Influence of plasticization on properties of polyesterurethane elastomers synthesized through the stage of epoxyurethane oligomers

Influencia de la plastificación en las propiedades de elastómeros de poliésteruretano sintetizados a través de la etapa de oligómeros de epoxiuretano

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ABSTRACT

The introduction of such plasticizers as tributyl phosphate and di-(2-Ethylhexyl)-sebacate [DEHS] into the composition of polyurethane elastomers, synthesized through the stage of epoxyurethane oligomer can significantly reduce the glass transition temperature, which expands the operating temperature range. The peculiarities of changes in the basic properties of the studied elastomers during plasticization are determined by their two-phase structure, which is characterized by hard urethane hydroxyl blocks.

Keywords: Epoxyurethane oligomers, Plasticization, Strength, Deformation, Hard blocks

RESUMEN

La introducción de plastificantes como el fosfato de tributilo y el sebacato de di-(2-etilhexilo) [DEHS] en la composición de elastómeros de poliuretano, sintetizados a través de la etapa de oligómero de epoxiuretano, puede reducir significativamente la temperatura de transición vítrea, lo que amplía el rango de temperatura de funcionamiento. Las peculiaridades de los cambios en las propiedades básicas de los elastómeros estudiados durante la plastificación están determinadas por su estructura de dos fases, que se caracteriza por bloques de hidroxilo de uretano duro.

Palabras clave: Oligómeros de epoxiuretano, Plastificación, Resistencia, Deformación, Bloques duros.

1. INTRODUCTION

Urethane-containing elastomers, polyurethanes and polyurethane ureas, are widely used in various fields of industry and medicine due to their high strength and strain properties, wear resistance, and resistance to absorption of many organic oils (Hepburn, 2012; Volkova, Tereshatov & Karmanov, 2011). They are made based on oligodiisocyanates [OD] and low-molecular-weight chain extenders: amines and alcohols. The properties of such materials can be controlled within wide limits due to the use of various reagents in their synthesis (Akindoyo, Beg, Ghazali & Islam, 2016).

To reduce the toxicity of precursors and the negative effect of moisture on the final properties of urethane-containing elastomers, one should perform the synthesis of such elastomers through the stage of epoxyurethane oligomers [EUOs]. These oligomers are synthesized using a chemical reaction of OD with glycidol. Unlike OD, EUO-based compositions are insensitive to moisture, which is essential for large monolithic products. Amines, dicarboxylic acid anhydrides, and compounds with carboxyl groups are used as hardeners for epoxyurethane oligomers. Good dielectric properties and mechanical characteristics distinguish elastic materials obtained based on EUOs; they can be used as adhesives (the basis of low-modulus potting compounds for various purposes) and biomedical materials (Chuvilina, Simunova, Zajchenko, Kuprijanov & Potsepnja, 2007; Elchueva, Nazipov, Tabachkov & Liakumovich, 2003; Hsia, Ma & Chen, 1994; Mathew, Kurmvanshi, Mohanty & Nayak, 2018; Sidorov et al., 2012).

The structure of polyurethanes based on EUOs includes alternating soft and urethane hydroxyl hard blocks, the difference in polarity of which leads to their microphase separation with the formation of a separate phase with domains serving as a reinforcing nano-dispersed filler and cross-linkages of a specific physical network, which is essential for ensuring high strength characteristics of the materials being developed (Hsia, Ma & Chen, 1994). The chemical structure of the soft segments is determined by the oligodiols used in the synthesis. The list of the most well-known epoxyurethane oligomers includes the following products: PEF-3A – synthesized based on oligotetramethylene oxide diol, PPG-3A – based on oligopropyleneoxidol, and PDI-3AK – based on oligodivinilisoprenediol; all of them are synthesized using 2,4-toluene diisocyanate. However, the elastomers synthesized based on the EUOs mentioned above are characterized by insufficient oil and petrol resistance. Thus, one should use oligoesterdiols for synthesis (Osman, Satti, Luqman & Hasan, 2018).

At the same time (Tun, Lyamkin, Shumskaya & Vasilyev, 2007), urethane-containing elastomers based on complex oligoesters are characterized by a sufficiently high glass transition temperature (Fedchenko & Tereshatov, 2007), which limits the possibilities of using this type of materials. The problem of lowering the temperature range of the operation of elastomers can be solved using plasticization, which is one of the methods of physical modification of polymers. Since urethane-containing elastomers are often biphasic materials, it cannot be assumed that the introduction of any plasticizers should cause an unequivocal decrease in the glass transition temperature. According to modern concepts of plasticization of block copolymers, a special role in the effect of certain plasticizers is played by their thermodynamic affinity for hard and elastic segments of polymer chains (Makarova et al., 2015). The corresponding data are fragmentary for the described polymers, which does not allow a qualitative assessment of the plasticization efficiency. Similarly, there is practically no data on the effect of plasticizers on the physical and mechanical characteristics of the corresponding elastomers.

The paper aims to reveal the regularities of the effect of plasticizers on the physical and physic-mechanical properties of polyurethane elastomers synthesized based on oligoesterdiols through the stage of epoxyurethane oligomers.

2. MATERIALS AND METHODS

The starting oligomeric diol was an oligoester OMA-2100 synthesized using adipic acid and ethylene glycol (the mass fraction of hydroxyl groups in the polyester is 1.85%). The first stage of the synthesis contains a reaction between this diol and 2.4-toluene diisocyanate. This reaction was provided with the ratio between NCO and OH groups being equal to 2.05:1. As a result, an oligodiisocyanate [OD] with terminal functional isocyanate groups was obtained. An epoxyurethane oligomer with terminal epoxy groups was synthesized based on OD and epoxy alcohol - glycidol.

The polyester was preliminarily dried at 80°C with stirring in a vacuum (residual pressure was 1–2 kPa). The synthesis was done in a conditionally hermetically sealed laboratory mixer with a heating jacket. After loading the components, the temperature was maintained at 60°C for 1 hour, then it rose to 80°C and was maintained at that level with stirring for 6 hours. In this case, the catalyst dibutyltin dilaurate (0.02% of the mass of the reaction mixture) was added. The accomplishment of a constant content of isocyanate groups was controlled using the method of back titration in accordance with ASTM D2572-08. At the stage of ECO synthesis, the obtained OD interacted with glycidol taken with a double excess. The synthesis mode provided for keeping the reaction mixture with stirring for 4 hours at 80°C. The control of the mass content of epoxy groups of the obtained oligomer was done in accordance with the Russian standard GOST R 56752-2015.

We used the synthesized oligomer to obtain cured samples to study physical, mechanical, and other functional properties. We used two liquid cycloaliphatic amines, aminoethylpiperazine [AEP] and isophorone diamine [IPDA], as hardeners. Tri-n-butyl phosphate [TBP] and di-(2-Ethylhexyl)-sebacate [DEHS] were used as plasticizers. The molar ratio between EUO and amine was 1:0.87 when using AEP and when using IFDA, it was 1:0.75. We prepared a reaction mixture of EUO, a plasticizer, and a hardener for 10 min under vacuum (residual pressure 1–2 kPa) at 90 ± 1°C. We cured the resulting mixture for 48 hours at 90 ± 1°C. The curing time was preliminarily established by monitoring the completeness of the conversion of epoxy groups by FTIR spectroscopy by the disappearance of the absorption band at 910 cm^{-1} (Tun, Lyamkin, Shumskaya & Vasilyev, 2007). The compositions of the synthesized series are shown in Table 1.

Table 1: Composition of synthesized series

	Sample	Hardener	Plasticizer	Mass fraction of plasticizer in the mix with oligomer, %
1	DF-0	IPDA	-	0
2	DF-10T	IPDA	TBP	10
3	DF-20T	IPDA	TBP	20
4	DF-10S	IPDA	DEHS	10
5	DF-20S	IPDA	DEHS	20
6	DA-0	AEP	-	0
7	DA-10T	AEP	TBP	10
8	DA-20T	AEP	TBP	20
9	DA-10S	AEP	DEHS	10
10	DA-20S	AEP	DEHS	20

We determined glass transition temperature [Tgs] using a Mettler Toledo DSC 822e differential scanning calorimeter at a scan rate of 0.08 deg s^{-1}. FTIR spectra of the initial epoxy-containing oligomers were recorded in the range 4000–400 cm^{-1} on a Bruker IFS-66 / S FT-IR spectrometer at a resolution of 1 cm^{-1}. For the convenience of comparison, the spectral curves were normalized to the 1600 cm^{-1} band, which corresponds to the vibrations of the aryl ring of the diisocyanate (Tereshatov, Makarova & Senichev, 2015). The FTIR spectra of the surface of the cured samples in the region of carbonyl stretching vibrations

(wavenumber range ν = 4000–400 cm^{-1}) were recorded using the ATR module A 225/Q (Platinum ATR diamonds F) with a single reflection diamond crystal. Mechanical tests of elastomer samples were carried out on a universal testing machine INSTRON 3365 at a strain rate υ = 0.28 s^{-1} at a temperature of 25 ± 1°C, in accordance with ISO 37–2013. Conditional strength σ_k (maximum stress calculated for the initial section of the sample), relative critical strain ε_k (%), and conditional modulus E_{100} (stress at the relative strain of the sample ε = 100%) were determined.

3. RESULTS AND DISCUSSION

The use of different hardeners for EUOs in the synthesis of polyurethanes leads to the formation of two types of urethane hydroxyl hard blocks. Their structure is shown in Fig. 1, 2:
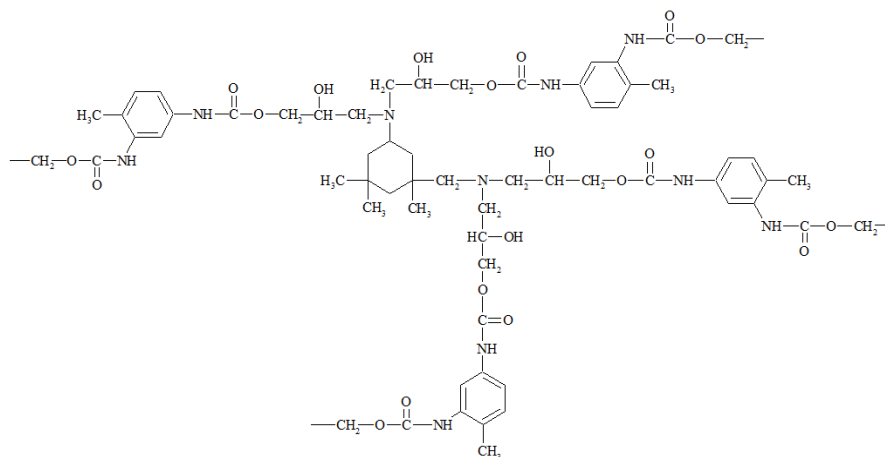

Fig. 1: Structure of HB-1 hard blocks based on IPDA, glycidol, and 2,4-toluenediisocyanate.
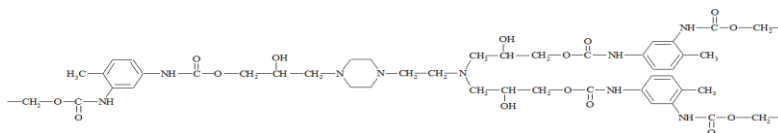

Fig. 2: Structure of HB-2 hard blocks based on AEP, glycidol, and 2,4-toluenediisocyanate

Differences in the structure of hard blocks [HBs] can significantly affect the supramolecular structure of the polymer (Tereshatov et al., 2016). Analysis of the FTIR spectra in the region of carbonyl stretching vibrations (the range of wavenumbers ν = 1600–1760 cm^{-1}) allowed to reveal essential features of the structural organization of the synthesized elastomers (Fig. 3, 4). The position of carbonyl absorption bands in the FTIR spectra of the studied elastomers can be slightly shifted for compositions with various diisocyanates and diamines. Thus, the absorption band of hydrogen-bonded carbonyl self-associates of urethane groups in urethane hydroxyl hard blocks localized in the hard phase of the polymer for elastomers with the first type of hard blocks appears at 1,644–1,650 cm^{-1}, and that with the second type of hard blocks appears at 1,712 cm^{-1} (Senichev et al., 2019). Regardless of the hard block type, the absorption band at 1,730–1,732 cm^{-1} refers to the absorption of the carbonyl of the free urethane group that characterizes hard blocks dissolved in the soft phase.

A higher degree of microphase separation is implemented for systems with the first type of hard blocks (Senichev et al., 2019). This fact should determine the difference in glass transition temperatures of these elastomers; it is confirmed experimentally: analysis of DSC thermograms of unplasticized elastomers (Fig. 5, 6) shows that the difference in glass transition temperature of unplasticized samples is about 8°C (Table

2). At the same time, despite the higher degree of microphase separation, the elastomer with the first type of hard blocks lacks crystallization of the soft phase, which, in our opinion, is associated with steric hindrances related to the more bulky structure of HB-1. The presence of partial crystallization of the soft phase in the DA-0 sample determines its higher mechanical characteristics: the strength and the conditional modulus are more than 2.5 times higher than in the DF-0 sample (Table 2).

Analysis of the FTIR spectra of plasticized samples (Fig. 3, 4) shows that the use of di-Ethylhexyl sebacate, regardless of the type of hard block, leads to a decrease in the amount of dissolved hard blocks in the soft phase, as indicated by a slight decrease in the intensity of the absorption band at 1730 cm^{-1}. In this case, the absorption band at 1,695 cm^{-1} practically does not change. When using TBP, which can play the role of a "solvent" of hard blocks, in addition to a similar effect, the degree of microphase separation decreases (a decrease in the intensity of the absorption band at 1,695 cm^{-1}, 1,646 cm^{-1}). When the mass fraction of this plasticizer is 20% (sample DF-20T, DA-20T), the material becomes practically single-phase.

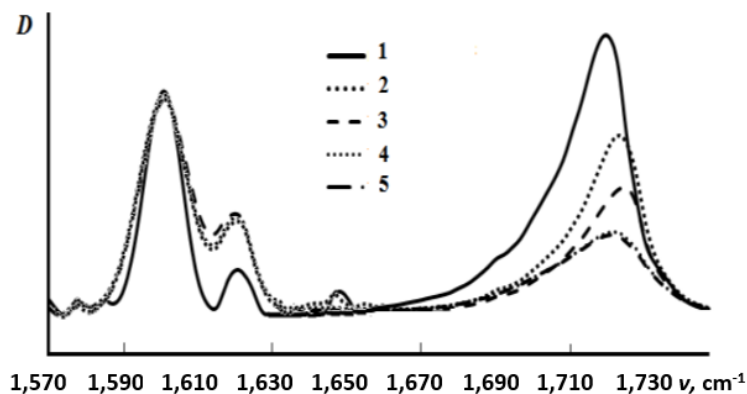Fig. 3: A fragment of FTIR-spectra of samples for the DF series: **1-** DF-0**, 2-** DF-10T**, 3-** DF-20T**, 4-** DF-10S**, 5-** DF-20S
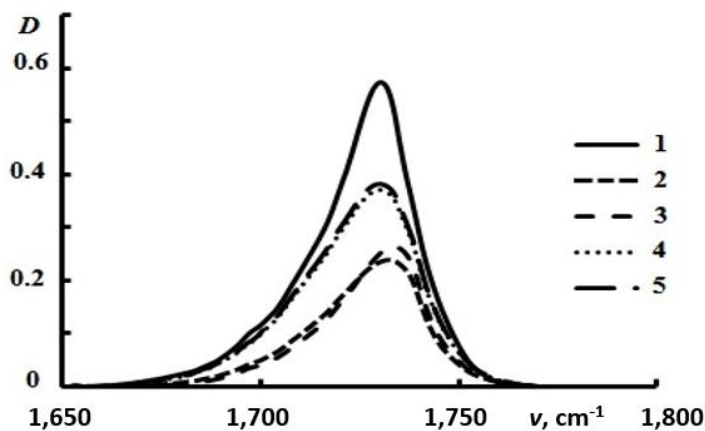

Fig. 4: A fragment of FTIR-spectra of samples for the DA series: **1-** DA-0**, 2-** DA-10T**, 3-** DA-20T**, 4-** DA-10S**, 5-** DA-20S

DSC analysis of thermograms of synthesized elastomers (Figs 5, 6) shows that the use of plasticizers leads to a decrease in the glass transition temperature of the soft phase. The use of di-Ethylhexyl sebacate

decreases this value down to -27°C for compositions with IPDA. We found less effect (-17°C) for those cured with AEP. A more complex effect can be observed when tri-n-butyl phosphate is used as a plasticizer. For samples cured by IPDA (type of hard block HB-1), the glass transition temperature decreases from -23°C down to -36°C (for 10% plasticizer), and then to -49°C (for 20% plasticizer). In this case, a peak characterizing the crystallization of the soft phase appears. For samples cured with AEP, the glass transition temperature decreases by 40°C from -15°C down to -55°C.

Table 2 shows the values of the physical and mechanical characteristics of plasticized samples.
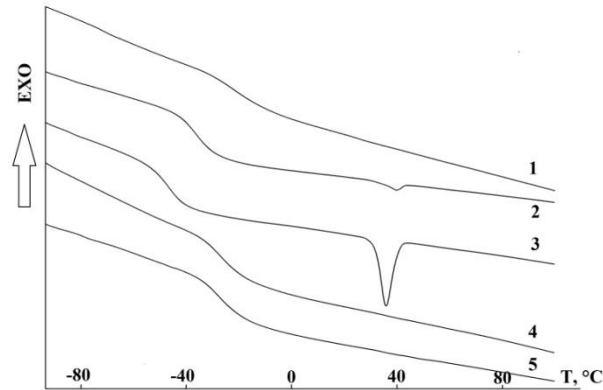

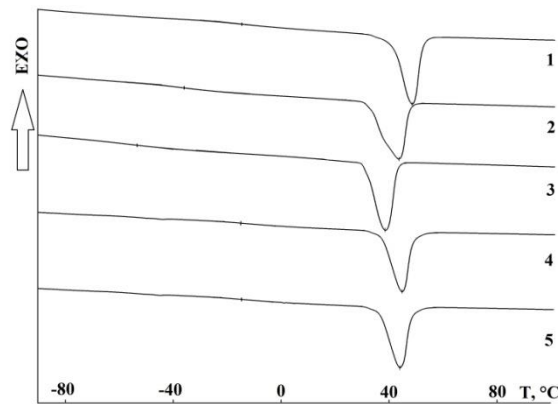Fig. 5: DF series: 1-DF-0, 2- DF-10T,3- DF-20T, 4- DF-10S, 5- DF-20S

Fig. 6: DA series: 1 - DA-0, 2- DA-10T, 3- DA-20T, 4 - DA-10S, 5 - DA-20S

Table 2: The main properties of investigated elastomers

Sample		Tensile strength, MPa		Relative critical strain, %		Conditional modulus, MPa		Glass transition temperature, Tgs, °C
Testing temperature, °C		25	-40	25	-40	25	-40	
1	DF-0	4.22	0	340	0	0.97	0	-23
2	DF-10T	5.55	47.1	444	13	0.86		-36
3	DF-	4.51	31.3	379	193	1.16	15.8	-46

	20T							
4	DF-10S	4.73	41.3	378	8	0.99	-	-27
5	DF-20S	3.60	42.8	348	11	0.96	-	-27
6	DA-0	11.09	0	362	0	6.1	0	-15
7	DA-10T	10.34	14.8	398	2	5.2	-	-37
8	DA-20T	4.97	36.5	380	37	4.08	27.4	-55
9	DA-10S	9.52	-	368	-	5.62	-	-16
10	DA-20S	5.65	-	320	-	5.31	-	-16

The obtained data shows that all versions of the proposed plasticized binders provide a structural glass transition temperature of the polymer matrix not higher than -30°C. At the same time, the appearance of crystallization in the samples was plasticized. In this case, the maximum strength was observed for the samples plasticized with di-(2-Ethylhexyl)-sebacate in an amount of 10%, which is associated with a slight increase in the mobility of polymer chains while maintaining microphase separation. Moreover, the conditional modulus of the DA-20T sample increases due to the appearance of crystallization of the soft phase. Samples cured with IPDA are significantly superior in strength compared to those cured with AEP at the same amount of plasticizer. The best combination of frost resistance and mechanical properties is achieved when plasticizing elastomers with the first type of hard blocks.

4. CONCLUSION

We synthesized a new epoxyurethane oligomer necessary for oil-resistant binders based on an oligoester of adipic acid and ethylene glycol, isophorone diisocyanate, and glycidol. This oligomer is cured using an epoxy-amine curing system. Isophorone diamine and aminoethylpiperazine were used as hardeners. To reduce the glass transition temperature, we implemented a structural modification of the binder using plasticization.

A higher degree of microphase separation between soft and hard blocks of an unplasticized urethane epoxy binder contributes to a lower glass transition temperature and higher strength and the possibility of manifestation of the crystallization effect of the soft phase.

In addition, plasticization of a microheterogeneous urethane-containing binder based on polyester and urethane hydroxyl hard blocks leads to a significant increase in its frost resistance: the glass transition temperature of the soft phase decreases by 14–56°C

REFERENCES

Akindoyo, J. O., Beg, M., Ghazali, S., & Islam, M. R. (2016). Polyurethane types, Synthesis, and applications: A review. RSC Advances, 6(115), 114453-114482.

Chuvilina, L. F., Simunova, S. S., Zajchenko, I. I., Kuprijanov, A. I., & Potsepnja, O. A. (2007). Compound and method of preparation thereof, RU 2291176. Moscow, Russia: Rospatent.

Elchueva, A. D., Nazipov, M. M., Tabachkov, A. A., & Liakumovich, A. G. (2003). Sealants based on oligodiene urethane epoxides. Russian Journal of Applied Chemistry, 76(3), 487-490.

Fedchenko, V. V., & Tereshatov, V. V. (2007). Liquid hardener for Polyurethane Systems, RU 2292358C1. Moscow, Russia: Rospatent.

Hepburn, C. (2012). Polyurethane Elastomers. Cham, Switzerland: Springer.

Hsia, H. C., Ma, C. C. M., & Chen, D. S. (1994). Adhesion properties and phase separation behavior of glycidyl-terminated polyurethanes. Macromolecular Materials and Engineering, 220(1), 133-149.

Makarova, M. A., Tereshatov, V. V., Slobodinyuk, A. I., Senichev, V. Yu., Volkova, E. R., & Fedoseev, M. S. (2015). Plasticization effect on the stability of the physicomechanical properties of polyetherurethane in a humid medium. Russian Journal of Applied Chemistry, 88, 633-637.

Mathew, A., Kurmvanshi, S., Mohanty, S., & Nayak, S. N. (2018). Sustainable production of polyurethane from castor oil, functionalized with epoxy-and hydroxyl-terminated poly (dimethyl siloxane) for biomedical applications. Journal of Materials Science, 53(5), 3119-3130.

Osman, M., Satti, S. M., Luqman, A., & Hasan, F. (2018). Degradation of polyester polyurethane by aspergillus sp. strain s45 isolated from soil. Journal of Polymers and the Environment, 26(1), 301-310.

Senichev, V. Y., Slobodinyuk, A. I., Makarova, M. A., Smirnova, V. E., Popova, E. N., Vaganov, G. V., … Kudryavtsev, V. V. (2019). The effect of hard segments structure on the functional properties of polyurethane elastomers based on oligoesterurethane epoxides. Journal of Physics: Conference Series 1399(4), 044060–1-044060–7.

Sidorov, O. I., Milekhin, Yu. M., Matveev, A. A., Poisova, T. P., Bykova, K. A., & Sadchikov, N. V. (2012). Plasticizer-resistant fixing compound based on polyethyruretane rubber with end epoxyurethane groups. Sealants. Technologies, 9, 15-21.

Tereshatov, V. V., Makarova, M. A., & Senichev, V. Y. (2015). The role of the soft phase in the hardening effect and the rate dependence of the ultimate physico-mechanical properties of urethane-containing segmented elastomers. Colloid and Polymer Science, 293(1), 153–164.

Tereshatov, V., Vnutskikh, Z., Slobodinyuk,. A, Vnutskikh, Zh. A., Slobodinyuk, A. I., & Savchuk, A. V. (2016). New multi-block isophorone diisocyanate-based copolymers with urethane urea hard segments. Journal of Elastomers and Plastics, 48(4), 289-304.

Tun, T. K., Lyamkin, D. I., Shumskaya, A. N., & Vasilyev, N. S. (2007). The role of the domain structure in the formation of thermomechanical and fatigue properties of microcellular polyurethanes. Connections Ser A, 49(6), 1043-1048.

Volkova, E. R., Tereshatov, V.V., & Karmanov, V. I. (2011). Influence of the concentration of Iron (III) tris(acetylacetonate) used as urethane formation catalyst on the structure and properties of cold-cure polyurethanes. Russ. J. Appl. Chem, 84(8), 1414-1417.