

УДК 678.028.2

V. A. Sedykh, PhD (Engineering), assistant professor (VSUET);
 O. V. Karmanova, D. Sc. (Engineering), professor, (VSUET);
 A. V. Kasperovich, PhD (Engineering), assistant professor (BSTU);
 A. S. Moskalyov, PhD student (VSUET)

BUTADIENE-STYRENE THERMOPLASTIC ELASTOMER WITH SPECIAL PROPERTIES

Structure and rheology of thermoplastic elastomers with stiff links of styrene in polybutadiene unit are examined. Molecular and structural characteristics TPE with the high vinyl links of polybutadiene are shown. Structure and technological properties of the thermoplastic elastomers modified in the synthesis stage are compared.

Introduction. Three-block copolymers in which the central block possesses a sufficiently high flexibility of the polymer chains, and end blocks are rigid, exhibit the properties of thermoplastic elastomers (TPE) [1].

Polymeric materials based on block copolymers of styrene and butadiene of styrene-butadiene-styrene type (SBS) occupy about 50% of the world market of thermoplastic elastomers [2]. TPE comprising 15–50% of bound styrene are used as the polymer base.

Modification of the properties of the TPE at the synthesis stage is developed mainly in three steps: changing nature of flexible links (polybutadiene, polyisoprene or polypiperylene) [3] and hard (Polystyrene or poly-alpha-methyl styrene) blocks; introduction of rigid styrene links in a flexible polybutadiene block [4–5]; an increase in the content of 1, 2-links butadiene in polybutadiene block.

Changes in the structure of the flexible block can significantly affect the technical properties of thermoplastic elastomers.

The materials based and using TPE, containing more than 50% of bound styrene are of great interest.

It is proved by the series of products of STYROLUX company BASF – The Chemical Company [4] containing about 75% bound styrene, processed by pressure molding, extrusion and thermofforming transparent shock-resistant products.

The results of these products application for the polystyrene modification without noticeable deterioration in its transparency are of special importance.

Main part. StyroTPE. Recently there appeared domestic high quality styrene TPE of brand TPE70, containing about 70% bound styrene in the Russian market [4].

According to the results of derivatography [6] StyroTPE-70 is resistant to the heat-flow influence under the conditions of dynamic on-heating to 260°C.

Analysis of TGA and DTA diagrams in the range of 260–320°C indicates the development of the thermal oxidative degradation process of TPE.

The subsequent course of the DTA curve indicates a preferential flow of the process of thermal depolymerization of its macromolecules in the temperature range of 320–410°C.

The studies [6] have allowed to establish molecular characteristics of StiroTPE-70, to identify their morphological and supramolecular structure and to treat them as polystyrene static copoly (butadiene/styrene/-1.2-butadiene)-polystyrene.

The structure of StiroTPE-65 (a mixture of 95% m. of StiroTPE-70 and 5% of the DST-30-01) allows to subject it to further chemical modification.

Thus, the short-term heat of TPE in the presence of structuring agent – brominated vinylcyclohexene (Br-VCH) greatly changes its elastic-strength indicators.

It is established that with increase of content of Br-VCH from 2 to 10% by weight in StiroTPE-65, after rapid heating at 190°C, there observed a decrease in both rupture resistance from 16.8 to 4.3 MPa and relative elongation at a rupture from 770% to 30%.

Apparently, the product of decomposition Br-VCH chemically reacts with butadiene links StiroTPE-65. This is due to two parallel processes in polymer- the destruction and structuring. The results are shown in Table 1. Linear DST-30-01B with a higher content of vinyl links. The increase in the content of 1, 2 links of -butadiene in polybutadiene block to 30–40% in the DST-30-01B (pilot batch of “Voronezhskintezkav-chuk”) caused a change in microstructure and elastic-strength indicators of TPE. TPE melt is pseudo-plastic fluid, the phenomenon of anomaly of viscosity is revealed at rather low intensity of its deformation.

When choosing a method and a processing temperature of StiroTPE-70 it is important to determine the effect of temperature and time of the heat flow on its fluidity (PTR). It is established that at the expected PTR general dependence on the temperature there appeared two temperature ranges with different intensity of PTR changing [6–8].

Table 1

Influence of Br-VCH content on elastic-strength indicators of Stiro TPE-65, heated to 190°C

Indicator	Content Br-VCH (wt %) in Stiro TPE-65			
	Without additive	2%	5%	10%
Tensile strength, MPa	16.8	14.6	13.2	4.2
Relative elongation at a break, %	770	750	650	30

Melt flow of TPE in the range of shear rates of 40–110 C^{-1} is described by the equation $\tau = K \cdot \dot{\gamma}^n$, where $K = 17.8 \text{ kPa s}^{0.37}$.

Studies were carried out [9] on the reometer SmartRheo-1000 with software “Ceast VIEW 5.94-4D”. Granules of StiroTPE-65 were heated in the device chamber at 190 and 200°C. Thermoplastic melt was extruded through a calibrated capillary diameter of which was 1 mm and a length of 5 mm and 30 mm with the increasing speed.

It is found that with increasing shear rate from 100 to 400 s^{-1} shear tension $\dot{\gamma}$ increased by a linear dependence. An increase in the temperature to 10°C resulted in a decrease in the shear tension ratio (B, Pa) and in an index of frequency rate of its change A (Pa·s) at the capillary length of 5 mm by 1.1 times, and the capillary length of 30 mm by 1.3 times 3 fold. It is noted that the increase in the length of the capillary by 6 times at 200°C caused a decrease in A index by 1.2 times but at 190°C it virtually remained unchanged (Table 2).

Table 2

Effect of shear rate τ (c^{-1}), melt temperature and length of the capillary on the index of multiplicity of tension changes of shear melt A (Pa·s)

Test temperature (capillary length)	Regression equation coefficients $Y = A \cdot \tau + B$	
	A, Pa · c	B, Pa
190° C (5 mm)	136.5	25.177
190°C (30 mm)	132.0	18.271
200°C (5 mm)	124.8	14.759
200°C (30 mm)	104.2	14.019

An increase in the shear rate led to a decrease in the melt viscosity (Table 3). It is confirmed that the nature of the melt flow of StiroTPE-65 corresponds to pseudo-plastic fluids. The temperature increase by 10°C resulted in a decrease in viscosity and refractive multiplicity of change K ($Pa \cdot s^2$) at a

capillary length of 5 mm by 1.7 times, and at 30 mm in 1.3 times. The length increase of the capillary by 6 times at 190°C caused a reduction in K factor to 1.4, but at 200°C index K did not depend on changes in the length of the capillary.

It can be assumed that the presence of linear DST-30-01B with a higher content of 1.2 links of butadiene in the pavement must also improve tire adhesion to the road.

Table 3

Effect of shear rate τ (c^{-1}), the melt temperature and the capillary length on the index of the multiplicity of changes in melt viscosity K ($Pa \cdot s^2$)

The test temperature (capillary length)	Coefficient of regression equation $Y = C \cdot \tau + D$	
	K, $Pa \cdot s^2$	D, Pa · s
190°C (5 mm)	-0.53	391
190°C (30 mm)	-0.39	319
200°C (5 mm)	-0.31	274
200°C (30 mm)	-0.31	249

It should be noted that high indexes of microstructure having vinyl links was 36–39%, and 29–30% of bound styrene.

It is known that styrene-butadiene co-polymers having a higher content 1.2-butadiene, give the tires (based on DSSK, SBR) a unique combination of properties of good adhesion to the road surface and low-rolling resistance [10–14].

According to GPH an average molecular mass M_w of the DST-30-01B varied for different parties in the range of $80 \cdot 10^3$ – $90 \cdot 10^3$, that corresponded to an intrinsic viscosity values of 1.0–1.1 dl / g, which were optimum for receiving polymer-bitumen binders (Table 4). The polydispersity of $M_w / M_n = 1.15$ –1.19, two blocks content is about 10% as well as for industrial linear TPE DST-30-01 (Table 5).

Physical-mechanical parameters for DST-30-01B were defined (Table 6).

Table 4

Microstructure and Properties of the linear DST-30-01 B

Indexes	intrinsic, viscosity dl/g	Mass fraction, %				pH aqueous extract of TEP
		1,2-links of butadiene	bound styrene	ashes	Antioxidant Agidol-1	
maximum	1.1	39.0	31.5	0.3	0.38	9.6
Minimum	0.9	29.4	27.0	0.2	0.24	1.3
Average	1.0	36.8	29.8	0.26	0.35	7.4

Table 5

Molecular-mass characteristics of the linear DST-30-01B

Values	$M_n \cdot 10^{-3}$	$M_w \cdot 10^{-3}$	M_w / M_n	Content of the two-block, wt %	Content of gomopolystyrene, wt %
maximum	77	91	1.19	11.3	1.8
Minimum	66	78	1.15	10.0	1.1
Average	69.7	81.9	1.2	10.6	1.6

Table 6

Physical mechanical indexes of the linear DST -30-01B

Name of an index	Indexes		
	Average	Minimum	maximum
The conv. stress at lengthening 300%, MPa	4.0	4.4	3.2
The conventional tensile strength, MPa	29.6	26.1	32.8
The relative elongation at a break, %	939	1,027	800
The relative residual deformation after a break, %	14	25	9
Rebound resilience, %	52	56	48
Shore hardness, °ShR	76	78	74

Table 7

Resilient and strength indexes of the modified TPE

Name of an index	DST-30-01 TC 38.103257-99	StiroTPE-65 (pilot batch)	DST-30-01B ((pilot batch))
The conventional tensile strength, MPa	Not less than 19.6	26	29
The specific elongation at a break, %	Not less than 650	520	860
The relative residual deformation, %	Not more than 25	–	12
Rebound resilience, %	Not less than 50	30	50
Shore hardness A, c. u.	Not less than 65	90	77

Conclusion. Introduction of styrene links in the flexible polybutadiene block of StiroTPE-65 has increased the hardness and durability at reducing the rebound resilience and relative elongation at break compared to the DST-30-01. Increase in the content of 1.2 links of butadiene in polybutadiene block up to 30–40% in the DST-30-01V led to a further increase in tensile strength and relative elongation at break (Table 7).

Butadiene-styrene TPEs are widely used not only as additives which improve the properties of roofing and road surfaces, but also as materials for precision and complex parts, components of medical devices and packages. Ease of processing allows their use in the manufacture of toys, advertising design, transparent films and details of office fixtures.

References

1. Термоэластопласты / В. Н. Вострякова [и др.]; под ред. В. В. Моисеева. М.: Химия, 1985. 184 с.
2. Ашпина, О., Салихов И. Перерабатываем шины // The Chemical Journal. 2011. № 1–2, С. 58–61.
3. Термоэластопласты на основе бутадиена, пиперилена и стирола / В. С. Глуховская [и др.] // Промышленное производство и использование эластомеров. 2008. № 4. С. 13–15.
4. Стиролюкс общая презентация. / BASF в РФ [Электронный ресурс] // ООО «БАСФ». – Москва, 2013. URL: <http://www.basf.ru>. (дата обращения: 25.03.2013).
5. Продукция. СтироТЭП-70 // Воронежский филиал ФГУП «НИИ синтетического каучука». Воронеж, 2013. URL: <http://www.niisk.vrn.ru>. (дата обращения: 25.03.2013).
6. Свойства высокостирольного бутадиен-стирольного блок-сополимера / А. А. Алексеев [и др.] // Пластические массы. 2013. № 3. С. 12–15.

7. Свойства блок-сополимера стирола и бутадиена марки «СтироТЭП-70» / А. В. Лобанов [и др.] // Успехи в химии и химической технологии. 2012. Т. XXVI. № 4. С. 23–36.

8. Свойства бутадиен-стирольных блок-сополимеров / А. В. Лобанов [и др.] // Успехи в химии и химической технологии, 2013. Т. XXVII. № 3. С. 82–86.

9. Изучение технических и технологических свойств СтироТЭП-65 / В. А. Седых [и др.] // Вестник воронежского государственного университета инженерных технологий. 2013. № 4. С. 175–178.

10. Влияние содержания винильных звеньев на свойства статистических бутадиен-стирольных сополимеров с аминными группами на концах цепи / А. В. Гусев [и др.] // Международная конференция по каучуку и резине IRC'04, Москва. 2004. С. 10–12.

11. Джибера С. Дж. Технология и очерки будущего наших полимеров // Гудьер Тайр энд Раббер Ко: Доклад на 38-м заседании Совета директоров ИИСПП. 1997. 8 с.

12. Куперман Ф. Е. Состояние и перспективы работ по новым каучукам для шин // Производство и использование эластомеров. 1997. № 10, 11. С. 5–19.

13. Свойства шин, получаемых с применением бутадиен-стирольного каучука с повышенным содержанием бутадиена структуры 1,2 / Ф. Е. Куперман [и др.] // Каучук и резина. 1994. № 2. С. 12–14.

14. Свойства и применение растворного БСК в шинной промышленности / Ф. Е. Куперман [и др.] // Производство шин: тематический обзор. М.: ЦНИИТЭнефтехим, 1982. 60 с.

Received 26.02.20