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Effect of polyols on the physico-mechanical properties of some polyurethanes

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Polyester and polyether polyols have been used to manufacture high quality products since the earliest days of the polyurethane era. They are cost effective raw materials which impart excellent abrasion and solvent resistance, oxidative stability, tear and tensile strength to the polyurethane. In this report, a series of three polyurethane (PUs) based on a mixture of two polyols (polyethyleneadipate diol-PEA 2000 and polytetrahydrofuran PTHF 1400) was prepared. Diphenylmethane diisocyanate (MDI) was utilized in the preparation of PUs. Ethylene glycol (EG) and Glycerin (Gly) were used as chain extenders. The physico-mechanical properties (hardness, stress-strain, resilience, and abrasion resistance) of this PUs were measured according to standard methods. Thermal analysis (TGA and DSC) were used for characterization. The structures were confirmed by infra-red analysis (IR).

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1. Introduction

Polyurethanes form a versatile class of polymers, which are used in a broad range of applications like elastomers, foams, coatings, fibers and biomedical materials. The group of polyurethanes comprises all polymers that contain urethane, urea or other isocyanate derived groups. The generally used reactants for segmented polyurethanes are a diisocyanate, a polyol and an extender. Segmented polyurethanes can be considered as multiblock-copolymers, consisting of a hard and a soft block (segment). The hard segment originates from the diisocyanate and chain extender, whereas the soft segment usually is the polyol. Polyurethanes (PUs) have a unique property of shape memory. This polymers basically consists of two phases, a frozen phase and a reversible phase [1-5]. Thermally reversible phase maintains a transient shape while fixed structure allows the recovery of the original shape. Shape memory property is governed by glass transition and melting temperature of polymer segments [6].

Polyurethanes are formed by linear polymeric chains of segmented structure. They are prepared by the addition reaction of bifunctional isocyanates, chain extenders and long chain polyols. Most of conventional PUs are based either on polyester or polyether polyols, 4, 4-diphenylmethane diisocyanate (MDI) as an isocyanate component and 1, 4-butanediol (BD) as a chain extender [7]. Development of soft grades of PUs (having hardness about 70-85 Shore A) has been reported among the latest trends that are taking place in the PU market. The main interest of researchers is focused on the polyol components saturated [8] and unsaturated [9]. Polyurethanes based on polybutadiene polyols could fall into this category. Moreover, they are known for excellent hydrophobicity, hydrolytic and chemical resistance, electrical insulation properties and low-temperature elasticity [10,11]. However, most of the commercially available large-scale hydroxyl terminated polybutadienes are manufactured by a free radical polymerization technology. This technology yields polyols with functionality exceeding the value 2.0, that are not applicable in PUs systems [6].

2. Experimental

2.1. Materials

- Polyethylene adipate diol (PEA), polyester polyol, Mw 2000, C_{OH} 56,1 mgKOH/g, mp 50-55 ^{o}C, d 1.175 g/cm^3;
- Polytetrahydrofurane (PTHF), polyether polyol, Mw 1400, C_{OH} 83 mgKOH/g, mp 33-36 ^{o}C, bp >110 ^{o}C, d 0.973;
- Ethylene glycol (EG), Mw 62,07, mp -13 ^{o}C, bp 196-198 ^{o}C, d 1,113 g/cm^3, n_d^{20} 1,4310;
- Glycerin (Gly), Mw 92,9, bp 182 ^{o}C, d 1,261 g/cm^3, n_d^{20} 1.4740;
- 4,4' diphenyl methane diisocyanate (MDI), Mw 250,14, mp 42-44 ^{o}C, bp 152-156 ^{o}C / 0,2-0,3mmHg;

PEA, PTHF and chain extenders were checked for the content of moisture and, if it would be necessary, dried under a vacuum until the content of water were below 0.03%.

2.2. Preparation of polyurethanes

All the polyurethane elastomers, utilized in this work, were synthesized by bulk polymerization. The synthesis of PUs was performed in a glass reactor (100 cm^3) at normal pressure, under nitrogen blanket and vigorous agitation.

The NCO/OH ratio of all formulations was 1.03-1.05. In the case of the prepolymer procedure, polyester and polyether diol mixture was reacted with a diisocyanate at 80 ^{o}C for 1 hour to yield a prepolymer that was mixed in the second step with a chain extender at 90 ^{o}C for 10 minutes. The resulting material was poured into a mold and left to cure at 100 ^{o}C for 20 hours, post-curing of the PU proceeded at laboratory temperature for 7 days. Under these conditions the addition of catalyst was not necessary.

The polyurethane sheets thus prepared were used for the determination of mechanical and physical properties.

2.3. Measurements

IR spectra were recorded on a Specord M80 Carl Zeiss Jena Spectrometer using KBr pellet technique.

Hardness was measured on Instron Shore Durometer using scale A.

Stress-strain measurements were performed on dumbbell-shaped samples cut from thin films at room temperature on a TIRA test 2161 apparatus, Maschinenbau GmbH Ravenstein Germany. Measurements were run at an extension rate of 10 mm/min, at 25 ^{o}C. All samples were measured three times and the averages were obtained.

Thermogravimetric analyses were performed on a DERIVATOGRAF Q-1500 D apparatus (Hungary) in a temperature range from 0-700 ^{o}C. The heating rate was 10^{o}C/min in air atmosphere and sample size was 50 mg.

Differential scanning calorimetry (DSC) determinations were performed by a Mettler TA instrument DSC 12E (T start: +20 ^{o}C, T end: +400 ^{o}C, heating rate: 10 ^{o}C/min, range: 50 μV).

3. Results and discussion

The following parameters of the formulation were tested in order to find out the structure-property relationship of the polyols (polyester and polyether) based PUs (Table 1):

- Type of polyols (polyesters and polyether);
- Composition of polyols mixture;

The polyol component of polyurethane elastomers has a significant effect on the hydrolytic stability and mechanical properties of these materials. In general, hydrolytic degradation of polyurethanes occurs when water reacts with the ester, urea**,** and amide or urethanes linkage of the polymer. The mechanical properties of the polyurethane elastomers based on polyesters are superior in opposition with polyurethane elastomers based on polyethers. These fact it is result of increase of the intermolecular force, realized by ester groups and the blocked of the tendency of the crystallization [12,13]. Thus, a polyurethane based on polyethylene glycol (PEG) have tensile stress at break of 40 MPa, based on PEA of 52 MPa, and based on poly(ethylene-azelat) the tensile stress at break it is of 29 MPa [14]. It is recognized that the hydrolytic stability of the polyurethanes based on polyethers are better than the polyurethane based on polyesters. The polyether component into mixture of polyols gives an increase of the hydrolytic stability of the polymer. The hydrolytic stability of these polyurethanes is outstanding and their mechanical properties (tensile strength, modulus, elongation) remain practically unchanged after four days of exposure to 85° C steam. Similarly, air aging for two days at 128° C affects only in a limited measure the mechanical properties.

Table 1. Polyurethanes composition and yours hardness.

Nr.	Designation	Ratio of Polyols/ Diisocyanate/ Chain extenders	Ratio of Polyester/ Polyether	Polyol Molecular weight		Chain extenders	Hardness Shore A
				PEA	PTHF		
1.	Sample 3	1:3:2	1:0.1	2000	1400	EG+Gly	70
2.	Sample 5	1:3:2	1:0.2	2000	1400	EG+Gly	73
3.	Sample 7	1:3:2	1:0.4	2000	1400	EG+Gly	66

The Fig. 1 showed the evolution of hardness function of polyester-polyether proportion. The formulation based on mixture of polyester and polyether in molar ratio presented in Table 1 lead polyurethanes with hardness between 66 and 73 ^{o}ShA. The hardness value of the polyurethane elastomers are close to 70 ^{o}ShA that may be classified as soft grade PUs. Their mechanical properties are comparable with those of good quality general purpose rubber materials. The polyurethane elastomers based on a mixture of polyester and polyether diol have similar properties. However, the uses of polyether diol in polyurethane compounds determine a good elongation and high resilience.

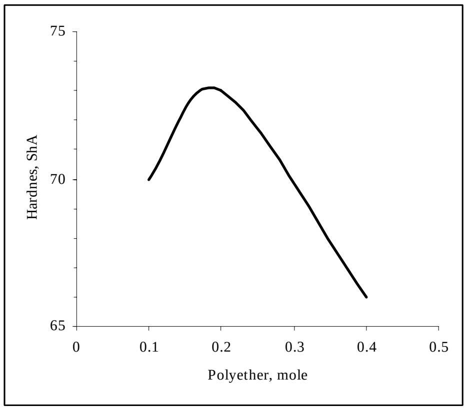

Fig. 1. Evolution of hardness function of polyester-polyether proportion.

3.1. IR Spectroscopy

IR spectra of the polymers were used to confirm the formation of PUs (Fig. 2). Formation of the polymer was confirmed by the disappearance of OH stretch (broad peak) at 3350 cm^{-1}. Appearance of new sharp peak for N-H stretch and for NHCOO (urethane) at 1540 cm^{-1} verifies the formation of polyurethane.

The CO stretching frequency at 1740 cm^{-1} for ester and respectively at 1070-1170 cm^{-1} for ether groups with the inclusion of polyol mixture in the polymer chain. Similarly the peak for CH_2 stretch appears to 2940 cm^{-1}.

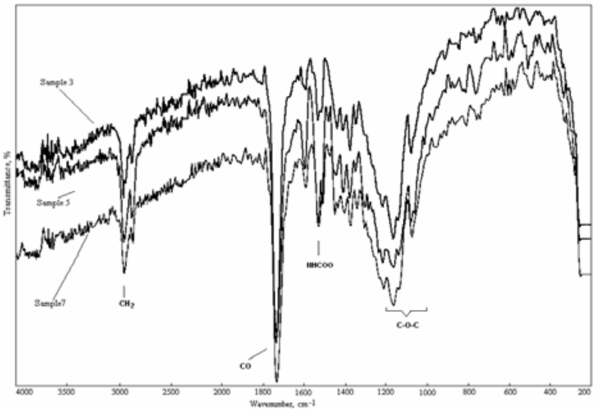

Fig. 2. IR spectra of polyurethane based on polyester and polyether mixture.

The MDI based system can also have more complete micro phase separation. The physical crosslinks are important in providing dimensional stability and stopping cold flow in the uncured materials. The effect of restricting segmental motion in a three dimensional network by chemical crosslink sites is similar to that of micro domain physical crosslinks excepting that the former is irreversible. The crystalline polyester domain acts as an additional physical crosslink site below the melting temperature.

3.2. Thermogravimetric analysis

Representative thermogravimetric (TGA and DTA) curves for polyurethanes based on polyester-polyether mixtures have been reproduced in Fig. 4. However details of degradation temperatures have been elaborated in Table 2. The thermal stability is a function of the components present in the formulation.

The open-air TGA was used to study some linear polyester urethanes attempting to outline the increase in the thermal stability brought by components from their structure. To achieve this, the same testing conditions were used for all the polyurethanes samples being analyzed. The onset (T_i) degradation temperature was defined as the initial temperature of degradation, corresponding to the intersection of the tangent drawn at the inflection point of the decomposition step with the horizontal zero-line of the TG curve [15, 16].

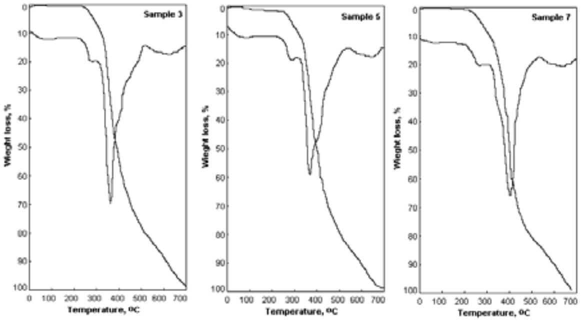

Fig. 4. TG and DTG curves of polyurethanes based on polyester-polyether mixture.

The thermal behavior of the PUs was assessed in terms of percent loss in weight at different temperatures. The results are reported in Table 2. It is evident that all the PUs based on polyester-polyether blends are stable up to 200 ^{o}C, lose weight rapidly around 350-450 ^{o}C, and decompose completely beyond 650 ^{o}C.

Table 2. Thermogravimetric data for PUs based on polyester-polyether blends.

Sample Code	Reaction order*	Percent weight loss at the temperature, ^{o}C									Energy of activation* kJ/mol
		250	300	350	400	450	500	550	600	650	
3	1.4	1.6	7.2	32.4	61.6	74	79.6	85.2	92	98.6	85.98
5	1.2	1.4	7.2	25.2	59.2	74	81.6	85.2	92.8	99	67.96
7	1.0	1.2	7.2	17.6	52.4	73.6	82	85	92	99	60.45

* Calculated through Reich-Levi method.

It can be observed from our study of PUs based on polyester-polyether mixture that this PUs have superior thermal stability. Increasing of the amount of polyether into PUs produces an increase of the thermal stability. All products decompose in two steps.

The general reaction orders for all PUs thermal decomposition are close to unity. This suggests that some diffusion processes might accompany the decomposition reactions. The dependence of the activation energy (Reich-Levi method) versus conversion degree is presented in Fig. 5.

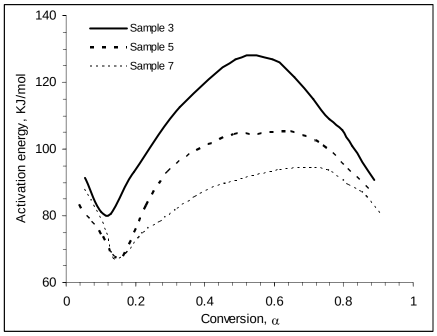

Fig. 5. Activation Energy vs. Conversion for PUs based on polyester-polyether mixture.

In Fig. 5 we can remark the fact that the energy of activation decreases until a conversion between α=0.12…0.16, after that increases up to α=0.6…0.7, and finally decreases again.

For α< 0.12 it appears an important depression in activation energy values versus conversion. This suggests that at the beginning, the reaction have an autocatalytic behavior. In connection with this, one should note that the oxygen traces in the polymer run as a catalyst for the decomposition process (the oxygen is the initiator of the thermal or thermoxidative reactions).

The Table 3 presents the overall kinetics parameters for thermoxidative decomposition of PUs based on polyester-polyether blends.

Table 3. Overall kinetic parameters for thermoxidative decomposition of PUs.

Sample	*E_{CR} (kJ/mol)*	*lnA_{CR}*	*n_{CR}*	*E_{LR} (KJ/mol)*	*T_m(°C) DTG*	*T_{iso} (°C)*	*T_i (°C)*	*T_f (°C)*	*w% final*
3	85.98	4.26	1.5	43.65	352.5	350.6	200	500	80
5	67.96	3.95	1.4	38.74	360	376.6	200	550	84
7	60.45	6.31	1.2	35.48	400	431.5	200	500	84

E- overall activation energy evaluated by various methods denoted by subscript; *A*- pre-exponential factor; *n*-reaction order; T_i - *initial* temperature; T_m- temperature corresponding to the maximum rate of weight loss; T_f - final temperature, T_{iso}- isokinetic temperature; w_{final}- final weight loss.

We can observe that the PUs based on polyester-polyether mixture present temperatures corresponding to the maximum rate of weight loss at PUs up to 500 °C. Influence of the amount of polyether into PUs is the increase of the thermal stability. The concordance of the overall values of the kinetically parameters obtained by both, differential and integral methods, makes possible an evaluation of the decomposition behavior of this products.

Generally, polyurethanes analyzed decomposed in two steps and the temperature which the weight losses were maximum is 300-480 °C. Increase of flexible chain lead to relative stability, because the posibility of order the molecular chain is high, folowing a accentuated decompositions.

Polyurethanes show two-step thermal degradation. The first stage was associated with lost of the humidity and degasification, and the second with the degradation of polyurethane structure. The polyether amount of polyol blends and the presence of glycerin linkages increased the polyurethane thermal stability. In the DTG curve of polyurethanes, an inflexion is present to around 400 °C.

The increase of the maxim point of temperature indicates a lower rate of diffusion of the degraded products out of the matrix as indicated by the lower peak degradation rates exhibited at these temperatures. Thus, it is evident that the cross linking bonds restrict the diffusion of the degradation products from the matrix.

3.3. Differential scanning calorimetry for polyurethanes

In Fig. 6 are presented DSC curves of polyurethane based on polyester and polyether blend. During the test, the temperature ranges from 20 to 300 °C by a heating rate of 10 °C/min under air. For the specimens prepared in this work confirm an endothermic peak between 240-260 °C, function of amount of polyether from polyol blend. The appearance of an endothermic peak indicates the beginning of a thermodegradation reaction. The increase of the amount of polyether diol in polyurethane determines an increase of degradation temperature. All samples present the T_g around 60 °C, which represented T_g for polyurethane structure for this interval of temperature.

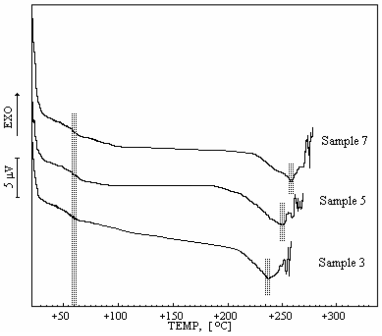

Fig. 6. DSC diagrams of polyurethane based on polyols mixture.

3.4. Mechanical properties

Physical and mechanical properties of polyurethane elastomers were evaluated by the following test methods:

- Shore hardness
- Tensile stress-strain properties (Fig. 7)

Physico-mechanical analyses evidence the extent of the supermolecular modifications of polyurethanes obtained as a function of their structural modifications [17,18].

Stress-strain, modulus and elongation are important for polymer characterization, depending on their structure by varying the polyol and/or diisocyanate molecular weight, as well as variation of chain extenders structure, leading to modifications of stress-strain, modulus and elongation [19,20].

The results of physico-mechanical measurements are presented in Table 4, evidencing that an increase of the amount of the polyether in polyurethane structures leads to a lower tensile strength, which may be explained by decreasing concentration of the ester groups on the macromolecular chain.

Table 4. Tensile properties of polyurethanes obtained with polyester-polyether mixture.

Sample	E$_1$, MPa	L$_1$, %	FR, MPa	AR, %	FM, MPa	AM, %	E, MPa
3	11.59	33.91	68.64	282.02	70.67	281.85	44.33
5	10.16	35.91	59.01	242.76	59.14	242.62	39.3
7	9.96	34.11	45.1	201.46	46.28	201.14	41.42

where:
E$_1$ – effective modulus to first transformation of phase
L1- elongation to first transformation of phase
FR- tensile stress at break
AR- elongation at break
FM- tensile stress at maximum
AM – elongation at maximum
E- modulus

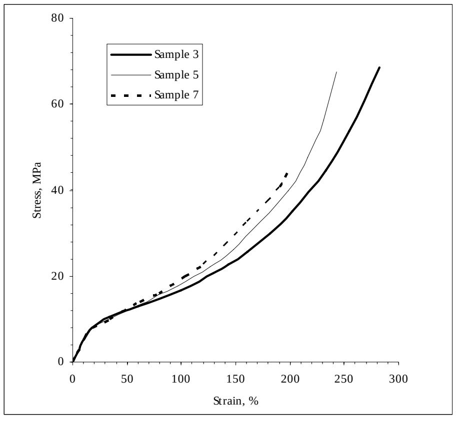

Fig. 7. Stress-strain measurements of polyurethanes based on polyester-polyether mixture.

The physico-mechanical properties depend largely on hydrogen bonds between polar groups of the polymeric chain, mainly among N-H groups (electron acceptors) and carbonyl groups (electron donors) of urea and urethane groups. Hydrogen bonds can also be formed among N-H groups and polyester carbonyl groups and, more difficultly, with polyether oxygen atoms (weak bonds). An ester group develops a cohesive molar energy of 2.9 Kcal/mole, while an ether group, only 1.00 Kcal/mole.

Effective moduli at 10 % elongation are presented in Table 4; lower moduli for sample 7, with bigger amount of polyether, may be observed, compared with the sample 3 with lower amount of polyether. This fact, can be explained by the formation of hydrogen bonds (NH...O=C<) with a much higher frequency in the case of sample 3. In segmented PUs hydrogen bridges are formed between active hydrogen atoms of -NH- urethane groups and -CO- urethane groups, with polyols polyester -CO- groups, and more difficultly with the oxygen atom of polyol polyethers. In polymers with high urethane concentration, hydrogen bridges between N-H groups and urethane -CO- groups are more frequent. Though, when urethane concentration is reduced, connections between N-H urethane groups and polyester -CO- groups become more important. Spectroscopic infrared analyses of polyester and polyether systems indicate that in polyester systems hydrogen bonds are formed mainly with polyester -CO- groups, while in polyether systems, such bonds are formed with urethane -CO- groups.

Therefore, with an increase of the applied stress, example sample 3, there is an increase of the forces impeding deformation, by the rearrangement of the macromolecules.

Because the crystalline regions play a similar role to cross links in improving mechanical properties, the tensile properties of crystallizable material are superior to non-crystallizable material. The influence of amount of polyether on the ultimate tensile properties on the polyurethane is very important. It is clear that, the content of the hard segment increases, and the cross linking density increase. Varying the composition of the polyol mixture affects the tensile properties of the polyurethanes and the cross linked materials.

4. Conclusions

A series of three polyurethanes based on polyester-polyether mixtures was obtained using the prepolymer procedure. The polyester utilized was polyethyleneadipate diol 2000, and the polyether was polytetrahydrofuran 1400. Ethylene glycol and glycerin were found to be a suitable chain extender for based PUs.

Depending on the amount of polyester-polyether blends, the resulting polyurethanes exhibited hardness about 65-75 Shore A making them prospective materials falling into the category of the soft grade polyurethanes.

The thermal stability is a function of the components present in the formulation. Polyurethanes show two-step thermal degradation. The first stage was associated with lost of the humidity and degasification, and the second with the degradation of polyurethane structure. The polyether amount of polyol blends and the presence of glycerin linkages increased the polyurethane thermal stability.

The results of physico-mechanical measurements evidence that an increase of the amount of the polyether in polyurethane structures leads to a lower tensile strength, which may be explained by decreasing of concentration of the ester groups on the macromolecular chain.

This study suggests the possibilities of enhancing the mechanical properties of the polyurethane material based on polyester-polyether blends.

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References

[1] H. M. Jeong, J. B. Lee, S. Y. Lee, B. K. Kim, J. Mater Sci; **35**, 279 (2000).
[2] S. Hayashi, Int Prog Urethanes; **6**, 90 (1993).
[3] B. K. Kim, Y. J. Shin, S. M. Cho, H. M. Jeong, J Polym Sci Part B: Polym Phys; **38**, 2652 (2000).
[4] F. Li, Y. Chen, W. Zhu, X. Zhang, M. Xu, Polymer; **39**, 6929 (1998).
[5] H. M. Jeong, B. K. Kim, Y. J. Choi, Polymer; **41**, 1849 (2000).
[6] H. M. Jeong, B. K. Ahn, B. K. Kim, Polym Int; **49**, 1714 (2000).
[7] T. Nishi, T. T. Wang, Macromolec; **8**, 909 (1975).
[8] S. Oprea, S. Vlad, J. Optoelectron. Adv. Mater. **8**(2), 675 (2006).
[9] S. Vlad, Romanian Patent, RO 116405.
[10] S. Lee, Thermoplastic Polyurethane Markets, in the EU: Production, Technology, Applications and Trends, Rapra Technology Limited, February (1998).
[11] H.-G. Hoppe, H.-G. Wusson, in: Polyurethane Handbook, G. Oertel editor, 2nd edition, Hanser Publishers (1994), p. 421.
[12] C. S. P. Sung, N. S. Schneider, Macromolec.**10**, 452 (1977).
[13] Y. Xiu, D. Wang, C.B. Hu, S.-K. Ying, J. Li, J. Appl. Polym. Sci. **48**, 867 (1993).
[14] Z. Kelemen, C. Chiriac, S. Vlad, Rev.Rom.Chim.**11**, 991 (1996).
[15] H. Hatakeyama, Y. Izuta, K. Kobashigawa, S. Hirose, I. Hatakeyama, Macromol. Symp. **130**, 127 (1998).
[16] K. Nakamura, T. Hatakeyama, H. Hatakeyama, Polym. Adv. Technol., **3,** 151 (1992).
[17] S. Oprea, Mat. Plast. **42**(1), 68 (2005).
[18] S. Vlad, Scientific Study & Research. **3**, 37 (2002).
[19] S. Oprea, S. Vlad, A. Stanciu, Polymer **42**, 7257 (2001).
[20] S. Vlad, Mat. Plast. **42**(1), 63 (2005).

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