UTILIZATION OF POLYETHYLENE TEREPHTHALATE IN ORDER TO OBTAIN POLYMERIC CORONA ELECTRETS

Kydyraliyeva A.Sh.[1], Beisenbayev O.K.[1], Nadirov K.S.[1*], Ibadullayev A.S.[2]
[1]M. Auezov South Kazakhstan University, Shymkent, Kazakhstan
[2]Tashkent chemical-engineering institute, Tashkent, Uzbekistan
[*]**Corresponding author's e-mail:** nadirovkazim@mail.ru

ABSTRACT

The possibility of recycling recycled polyethylene terephthalate (plastic) in order to obtain polymer corona electrets and compositions, sealing materials, compositions for corrosion protection was explored in this article.

Work objective is to study the effect of a dispersed filler - wollastonite and a stabilizing additive - technical gossypol, as well as savilen on the electret properties of a composite based on waste plastic materials - polyethylene terephthalate (PET). Technical gossypol, wollastonite of the Verkhnebadam deposit (Kazakhstan, Turkestan region), savilene - a copolymer of ethylene with vinyl acetate and a finished composite: mineral filler - wollastonite; sevilen; technical gossypol; PET - the rest were the objects of study. It has been established that the introduction of fillers into the composition of a PET-based composite leads to an increase in its density and degree of crystallinity in the composition of the composite and, as a result, to a decrease in its moisture permeability, which leads to a decrease in conductivity, and hence, an increase in the stability of the electret state of composite films. Changes in the surface structure of polyethylene terephthalate and its compositions with the above components during electretization were established using microscopy and infrared spectroscopy.

Additives of the above components to the composition of a composite based on recycled polyethylene terephthalate affect the electretization process, the effect of the interaction of various fillers can significantly change the stability of composite electrets, which seems promising for using the results obtained in the chemical and petrochemical industries.

Keywords: polymer corona electrets, polyethylene terephthalate, electret potential difference, technical gossypol, sevilen, wollastonite, crystallinity, melting point.

INTRODUCTION

At present, polymer electrets are becoming more and more widespread in technology (gas filters, microphones, dosimeters, electronic focusing systems, and others). The possibility of their use in these and other areas of application (sealing materials, corrosion protection systems, and others) requires an increase in the production of polymeric electret materials with specified electret and physical-mechanical properties and with a competitive cost. It is known that among structural materials, polymers occupy a fairly significant volume and are mainly dielectrics. Electrical polarization is their natural physical state. An electret is a dielectric that retains a polarized state for a long time after the removal of an external influence, which led to the polarization (or charging) of this dielectric, and creates a quasi-constant electric field in the surrounding space [1].

There are several ways to obtain them depending on the type of electret. Corona electrets are made by applying a corona discharge field to a dielectric. When charging, a high

voltage is applied to one of the electrodes, made in the form of a set of needles, causing the appearance of ionized air-plasma, while the dielectric must be in contact with a grounded metal electrode [1]. The latter method has proven itself well in terms of technical and economic indicators. Polyolefins are the most promising materials for producing corona electrets and products based on them, and their disadvantage, due to the low stability of the electret state, can be compensated for by introducing finely dispersed fillers of various kinds. However, at the moment, there is little information in the literature about the influence of the conditions for obtaining and processing methods of polymer composite materials on the manifestation of the electret effect in them. By linking the influence of the formulation and processing conditions on the structural parameters of polymers and composites, it becomes possible to add one more factor to the prediction and control of the electret properties of compositions based on polyolefins, and, therefore, to facilitate the task of obtaining an electret with desired properties. [2].

At the present stage, much attention in the oil-producing and oil-refining industry is paid to the design, creation and operation of equipment that is in direct contact with oil-bearing media. The creation of self-regulating assembly units and systems is promising direction in increasing the durability of machines and equipment in the oil and gas industry. This is especially true for sealing units, namely, polymeric elastomeric materials used as gaskets, seals, cuffs and other units and parts. Giving such products an electret state can help increase their service life, and, consequently, improve the reliability of machines, assemblies and equipment it is shown in the authors' work [3]. The effect of electric fields on sealed and separating media located in seal gaps underlies many sealing methods. Electric fields affect the wetting and spreading of liquids, largely determine the kinetics of the capillary flow of liquids through the gaps between the parts and the diffusion penetration of media through films, coatings and vessel walls, control the transfer of lubricating films in the friction zone.

It should be noted that most of the existing technologies for creating electrets are labor-intensive (as a rule, they are carried out in several technological stages), and based on the electretization of polymers already processed into products, which negatively affects energy costs and significantly increases the labor intensity and cost of the obtained final electret material. In addition, there is practically no information in the scientific literature about the change in the anticorrosion properties of polymer coatings in the electret state.

The objective of this work is to study the effect of a dispersed filler, wollastonite, and a stabilizing additive-technical gossypol and savilen, on the electret properties of a composite based on polyethylene terephthalate, a composition developed both for components and parts of equipment, and for an external anti-corrosion protective coating.

MATERIALS AND METHODS

Polyethylene terephthalate was used as objects of study in accordance with GOST 32686-2014. PET bottles for food liquids. General specifications, technical gossypol, a mixture of brown complex organic compounds are a by-product of the oil and fat industry (ГОСТР51424-99), wollastonite of the Verkhnebadam deposit [4], sevilen is a copolymer of ethylene with vinyl acetate (sevilen 11104-030). The finished composite consists of the composition of the masses. %: mineral filler - wollastonite - 10; sevilen - 8; gossypol technical - 15; polyethylene terephthalate - the rest.

Due to the fact that gossypol itself, isolated from cottonseed oil during its alkaline refining, has a very high cost, which can be several orders of magnitude higher than the cost

of the original technical product, in this work we used technical gossypol, which was obtained using the technology given in the authors' works. [5,6].

Polyethylene terephthalate is the most common member of the polyester class and is known by various brand names. Polycondensation product of ethylene glycol with terephthalic acid; solid, colorless, transparent substance in the amorphous state and white, opaque in the crystalline state [7,8]. It should be noted that the disposal of products, that is, plastic containers based on polyethylene terephthalate, is also associated with serious costs, since the accumulation of this material leads to environmental pollution. The used plastic is not destroyed completely, but breaks up into miniature segments that fall to the inhabitants of the seas and oceans. We used crushed PET plastic as a filler to obtain a composition of a composite coating and a polymeric electret material.

An AND HL-100 technical balance was used to weigh granular polymers and powdered fillers. The distribution quality and particle size of the filler in polymers were studied under an optical microscope, according to GOST R ISO 18553-2013. Polymer compositions were obtained by mixing polyethylene terephthalate with a filler on a VK-4 laboratory microroller with controlled electric heating. Roll rotation speed is 12.5 m/min, friction is 1:1.2. Rolling was carried out for 300 s. The samples were made in the form of 0.5 mm plates and thick by pressing on a PG-60 hydraulic press. Technological parameters of pressing: pressing temperature 170 is 210 °C, pressing pressure is 15 MPa, preheating time is 10 min, holding time under pressure is 5 min, cooling time is 5 min. Extrusion of the polymer with fillers was carried out in the melt in a laboratory desktop multifunctional twin-screw extruder UR-TC with modular screws and a modular barrel.

Electrets were obtained by the corona discharge method. To do this, pressed plates from composites of various compositions were placed in a thermal cabinet heated to a temperature of 100°C and kept for 10 minutes. After that, the samples were transferred to a corona cell with an electrode consisting of 225 pointed needles evenly spaced over an area of 64 cm2 in the square form. The samples were cooled in the field of a negative corona discharge at a voltage of 35 kV and a polarization time of 30 seconds. The technology for obtaining electrets was also used, which combines the processes of extrusion and polarization in a corona discharge according to the method [2]. Measurement of the electret potential difference of the samples Uerp was carried out by the non-contact induction method using a vibrating electrode according to GOST 25209-82. The removal of infrared spectra was carried out by the method of multiple frustrated total internal reflection on the Infrared Fourier - spectrometer "Infralum FT - 08" [9].

RESULTS AND DISCUSSION

In the IR spectrum of the resulting composite composition (Figure 1) at above the specified temperature, the deformation (δ) vibrations of C–H bonds of these groups correspond to bands with maxima at 1454 cm^{-1} (δ_{asym}. CH^3), as well as 1373 cm^{-1} (δ_{symm} .CH_3 and CH_2). The peak at 1800–1778 cm^{-1} can be attributed to aromatic carboxylic acids and phthalic acid derivatives. An increase in the absorption intensity from 78 to 54% in the region of the 1300–2800 cm^{-1} bands belonging to the naphthalene nuclei of gossypol and its derivatives indicates its partial conversion in this mixture. As a result of the heat treatment of the components as a whole, a change in intensity is observed in the range of absorption bands from 1778 to 1700 cm^{-1}. It is noticeable that additional peaks appear at 2400 – 2370 cm^{-1} in the modified product. In general, it can be said that in the resulting composition at temperatures of 170-210 ° C a rather stable mixture is formed, which can retain its properties

in aggressive environments when used as part of hermetic materials, as well as various coatings.

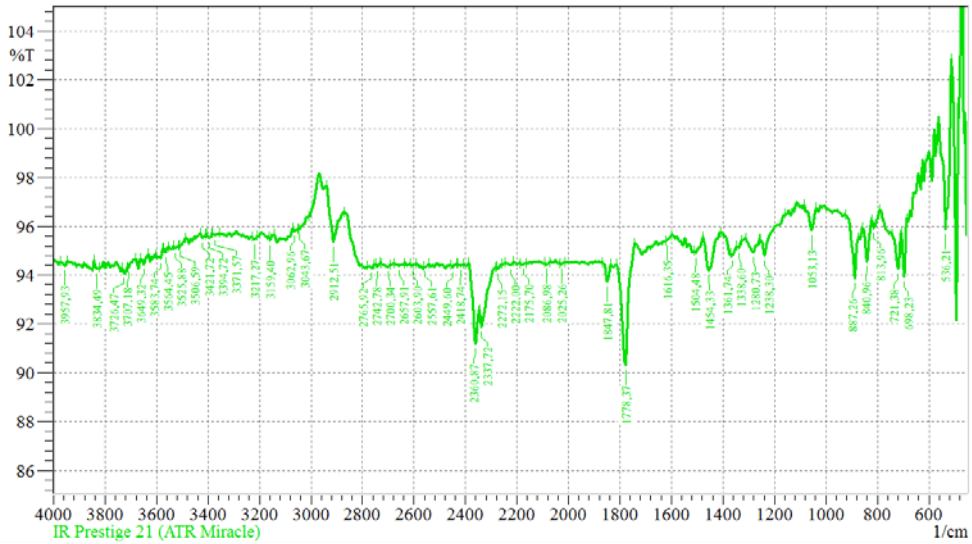


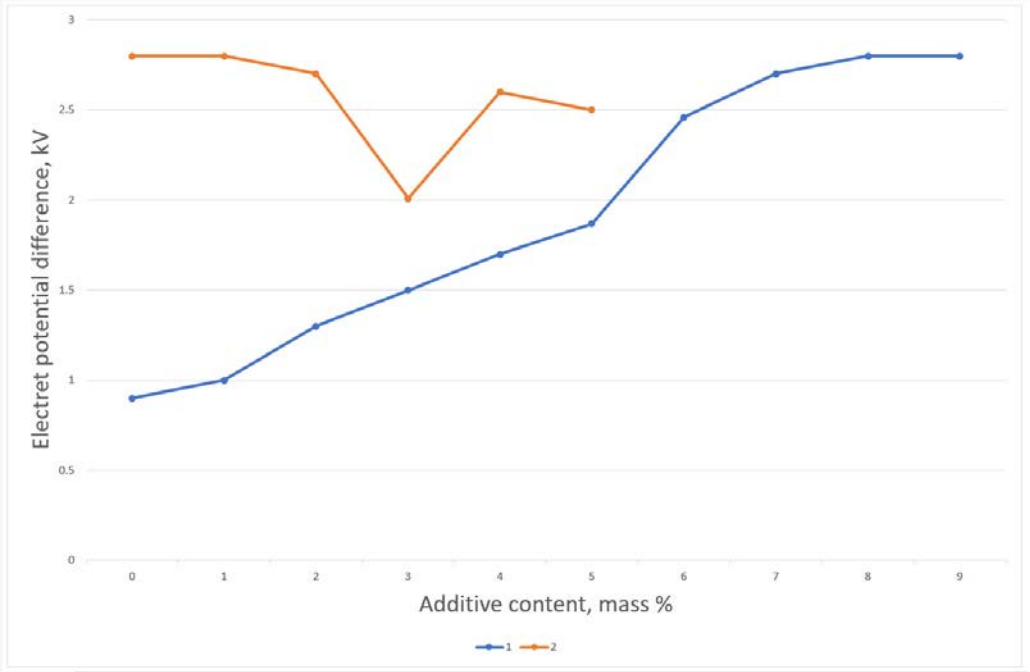
Fig. 1. Infrared spectra of a composition based on polyethylene terephthalate and additives.

Microscopic images of the resulting composite composition based on the mineral filler wollastonite, savilen, technical gossypol and polyethylene terephthalate are shown in figure 2. In general, the coating is uneven, white areas, apparently related to wollastanite and unreacted plastic.

Fig. 2. Microscopic images of the composition based on polyethylene terephthalate and additives.

The dependence of the electret potential difference of the composite on the content of wollastonite, savilene, and technical gossypol is shown in Figure 3. The concentration of

additives was changed within the limits that retained the functional properties of the composite. The general behavior of electrical potential difference dependencies of polyethylene composites on the content of fillers can be explained as follows. The obtained dependences indicate an increase in the electret potential difference with an increase in the content of wollastonite and savilene in the composition (curve 1) and its slight decrease with an increase in the concentration of technical gossypol in the mixture (curve 2).



The composition of the composite, wt %: 1 - wollastonite -8; sevilen - 8; gossypol - 10; PET - the rest; 2 - wollastonite - 10; sevilen - 10; gossypol 15; PET - the rest.

Fig. 3. The dependence of the electret potential difference of the composite based on PET.

To determine the reasons for such an effect, the contribution of various fillers to the thermophysical properties of the polyethylene matrix was estimated by differential scanning calorimetry. To study the processes associated with physical transitions, the samples were subjected to melting twice. Film samples were obtained by thermal pressing with rapid cooling. During rapid cooling, fine crystallites are predominantly formed. In this regard, after the first melting in the materials during slow cooling, larger and more perfect crystallites were formed, the melting point of which is higher than that of fine crystallites (Table 1)

Table 1. Influence of the composition on the melting point and the crystallinity degree of the PET mixture with components' additives

Composition			Melting point, °C	Crystallinity degree, χ, %
Component content, wt.%				
Wollastonite	Savilen	Technical gossypol		
-	-	-	107.7	26.5
3	2	-	108.4	27.8

Table 1 continuation

6	4	-	109.8	27.3
8	6	-	107.6	29.5
10	8	-	106.4	28.9
10	8	-	107.5	28.1
10	8	-	105.8	30.7
10	8	8	106.7	29.6
10	8	10	105.8	31.3
10	8	13	104.5	32.4
10	8	15	105.7	32.5
10	8	18	105.9	31.6

The data in the table indicate that the fillers used have a certain effect on the crystallization process: they act as crystallization nuclei, so the degree of materials crystallinity with fillers is higher than that of a pure polymer, while there is a directly proportional relationship between the filler concentration and the measured parameter. It has been established that the crystallinity degree of the filled composites is different, which is due to the different degree of dispersion of the fillers. With the introduction of savilene into the composition, the crystallinity degree increases, and the melting point decreases, and a symbatic dependence of these changes on the concentration of sevilen is observed, however, with an increase in the concentration of savilene above 8%, an inversely proportional dependence is observed and the quality of the finished material, regardless of the type of filler, deteriorates according to mechanical indicators. With an increase in wollastonite concentration above 10%, the crystallization process changes its character, which gives incomparable results. The introduction of technical gossypol into the composition of the mixture slightly increases the melting point and the crystallinity degree, and only up to the content of gossypol up to 15%, then there is a sharp jump in the studied parameters change nature.

The issues of mineral fillers selection for the development of the composition of the outer layer of a three-layer coating of oil pipelines, as well as the study of the stabilizer and fillers effect on the thermal stability of polymer composites, were investigated by us in the works [10-12].

CONCLUSION

Thus, it was found that the introduction of fillers into the composition based on polyethylene terephthalate leads to an increase in its density and crystallinity degree in the composition of the composite and, as a result, to a decrease in its moisture permeability, which leads to a decrease in conductivity, and hence to an increase in the stability of the composite films' electret state. With the help of data obtained on the basis of IR spectroscopy and microscopy, changes in the surface structure of polyethylene terephthalate and its compositions with wollastonite during electretization were established. It is shown that with the introduction of wollastonite and technical gossypol and the use of polarization, the content of oxygen-containing groups on the surface of polymer films increases significantly. Dielectrics that retain polarization for a long time (electrets or electrical analogues of magnets) constitute a special class of materials that are distinguished by the property of being a source of a constant electric field. Therefore, the introduction into industrial production of

new compositions and technologies for obtaining polymer composite electrets with high and, most importantly, stable electret properties is very relevant and timely. Savilene additives also affect the process of electretization, the effect of the interaction of various fillers can significantly change the stability of composite electrets, which seems to be very promising both in theoretical and practical terms.

REFERENCES

1 Gorokhovatsky Yu.A. Elektretnyy effekt i yego primeneniye [Electret effect and its application]. Obrazovatel'nyy zhurnal Sorosa - Soros Educational Journal, 1997, No. 8, pp. 92-98.

2 Karimov I.A. Vliyaniye sostava, usloviy polucheniya i obrabotki poliolefinovykh kompozitsionnykh materialov na ikh elektretnyye svoystva. Diss…..kand. tekh. nauk. [Influence of composition, production and processing conditions of polyolefin composite materials on their electret properties. Diss…Cand.Tech.Scie]. Kazan, FSBEI HPE “KNRTU”, 2015. 147 p.

3 Pinchuk L.S., Goldade V.A. Elektretnyye materialy v mashinostroyenii [Electret materials in mechanical engineering. Gomel, Infotribo, 1998. 288 p.

4 V. A. Tyulnin, V. R. Tkach, V. I. Eirikh, and N. P. Starodubtsev. Vollastonit – unikal'noye mineral'noye syr'ye mnogotselevogo naznacheniya [Wollastonite is a unique multi-purpose mineral raw material]. Moscow, Publishing House "Ruda i metally", 2003. 152p.

5 Nadirov K.S. Polucheniye gossipola i yego proizvodnykh pri pererabotke semyan i khlopkovogo masla [Getting gossypol and its derivatives in the processing of seeds and cottonseed oil]. Shymkent: M. Auezov SKSU, 2012. 115 p.

6 Glushenkova A.I., Nazarova I.P. Gossipol, yego proizvodnyye i ikh primeneniye [Gossypol, its derivatives and their use]. Tashkent, Fam, 1993. 78 p.

7 N. A. Chainikov, P. S. Belyaev, A. B. Mozzhukhin, and V. V. Zharikov Resursosberegayushchiye tekhnologii proizvodstva metallopolimernykh materialov [Resource-saving technologies for the manufacture of metal-polymer materials]. Tambov, TSTU, 2003. 80 p.

8 Traven V.F. Organicheskaya khimiya v 2-kh tomakh. Tom 1. [Organic chemistry in 2 volumes. Volume 1]. Moscow, Akademkniga, 2004. 727p.

9 Tarasevich B.N. IK spektry osnovnykh klassov organicheskikh soyedineniy. Spravochnyye materialy [IR spectra of the main classes of organic compounds. Reference materials]. Moscow, MSU after name M.V. Lomonosov, 2012. 54 p.

10 Nadirov K.S., Sakybaev B.A., Bimbetova G.Zh., Zhantasov M.K. Otsenka effektivnosti ob"yedineniya otdel'nykh kompozitov v trekhsloynoye pokrytiye dlya zashchity nefteprovodov ot korrozii [Evaluation of the effectiveness of combining individual composites in a three-layer coating to protect oil pipelines from corrosion. Problemy i innovatsii sovremennogo obshchestva. Materialy 7-y nauchno-prakticheskoy konferentsii s mezhdunarodnym uchastiyem [Problems and innovations of the modern society. Materials of the 7th scientific-practical conference with international participation]. Astrakhan, 2015, pp. 349-353.

11 Nadirov K.S., Zhantasov M.K. Bimbetova G.Zh. Orynbasarov A.K., Ermenov S.M., Shegenova G.K., Kalmenov M.U., Ziyat A.Zh. Vybor mineral'nykh napolniteley dlya razrabotki sostava naruzhnogo sloya trekhsloynogo pokrytiya [The choice of mineral fillers for the development of the composition of the outer layer of a three-layer coating]. Materialy

XI mezinarodni vedecko-conference "Aktualni vymozenosti vedy - 2015".-Dil 6. Lekarstvi. Biological Vedy. Chemie a chemicka technjjljgie. Ecology. Zemedelstvi [Materials Xi international scientific conference "current achievements of science-2015". Dil 6. Medicine. Biological sciences. Chemistry and chemical technology. Ecology. Agriculture]. Prague, 2015, pp. 57-65.

12 Nadirov K.S., Akhmetov N.E. Bimbetova G.Zh. Zhantasov M.K. Orynbasarov A.K. Ziyat A.Zh., Kalmenov M.U. Issledovaniye vliyaniya stabilizatora i napolniteley na teplostoykost' PEVD i kompozitov na yego osnove dlya magistral'nykh nefteprovodov [Study of the effect of stabilizer and fillers on the heat resistance of LDPE and composites based on it for main oil pipelines]. Vestnik im. L.N. Gumilyova - Bulletin after name L.N. Gumilyov, 2016, No. 2, pp. 261-267.