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PROPERTIES OF COATINGS OF HIGH STYRENE THERMOPLASTIC ELASTOMERS AND THEIR MODIFICATIONS

Flexible fiber-optic cables, used to prevent stomach diseases, protected by disposable and transparent coatings reduce the duration of disassembly and sterilization. The aim of this work was to develop technologies for producing films, protective coatings of high-styrene block copolymers StyroTEP-65 and estimation of their technical parameters. It was determined the impact of the multiplicity of dippings in polymer solution and polymer solution concentration, layer thickness and nature of the substrate on the elastic strength properties of the films. The manifestation of the anisotropy of the properties in the longitudinal and transverse cross section of the membranes is fixed. The increase in the thickness of the membranes resulted in a slight decrease in light transmission in the visible and infrared wavelength range. Results of physico-mechanical properties of the films StyroTEP-65 in the presence of polyvinylcarbazole additives are presented. Method for casting membranes is developed, their optimal thickness is determined, the effect of the anisotropy properties of the membranes in the longitudinal and transverse cross-section is observed.

Keywords: thermoplastic elastomer film StyroTEP-65, endoscope, cable, block copolymer, strength, relative elongation, toluene, photoelectric gloss meter, PVC additive, thermodynamic compatibility, polystyrene domains.

Introduction. Currently, endoscopes for various purposes are widely used for the prevention of gastric diseases. The most important endoscope element is the flexible endoscope optic fiber bundle with a camera and lights. After removing the device from the stomach it is subjected to lengthy disassembly and sterilization. Reducing the duration of bundle preparation is relevant.

One of the solutions to this problem is to dress up a flexible optic fiber bundle with protective disposable and transparent shell. As a material suitable for the shell, it can be recommended high styrene block copolymer StyroTEP-65 developed by the Voronezh branch of FSUE "NIISK" [1–8]. The films of the block copolymer are characterized by acceptable strength, flexibility, and most importantly, transparency.

The aim of the work is to develop technologies for the film production, protective shells from StyroTEP-65 and its compositions with polyvinylcarbazole and evaluation of their technical indicators.

Main part. As a standard of comparison it was tested the film StyroTEP-65 obtained by extrusion from melt through a flat head (Table 1). The indicators of the strength at break f_p, the relative E_p, and adjusted E_p / f_p elongation at break as well as residual relative E_{res} and adjusted E_{res} / E_p elongation after rupture were identified.

The test results revealed the effect of the anisotropy properties of the film along and across the sleeve i.e. the difference in strength, elongation at break. This was due to the orientation of the polymer macromolecules along the sleeve in the process of drawing.

Studying the properties of thermoelastoplastic solutions. It is known [9] that with increasing concentration of polymer solutions their viscosity goes up. It was investigated the effect of the concentration of the solution StyroTEP-65 in toluene and spindle speed rate (s62) Brookfield viscometer PV-E on their viscosity. It was confirmed that concentration increase from 19.0 to 26.8 wt % (by 1.4 times) the viscosity level increased from 104 to 330 mPa · s (by 3.2 times).

Table 1

The elastic-strength characteristics of the extruded film StyroTEP-65 along and across the sleeves (thickness 0.03–0.05 mm)

Thickness, mm	The direction of stretching	Strength at break f_p, MPa	Elongation at rupture		The permanent elongation after rupture	
			Relative E_p, %	Adjusted E_p / f_p	Relative E_{res}, %	Adjusted E_{res} / E_p
0,04–0,05	Along	63.1	73	1.6	13	0.17
0,03–0,04	Across	22.3	136	6.0	20	0.15

It was found that with increasing of spindle speed from 2.0 to 10.0 min^{-1}, the viscosity of the solution increased regardless of the concentration. It was explained by the manifestation of thixotropy due to the effect of structural viscosity of the polymer solution. Therefore, at slow extraction of solution forms, solution layers will retain on the surface thereof. Further spindle speed increase from 10 up to 100 min^{-1} had no effect on the viscosity of the solutions, which is characteristic for ideal fluids.

Development of a technique of casting polymeric films and membranes from solutions. Films cast on a horizontal surface of the stretched cellophane from 10% toluene solution, are characterized by less strength than extruded, but differed in relative and residual larger elongation at break (Table 2).

The tubes from glass (D = 20 mm) or press mould PET (D = 30 mm), depending on the film thickness were loaded for 2–3 times into solution. The excess droplets of the solution were removed from the press moulds with a glass rod after each dipping.

Between dipping solution layers were dried in the open air for 10–15 min. Upon completion of the procedure, the samples were left under a fume hood in an inverted vertical position at 20°C for 24 hours. Further, the polymer shell tubes were kept in isopropyl alcohol for 24 hours and then removed from the alcohol to dry for 10–15 min and the shells were manually removed from forms.

Determining the influence of layer thickness, the concentration of the block copolymer solution and the nature of the substrate on the elastic-strength characteristics of membranes. It was found that the multiplicity of form dipping into the polymer solution and the concentration of the latter affected the elastic-strength indicators of obtained shells (Table 3). Maximum strength (f_p = 21.4 MPa) and the highest relative elongation at break (E_p = 437%) of membranes are achieved by the triple form dipping into a solution StyroTEP-65 at a concentration of 19.0 wt %.

The increase of strength and relative elongation at break of shells obtained from dilute solutions, was explained by reducing their thickness spread, which at dipping number equal to 3 for a concentration of 28.6 wt % was in the range of 0.20–0.28 mm, while for a concentration of 19.0 wt % – 0.09–0.11 mm.

The increase in the multiplicity of form dipping in the solution reduced the spread of the shell thickness, because there was a “healing” of film defects.

At a larger increase in the form diameter the anisotropic effect was recorded by the appearance of properties in the longitudinal and cross-sectional membranes (Table 4). Thus, the tensile strength perpendicularly to the tensile direction is different by 47.7%, the indicator of elongation at break – by 55.5%. This was due to the orientation of the polymer macromolecules in the transverse perimeter of the shell as a result of constrained shrinkage during solvent volatilization.

The study of shell light-transmitting capacity. A more detailed study of light transmission of the films was carried out with Mono-Spectrum SF-56.

It is found that increasing of the shell thickness StyroTEP-65 from 0.14 to 0.19 mm led to a slight decrease in transmittance within the visible and infrared wavelength range from 450 to 750 nm, i.e. it wasn’t a limiting factor.

Table 2

The elastic-strength characteristics of films (thickness 0.15–0.18 mm) StyroTEP-65 molded on cellophane from a 10% solution of toluene

Tensile strength, MPa	Elongation at rupture		The permanent elongation after rupture	
	Relative E_p, %	Adjusted E_p / f_p	Relative E_{res}, %	Adjusted E_{res} / E_p
17.9	717	40.1	77	0.11

Table 3

Influence of glass mould dipping multiplicity and concentration of the solution on the elastic-strength characteristics of shells StyroTEP-65

Thickness, mm	Number of dipping	Strength at break f_p, MPa	Elongation at rupture		The permanent elongation after rupture	
			Relative E_p, %	Adjusted E_p / f_p	Relative E_{res}, %	Adjusted E_{res} / E_p
26.8 wt % in toluene						
0.04–0.05	1	15.6	433	27.7	91	0.21
0.12–0.19	2	6.4	190	29.7	36	0.19
0.20–0.28	3	9.4	227	24.1	60	0.26
19.0 wt % in toluene						
0.06–0.08	2	11.6	175	15.1	21	0.12
0.09–0.11	3	21.4	437	20.4	103	0.24

Table 4

Influence of stretching direction on the elastic-strength characteristics of shells StyroTEP-65, cast on PET press mould from 19% solution in toluene (twofold dipping)

Thickness, mm	The direction of sample stretching	Strength at break, fp, MPa	Elongation at rupture		The permanent elongation after rupture	
			Relative E_p, %	Adjusted E_p / f_p	Relative E_{res}, %	Adjusted E_{res} / E_p
0.10–0.18	Along	4.4	280	63.7	59	0.21
0.06–0.08	Across	6.5	180	27.7	36	0.20

Table 5

Influence of shell thickness StyroTEP-65, cast on glass from 26.8 wt % solution in toluene, on their light transmittance

Thickness, mm	Number of dipping	Light transmission (on white), mA
0.04	1	0.99
0.15	2	0.97
0.26	3	0.95

Table 6

Influence of the multiplicity of glass form dipping, concentration of the solution and the content of STC on the elastic-strength characteristics of shells StyroTEP-65

Thickness, mm	Number of dipping	Strength at break f_p, MPa	Elongation at rupture		The permanent elongation after rupture	
			Relative E_p, %	Adjusted E_p / f_p	Relative E_{res}, %	Adjusted E_{res} / E_p
1 wt % PVK on TIC (dry residue 18 wt %)						
0.05–0.12	2	15.3	418	27.3	94	0.22
0.09–0.14	3	20.2	490	24.3	99	0.20
5 wt % PVK on TIC (dry residue 16 wt %)						
0.05–0.10	2	12.6	223	17.7	68	0.30
0.14–0.19	3	18.5	342	18.5	110	0.32

Table 7

The elastic-strength characteristics of shells StyroTEP-65 in the presence of PVC, cast on PET press mould

Thickness, mm	The direction of stretching	Strength at break f_p, MPa	Elongation at rupture		The permanent elongation after rupture	
			Relative E_p, %	Adjusted E_p / f_p	Relative E_p, %	Adjusted E_p / f_p
1 wt % PVK on TIC (dry residue 18 wt %)						
0.05–0.10	Along	13.3	320	24.0	79	0.25
0.04–0.08	Across	21.8	440	20.2	94	0.21
5 wt % PVK on TIC (dry residue 16 wt %)						
0.06–0.10	Along	13.6	128	9.4	37	0.28
0.06–0.14	Across	15.8	280	17.7	108	0.38

It was confirmed that the increase in the shell thickness led to a decrease in light-transmitting capacity (Table 5) defined by an indirect method using a photoelectric gloss meter SE-2. A noticeable decrease in light transmission (2.0%) was found in the shell thickness greater than 0.15 mm.

Modification of thermoplastic membranes with PVC additives. The increase of strength and relative elongation at break, at increasing the thickness (number of dipping) is characterized for samples of shells based on StyroTEP-65 in the presence of 1% and 5 wt % polyvinylcarbazole (PVC (Table 6)).

Thus, at a concentration of 1 wt % PVC for two dipping tensile strength is 15.3 MPa, and for three – 20.2 MPa; at a concentration of 5 wt % tensile strength increases from 12.6 MPa at 2 dipping to 18.5 MPa at 3 dipping.

For samples containing PVC, the effect of anisotropy of elastic-strength characteristics along and across the membranes preserves (Table 7). It is explained by the transverse orientation of macromolecules perimeter of the shell as a result of constrained shrinkage during solvent volatilization StyroTEP-65.

The rise of PVC content from 1.0 to 5.0% reduces the strength from 21.8 MPa to 15.8 MPa, relative elongation at break from 440 to 280% and an increase of the relative residual elongation after fracture from 94 to 108% at the cross-tension.

Tensile strength with an increase of STC in the content to 5% decreases slightly (by 2.3%). The presence of PVC in StyroTEP-65 in the range from 1 to 5 wt % does not affect the adjusted residual elongation (Table 6).

It was cconfirmed thermodynamic compatibility of StiroTEP-65 and STC to a concentration of 1 wt %. Reducing the strength of shells StyroTEP-65 in the presence of PVC in the range from 1 to 5 wt % is explained by PVC macromolecules penetration in TEP polystyrene domains and a violation of its crystal structure. The presence of additives in PVC StyroTEP-65 in the wavelength range from 300 to 1100 nm reduced membrane light transmission by 25–35%.

Conclusion. It was developed the technique of shell casting for endoscope optic fiber bundles by multiple dipping of forms with different diameters into solutions StyroTEP-65.

The optimum thickness of the shells subject to the elastic-strength parameters and light transmission were determined. The effect of the anisotropy of the shell properties obtained by various methods as a result of the macromolecule orientation was identified. It was confirmed that StyroTEP-65 and polyvinylcarbazole with its content to 1% have thermodynamic compatibility. It was shown the drop in shell strength from 1 to 5%. It occurred due to the penetration of polyvinylcarbazole macromolecules in StyroTEP-65 polystyrene domains. The modification of film elastic strength properties StyroTEP-65 by introducing PVC additives was implemented.

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