and C=O groups of the oligoester block. The additional presence of aromatic groups in TDI contributes to an even greater growth of a number of physical bonds due to the possibility of π-π interaction between benzene rings of TDI in the matrix PU-4 (compare PU-2 with PU-4). This significantly improves its elastic properties.

The cross-linking agent TMP was used in the synthesis of PU, and therefore all the studied
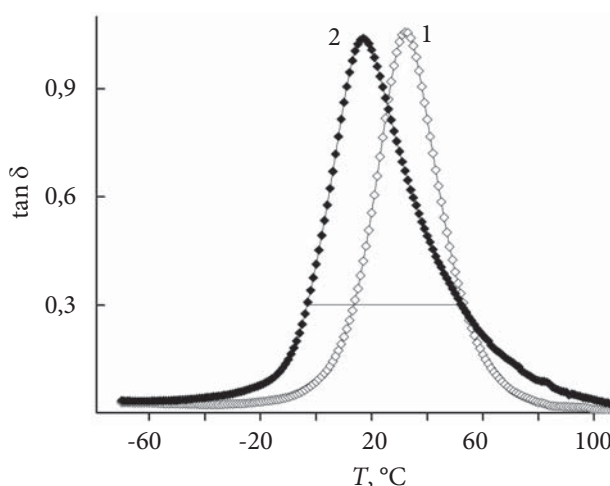
matrices have cross-linked topology. The value of the effective molecular weight of the chains between the crosslinks (M_c) was calculated according to the equation of elasticity:

$$M_c = 3\rho R T / E_e$$

where ρ is the density of the polymer, *R* is the universal gas constant, *T* is the value of the absolute temperature, E_e is the value of the storage modulus (*E'*) on the elasticity plateau, and it is determined from the temperature dependences of *E'*.

The calculated values of M_c are given in table 3. They indicate a significant effect of the molecular weight of the oligoester and the chemical nature of the diisocyanate on the density of crosslinks in
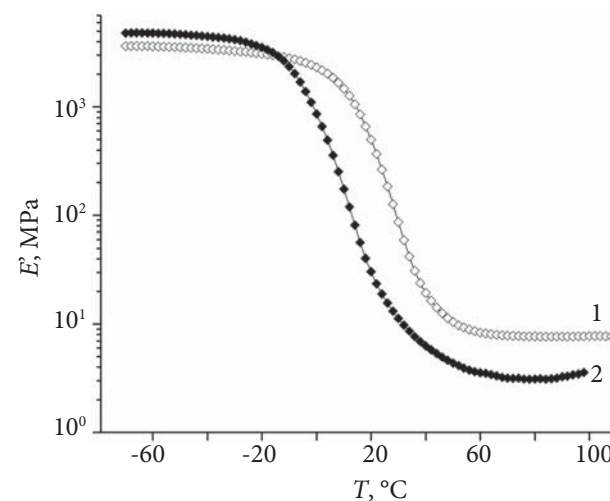
Fig. 6. Temperature dependences of *E'* for PU-4 (*1*) and PU-5 (*2*)

the PU matrix. The decrease in the values of M_c indicates an increase in the density of crosslinks for PU when a decrease in MM of ODA (PU-1 and PU-2, PU-3 and PU-4), and when replacing HMDI with TDI (PU-1 and PU-3, PU-2 and PU-4). The highest density of the crosslinked topology in the matrix PU-4 based on ODA with MM = 800 and TDI (this matrix has the lowest value of M_c) may be associated not only with a decrease in MM of oligoester, but also with aromatic nature of diisocyanate.

The replacement of the oligoester with the oligoether in PU also affects the viscoelastic properties and damping capacity of the material. Fig. 5–6 show the temperature dependences of tanδ and *E'* for PU matrices based on ODA (PU-4) and OPG (PU-5) with similar molecular weights and the same aromatic nature of the diisocyanate component (TDI).

It was found that the matrix PU-5 has a lower T_g and significantly lower value of *E'* compared to the corresponding values for PU-4 (table 2), due to the more flexible nature of the oligodiol component and weaker physical bonds between the polymer chains. For PU matrix based on OPG there is a decrease in the values E_e (Fig. 6) and, accordingly, the values of M_c for PU-5 are greater than for the matrix PU-4 based on ODA. This indicates that the polymer network of matrix based on oligoester (PU-4) is more crosslinked than one based on oligoether (PU-5).

However, the analysis of temperature dependences of tan δ (Fig. 5) shows that among all the studied matrices PU-5 has the widest temperature range of effective damping ($\Delta T = 56$), which extends from –3 to 53 °C (table 2). Therefore, the use of oligoether as the oligodiol component in the synthesis of PU, increases the flexibility of the material and significantly extends the effective damping in the range of temperatures at which, usually, the damping material is operated most often.

Conclusions

Therefore, transparent PU matrices with effective protection against UV rays and high damping ability were obtained. It is shown that the ranges of absorption in the UV range and effective damping depend significantly on the chemical nature of the constituent components of PU. Thus, PU matrices based on aliphatic diisocyanate absorb UV up to 250–280 nm, while UV absorption by PU matrices based on aromatic diisocyanate undergoes a bathochromic shift to 300–400 nm due to the presence of benzene rings. At the same time, the replacement of an aliphatic diisocyanate with an aromatic one leads to a shift in the range of effective damping of the PU material towards positive temperatures. It was established that the highest absorption in the UV range is observed for PU based on oligoesters, which is due to the greater absorption ability of ester groups relative to ether ones. A decrease in the molecular weight of the oligoester block contributes to greater absorption of UV rays. It was found that PU materials based on oligoester have better elastic properties as well, but PU matrix based on oligoether is characterized by a wider temperature range of effective damping. Thus, varying the chemical nature of PU constituents allows one to obtain materials with selective protection against UV radiation and an adjustable range of effective damping.

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УЛЬТРАФІОЛЕТОВИЙ ЗАХИСТ І ДЕМПФЕРНІ ВЛАСТИВОСТІ ПРОЗОРИХ ПОЛІУРЕТАНОВИХ МАТРИЦЬ ЗІ СКЛАДОВИМИ РІЗНОЇ ХІМІЧНОЇ ПРИРОДИ

Стаття присвячена дослідженню впливу хімічної природи складових поліуретанових матриць (ПУ) на їхні оптичні та в'язкопружні властивості з метою отримання полімерних матеріалів, що поєднують у собі кілька різних функціональних властивостей: високу прозорість, ефективний УФ-захист і високу демпферну здатність. Синтезовано ПУ матриці з різною хімічною будовою діізоціанатного (аліфатичного (гексаметилендіізоціанат) або ароматичного (толуїлендіізоціанат)) та олігоефірного (етерного (олігооксипропіленгліколь) або естерного (олігодіетиленглікольадипінат)) блоку, а також з різною молекулярною масою естеру (800 і 1500). Встановлено, що всі ПУ матриці мають досить високий (~90 %) коефіцієнт пропускання в діапазоні видимих довжин хвиль і блокування УФ. Проте, діапазон поглинання УФ істотно залежить від складових ПУ. Матриці на основі аліфатичного діізоціанату поглинають УФ до 250–280 нм. УФ-поглинання ПУ матрицями на основі ароматичного діізоціанату, незалежно від природи їхньої олігоефірної складової та її молекулярної маси, зазнає зсуву в довгохвильову область – до 300–400 нм, що зумовлено наявністю ароматичних кілець. Для ПУ з ароматичною складовою найбільше поглинання в УФ-області спостерігається для ПУ на основі олігоестерів, що пояснюється більшою поглинальною здатністю естерних груп відносно етерних. Виявлено, що ПУ матеріали на основі олігоестерів мають кращі пружні властивості, проте ПУ матриця на основі олігоетеру характеризується ширшим температурним інтервалом ефективного демпфування. Заміна аліфатичного діізоціанату на ароматичний зсуває область ефективного демпфування ПУ матеріалу в бік плюсових температур. Отже, змінюючи природу складових ПУ, а також молекулярну масу олігоефірної складової ПУ, можна отримувати прозорі матеріали з широким діапазоном температур ефективного демпфування у поєднанні з високим захистом від дії УФ випромінювання.

Ключові слова: поліуретани, ультрафіолетовий захист, демпферна здатність, в'язкопружні властивості, прозорість.