ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 6, pp. 1114−1116. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © V.V. Tereshatov, V.Yu. Senichev, S.F. Krasnosel'skikh, M.A. Makarova, I.S. Lamzina, 2008, published in Khimicheskaya Promyshlennost', 2008, Vol. 85, No. 8, pp. 392−394.

TECHNOLOGY OF ORGANIC AND INORGANIC CHEMISTRY

High-Dense Polymeric Compositions Based on the Thermoplastic Polyuretanes

V. V. Tereshatov[a], V. Yu. Senichev[a], S. F. Krasnosel'skikh[a], M. A. Makarova[a], and I. S. Lamzina[b]

[a]*Institute of Technical Chemistry, Ural Branch of Russian Academy of Sciences, Perm, Russia*
e-mail: tvvz@mail.ru
[b]*Central Scientific and Research Institute of Chemistry and Mechanics, Moscow, Russia*

Received September 13, 2008

Abstract—-The results of investigating the properties of high-dense pollution-free hybrid composites on the basis of the new type of polyurethane thermoplastics with the low-melting diurethane plasticizer are represented. The material is shown appropriate for the processing at low temperature. Strengthening of such materials is shown caused by the crystallization of the low-melting plasticizer.

DOI: 10.1134/S1070427209060366

INTRODUCTION

A number of the basic applications of lead is connected with its high gravimetric density (ammunition, the elements of radiation shielding, loads for the balancing, etc). Only in Russia hundreds ton per year of this highly toxic metal are expended to these purposes [1].

The task of replacing the toxic dense metal lead by the pollution-free composites can be solved by creation of the highly filled materials, which contain microdisperse tungsten, whose density 1.7 times higher than density of lead.

As a bonding agent for the highly filled composites can be used thermoplastic polyurethanes (TPU) with the low-melting plasticizers diuretanes, the products of the reaction of diisocyanates with alcohols. Diurethanes are crystalline substances with melting temperature from 46 to 50°C. They are thermodynamically compatible with polyuretanes and can be used as the plasticizers [2, 3]. The purpose of the work was a study of the properties of the dense thermoplastic composites with the low-melting plasticizer, filled with microdisperse tungsten.

EXPERIMENTAL

As the object of studies are used the samples of thermoplastic polyurethane (TPU), synthesized on the basis of oligotetramethyleneoxidediol with molecular weight 1000, diphenylmethane diisocyanate (MDI) and butanediol by a two-step procedure. During the first step (80°C, 4 h) was carried out the reaction of oligotetramethyleneoxidediol with MDI at the diizocyanate–diol mole ratio 2.5 : 1. In the second step (after the analysis of the obtained pseudo-prepolymer for the content of free NCO groups) into the composition was introduced the melted diurethane plasticizer (30% of the mass of the unfilled composition) and then added butanediol-1,4. In the experiences the calculated ratio of NCO and OH groups was 0.95 (for TPU-1) and 0.8 (for TPU-2). As the plasticizer into the composition was introduced in the melted form dibutyl(4-methylbenzyl-1,3-diyl)biscarbamate (BT), obtained by the reaction of 2,4-toluilenediizocyanate with butanol [3, 4]. As the fillers was used powdered tungsten of the fractions 0.8, 6, and 80 μm. It was introduced into the composition also at the second step of obtaining TPU.

The samples were solidified at 80 °C during 2 days. Mechanical characteristics were determined according to GOST 270-75. Calorimetric study of the solidified samples was carried out by the DSK method on a Mettler-Toledo 822 instrument with the rate of scanning 3°C/min. The thermomechanical analysis was carried out on the installation UIP-70.

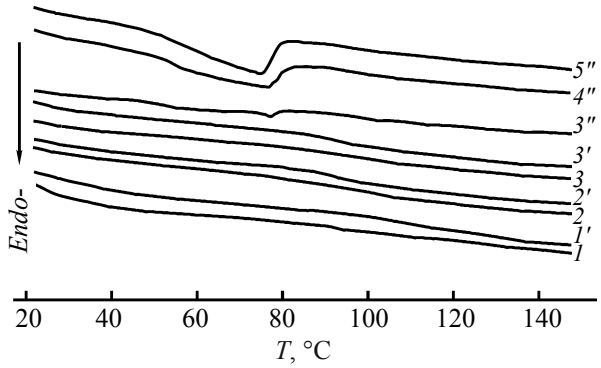

Fig. 1. DSK curves of the samples of TPU-1/0 after storage under different temperature conditions: (*1, 2, 3*) at 60°C, (*1′, 2′, 3′*) at 75°C. The storage time after solidification 1 day (*1, 1′*), 14 days (*2, 2′*) and 30 days (*3, 3′*). The samples *3″*, *4″*, *5″* were maintained at 25°C for 30, 60, and 90 days respectively.

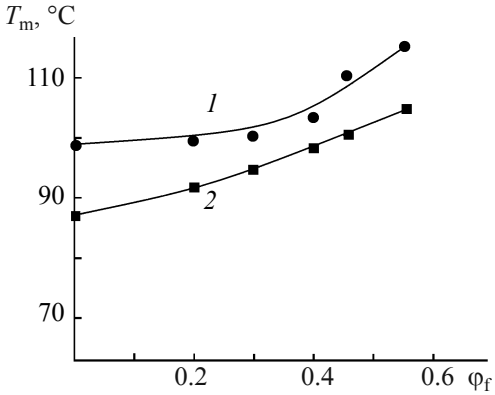

Fig. 2. The dependence of the softening temperature (T_m) of the samples of composites based on TPU-2 on the volume fraction of metallic filler (φ_f): (*1*) in the regime of dilatometry, (*2*) in the regime of penetration under the pressure 0.12 MPa.

RESULTS AND DISCUSSION

The obtained experimental data show that the ultimate strain of the elastomer is regularly reduced with an increase in the content of filler. However, even at the mass concentration of filler 95.6% the value of ε_c is higher than 30%, which is completely acceptable for producing elastic screens for the radiation protection of units and instruments (see the table).

Under the storage conditions at 25°C the strength σ_c of both filled and the unfilled materials grows without considerable reducing in their critical tensile strain, which contributes to an improvement in the working capacity of the developed composites. The causes for such behavior can be elucidated from the data obtained by the DSK method.

The temperature of the crystallization of plasticizer BT is 76–78°C. However, in the TPU samples at elevated temperatures close to the melting point of BT at 60°C and 72°C the crystallization of plasticizer practically is not manifested (curves *1,1′–3,3′* in Fig. 1).

But storage at 25°C leads to the crystallization of

Physicomechanical characteristics of composites on the basis of TPU filled with microdisperse tungsten

Base	Sample	Filler content, wt% (volume fraction)	ρ, kg/m^3	σ_c, MPa, (ε_c,%) after storage at 25 °C	
				2 days	90 days
TPU-1	TPU-1/0	0 (0)	1150	2.8 (162)	5.5 (163)
	TPU-1/1	87.8 (30)	6600	3.6 (92)	5.1 (90)
	TPU-1/2	91.8 (40)	8420	4.6 (46)	8.5 (42)
	TPU-1/3	93.5 (43.2)	9510	3.8 (42)	6.4 (43)
	TPU-1/4	95.6 (54.2)	11000	5.3(36)	8.2 (32)
TPU-2	TPU-2/0	0(0)	1150	6.0 (602)	7.6(570)
	TPU-2/1	87.8 (30)	6600	5.5 (120)	7.5 (113)
	TPU-2/2	91.8 (40)	8420	6.2(50)	8.4 (47)
	TPU-2/3	93.5 (43.2)	9510	6.5 (45)	7.9 (41)
	TPU-2/4	95.6 (54.2)	11000	7.2 (33)	8.2 (32)

plasticizer after only 60 days, that is evident from the wide peak of melting in the DSK curves in the range of 50–75°C (curve *4″* in Fig. 1). The transfer of the plasticizer into the crystalline state leads to strengthening of the material.

The influence of degree of filling on the softening temperature T_m of polyurethane composites is established by the method of thermomechanical analysis (Fig. 2). It is evident from the data obtained that an increase in the volume fraction of filler insignificantly increases the composite softening temperature. Its absolute value does not exceed 110°C at the filler volume fraction 0.56, that provides the composite density (11000 kg/m^3) at the density level of lead.

The lower limit of the range of the operation of polyurethane composites is defined by the glass transition temperature of the bonding agent. As showed working up of the corresponding DSK curves, the glass transition temperature of the plasticized polyurethane bonding agent falls to the range of 25–30°C regardless of the content of metallic filler.

Thus, it is for the first time shown that the use of low melting diurethane in the composition of thermoplastic polyurethane composite provides the possibility of obtaining a very dense pollution-free material appropriate for processing at low temperatures. It is established that the crystallization of diurethane plasticizer in the elastic composite leads to an increase in the strength of material without worsening in its deformation properties. Because of the high density of the new type hybrid functional material it is completely acceptable for the radiation protection of different units, instruments and population.

ACKNOWLEDGMENT

This work was financially supported by Russian foundation for Basic research (project no. 07–03–00240a).

THE ARBITRARY SYMBOLS

ε_c is ultimate strain at the tensile-strength of sample,
σ_c is tensile strength of sample,
T_m is temperature of softening,
φ_f is volume fraction of filler,
ρ is gravimetric density.

REFERENCES

1. Snakin, V.V., *Meditsina truda i promyshlennaya ekologiya* (Labour Medicine and Industrial Ecology), 1999, no. 5, pp. 21–27.
2. Tereshatov, V.V., Senichev, V.Yu., Krasnosel'skikh, S.F., Fedoseev, M.S., Makarova, M.A., and Volkova, E.R., Abstracts of Papers, X Vserossiiskaia nauchno-tekhnicheskaya konferentsiya "Aerokosmicheskaya tekhnika i vysokie tekhnologii-2007" (10th All-Russian Sci. Tech. Conf. "Aerospace Technique and High Technologies-2007), pp. 270–272.
3. Tereshatov, V.V., Senichev, V.Yu., Krasnosel'skikh, S.F., Fedoseev, M.S., Yakushev, R.M., Valeev, N.S., and Volkova, E.R., *XI Vserossiiskaia nauchno-tekhnicheskaya konferentsiya "Aerokosmicheskaya tekhnika i vysokie tekhnologii-2007"* (11th All-Russian Sci. Tech. Conf. "Aerospace Technique and High Technologies-2007), pp. 373–375.
4. Fu-Sen, Yen and Jin-Long, Hong, *Macromolecules*, 1997, vol. 30. pp. 7927–7938.