CHEMISTRY & CHEMICAL TECHNOLOGY

Vol. 7, No. 1, 2013 Chemistry

Svetlana Rusanova[1], Oleg Stoyanov[1], Svetlana Sofina[1] and Gennady Zaikov[2]

IR-STUDY OF SILANOL MODIFICATION OF ETHYLENE COPOLYMERS

[1]Kazan State Technological University,
68, K. Marx str., 420015 Kazan, Tatarstan, Russia; tpspk@kstu.ru, ov_stoyanov@mail.ru;
[2]Emanuel Institute of Biochemical Physics, Russian Academy of Sciences,
4, Kosygina str., 119991 Moscow, Russia; chembio@sky.chph.ras.ru

Received: March 13, 2012 / Revised: April 23, 2012 / Accepted: August 13, 2012

Abstract. The chemical interaction of organosilicon compounds and copolymers of ethylene with vinylacetate and copolymers of ethylene with vinylacetate and maleic anhydride was studied by IR-spectroscopy absorption and attenuated total reflection (ATR). An enrichment of the surface layers of polymers by siloxane phase was found, that may be useful in the design of the chemical structure of adhesive materials for different purposes.

Keywords: IR-spectroscopy, chemical interaction, ethylene copolymers, organosilicon compounds.

1. Introduction

It is possible to extend the sphere of application of ethylene copolymers by modification of the original polymer or by development of composite materials on their basis. Traditionally the compositions formation is effective in the presence of additives, interacting with the polymer during the processing. It results in the regulation of the material properties. One of the methods of chemical modification is introduction of organosilicon compounds into polyolefins.

Earlier [1, 2], we studied the modification of ethylene copolymers with vinylacetate by ethylsilicates containing various amounts of ester groups. Similar studies were conducted by V. Bounor-Legaré *et al.* [3], so it was of interest to study changes in the structure and properties of ethylene copolymers with vinylacetate containing other functional groups, such as anhydride, to identify general trends and specific differences during the modification of ethylene copolymers, containing different reactive segments, by limiting alkoxysilane.

2. Experimental

2.1. Materials

Copolymers of ethylene with vinylacetate (EVA) grades Evatane 2020 and Evatane 2805 (Arkema) and sevilen 11306-075 brand of JSC “Sevilen”; copolymer of ethylene with vinylacetate and maleic anhydride (EVAMA) grades Orevac 9305 and Orevac 9707 (Arkema) were used as the objects of the study. The main characteristics of the polymers are listed in the Table 1.

Ethylsilicate ETS-32 (ETS) being a mixture of tetraethoxysilane with geksaethoxydisiloxane with a small admixture of ethanol and oktaethoxytrisiloxane was used as a modifier. The silicon content in terms of silicon dioxide is 30–34 %, tetraethoxysilane – 50–65 %. Its density is 1.062 kg/m^3 and viscosity is 1.6 cP. Ethylsilicate is manufactured by Production JSC “Khimprom” of Novocheboksarsk.

Table 1

Main characteristics of the polymers

Characteristics	Sevilen 11306-075	Evatane 2020	Evatane 2805	Orevac 9305	Orevac 9307
Symbol	EVA 14	EVA 20	EVA 27	EVAMA 26	EVAMA 13
The content of vinyl acetate, %	14	19–21	27–29	26–30	12–14
Melt flow rate, g/10 min, 398 K	0.85	2.23	0.53	14.06	1.10
Density, kg/m^3	0.935	0.936	0.945	0.963	0.924
Melting temperature (max), K	370	355	345	340	363
Tensile strength, MPa	18.15	14.28	17.40	6.72	18.88
Breaking elongation, %	650	660	830	800	670

2.2. Samples Obtaining

Reactive blending of polymers with ethylsilicate was carried out on the laboratory rolls at the rotational rolls speed of 12.5 m/min and at the friction of 1:1.2 during 10 min in the range of 373–393 K. The content of the modifier was varied in the range of 0–10 mas %. The samples for investigations were prepared by the direct pressing in the restrictive frameworks. Pressing regime is under the temperature of 433 K and the unit pressure of 15 MPa; the time of preheating, injection boost time and the time of cooling is 1 min for each 1 mm of the sample thickness. After the pressing all the compositions were subjected to aging at a room temperature for 24 h.

When rolling two-component systems the products of the chemical interaction between the components and also the simple mechanical mixtures can be formed. That is why a purification of the modified polymers was carried out by fivefold reprecipitation under cold conditions by ethanol from the solution in CCl_4. The samples for IR-spectroscopy absorption were prepared by watering from solution in carbon tetrachloride on a substrate of KBr. The film samples with the thickness of 0.07–0.12 mm for IR-spectroscopy attenuated total reflection (ATR) were prepared by the direct pressing without restrictive frameworks on fluoroplastic plates.

2.3. Research Method

IR spectra were registered by the infrared Fourier spectrometer "Spectrum BXII" of Perkin Company by absorption spectroscopy in the range of 450–4000 cm^{-1} and with the method of ATR on the ZnSe crystal in the range of 650–4400 cm^{-1} with the subsequent transformation by Kubelka-Munk. All spectra were normalized according to an internal standard and the intensity of the band of 720 cm^{-1} related to the deformation vibrations of CH_2 groups of the main chain not involved in the chemical reaction was assumed as the internal standard [1, 4]. The original spectra in the coordinates of the optical density – wave number were processed using the software package ACD/SpecManager (ACD/UV-IR Manager & UV-IR Processor. Version 6.0 for Microsoft Windows) to separate the individual components of the spectrum in the areas corresponding to strongly overlapping absorption bands. The contours shape during the spectra simulation is a mixed Gaussian-Lorentzian. After converting the spectra to eliminate the influence of the penetration depth of radiation and automatically determine the main peaks position a preliminary decomposition of the spectrum on these bands was conducted. The first derivative of the experimental contour and the deviation of the calculated spectrum from the experimental spectrum were analyzed. The most probable position of the characteristic peaks not recorded in the preliminary decomposition was determined by the deviation of the resulting deviation from the zero level and the position of the peaks on the graph of the derivative, taking into account the literature data. The addition of a decomposition component was carried out step by step with the expansion of the spectrum conduction, taking into account the added peak and the deviations of the calculated spectrum analysis.

The melt flow rate (MFR) was determined by capillary viscometer IIRT-5M according to the standards under the temperature of 398 K and the load of 2.16 kg.

The intrinsic viscosity was determined by the standard method [5] in carbon tetrachloride solution at 298 K.

3. Results and Discussion

The change of the macromolecules chemical structure as a result of polymer-analogous transformations can be analyzed by various spectroscopic methods. Qualitative differences between the IR spectra of modified and unmodified samples confirm this fact (Figs. 1 and 2). On spectra of polymers modified with ethylsilicates the bands related to silicone fragments in the areas of 1020–1090 cm^{-1}, 780–830 cm^{-1}, specific for the stretching vibrations of Si–O, Si–O–Si, Si–O–C appears, as well as the band of 971 cm^{-1} appears, characterizing Si–O and Si–O–Si bonds in the cross-linked siloxane fragments. The difference in the nature of optical density changes is possibly due to the different structures formed during the reaction of organosilicon fragments.

It was established earlier [1, 2] that the introduction of tetraethoxysilane in the sevilen leads to a splitting in the IR spectra of characteristic band of 1240 cm^{-1} corresponding to the stretching vibrations of C–O bond in ester groups caused by the substitution of acetyl fragment of the copolymer for the remainder of organosilicon modifier. A similar splitting was observed for ethylene copolymers with vinylacetate and maleic anhydride (Fig. 3). The vibrations of C–O bonds are in strong interaction with the vibrations of C–C bonds due to small differences in power coefficients and the proximity of the atoms masses forming the bond. Therefore, the contour of the C–O bands is characterized by the presence of satellites due to rotational isomerism with respect to σ-bonds [6, 7]. The characteristic band shift of the stretching vibrations of C–O bond in the direction of higher frequencies during the substitution of the acetate fragment by the silicone is due to the tension connection by the steric interactions of volume replacement groups [8]. A decrease in the intensity of the characteristic band of 1462 cm^{-1} corresponding to the deformation vibrations of methyl groups in vinylacetate has been observed for EVAMA as well as in the modification of EVA (Fig. 4), which confirms the participation of both copolymers EVA and EVAMA in the transesterification reaction of acetyl fragment.

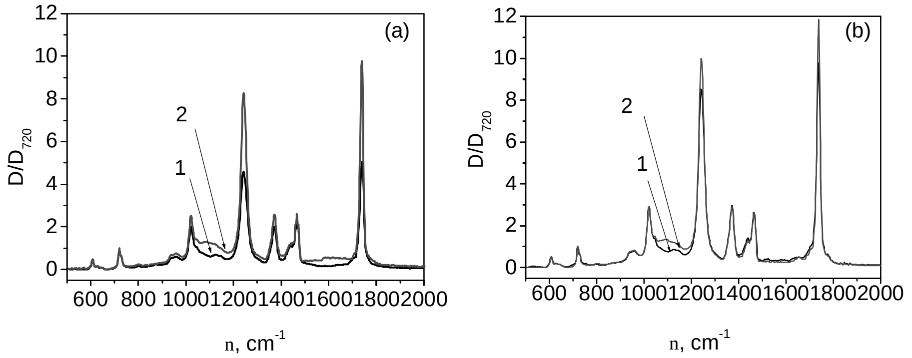

Fig. 1. IR spectra absorption of EVA 27 (a) and EVAMA 26 (b) initial (1) and modified by ethylsilicates (2)

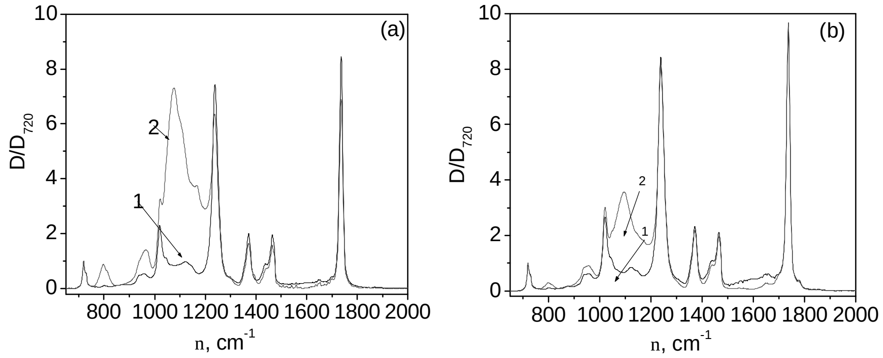

Fig. 2. IR-spectra ATR of EVA 27 (a) and EVAMA 26 (b) initial (1) and modified by ethylsilicates (2)

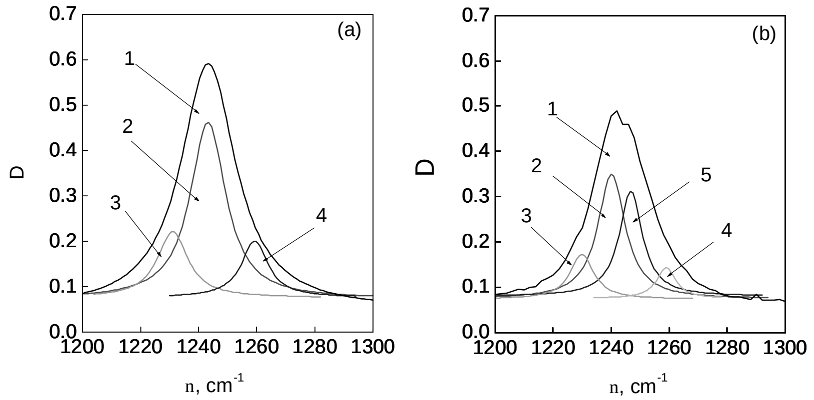

Fig. 3. Computer decomposition of the infrared spectra in the region of stretching vibrations of C–O bond in ester groups of EVAMA initial (a) and modified by ethylsilicates (b). Observed absorption band of 1240 cm^{-1} (1); individual components of the spectrum: 1240 cm^{-1} (2), 1230 cm^{-1} (3), 1259 cm^{-1} (4) and 1246 cm^{-1} (5)

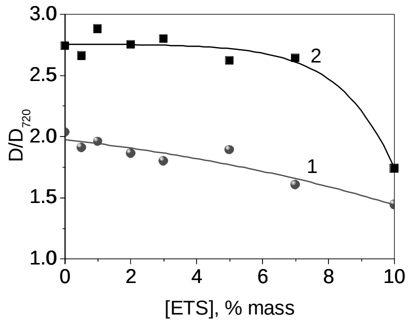

Fig. 4. Dependence of the relative optical density of the band of 1462 cm^{-1} in EVA 27 (1) and EVAMA 26 (2) on the content of ETS (IR-spectroscopy absorption)

The absence of characteristic bands doublets of 1790 cm^{-1} and 1850 cm^{-1} related to the stretching vibrations of C=O groups of maleic anhydride, both in the modified and unmodified terpolymer is of great interest, though in IR-spectra of films obtained from EVAMA granules, it is presented. We can assume that it is due to the intense thermomechanical effects in the oxygen environment during the rolling, which results in the anhydride cycle opening with the formation of carboxylic acid, reacting further with alkoxy groups of the modifier.

In the spectra of organosilicon compounds the band of 1070 cm^{-1} corresponding to the stretching vibrations of Si–O–Si groups is indicated vividly. This band is present, respectively, in the spectra of the modified copolymers. The introduction of the modifier into the polymer, naturally, leads to an increase of the optical density of this band corresponding to the total content of Si–O–Si links, which is in the direct ratio to the amount of the injected additive (Fig. 5). However, it was found that the surface layers of the polymer are enriched by siloxane phase, as evidenced by the differences in the growth of the characteristic band of 1070 cm^{-1} in the spectra obtained by ATR (surface layer) and by the absorption IR spectroscopy (integral). It was established earlier [9] that EVA modified by ethylsilicate is a two-component heterophase system. Since polysiloxanes and polyolefins have different segmental mobility and large differences in free surface energy, it was suggested that the migration of grafted siloxane fragments into the subsurface layers of material is possible during the formation of the samples. The saturation of the polymer surface layer during the silanol modification may be of great interest in the development of adhesive materials.

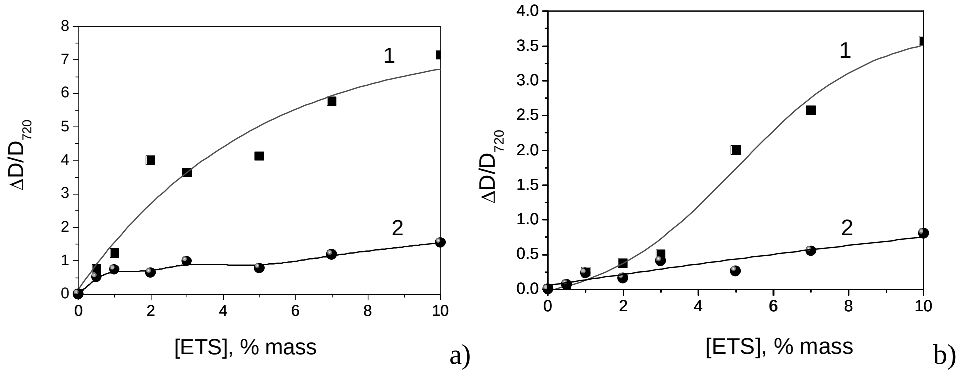

Fig. 5. Dependence of the relative optical density of the band of 1070 cm^{-1} in the ATR spectra (1) and IR spectra absorption (2) in EVA 27 (a) and EVAMA 26 (b) on the content of ETS

4. Conclusions

In the course of the studies, the effect of maleic anhydride contained in EVAMA on the chemical interaction between polymer and ethylsilicate and the change of the properties of copolymers in the process of silanol modification have not been detected, probably due to the small (not more than 2 %) amounts of the comonomer. Previously, it had been found that the introduction of the ethylsilicate into the polymer composites leads to a change in its phase structure [9] and to an increase of the adhesive strength of the material to the metal [1]. Therefore, the data of the effect of ETS on the chemical structure of modified polymers, as well as the fact of the enrichment of the polymers surface layers by the siloxane phase, may be useful in designing of the chemical structure of adhesive materials for different purposes.

References

[1] Rusanova S.: PhD thesis, Kazanski Gos. Texnol. Univ, Kazan 2000.

[2] Stoyanov O., Rusanova S., Petukhova O. and Remisov A.: Zh. Prikl. Khimii, 2001, **74**, 1174.

[3] Bounor-Legaré V., Ferreira I., Verbois A. *et al.*: Polymer, 2002, **43**, 6085.

[4] Bogatyrev V., Maksakova G., Villevald G. and Logvinenko V.: Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim., 1986, **2**, 104.

[5] Kurenkov V., Budarina L. and Zaikin A.: Praktikum po Phizike i Khimii Polimerov. Khimiya-Koloss, Moskwa 2008.

[6] Barnsa A. and Orvill T. (Eds): Kolebatelnaya Spektroskopiya. Sovremennye Vozzreniya. Tendencii Razvitiya. Mir, Moskwa 1981.

[7] Orvill T. (Ed): Vnutrennee Vrashenie Molecul. Mir, Moskwa 1987.

[8] Belopolskaya T.: Vysokomol. Soed., 1972, **14**, 640.

[9] Chalykh A., Gerasimov V., Rusanova S. *et al.*: Vysokomol. Soed. A, 2006, **48,** 1801.

ІЧ-СПЕКТРОСКОПІЧНЕ ДОСЛІДЖЕННЯ СИЛАНОЛЬНОЇ МОДИФІКАЦІЇ КОПОЛІМЕРІВ ЕТИЛЕНУ

Анотація. *Методом абсорбційної ІЧ-спектроскопії та розсіяного загального відбиття вивчено взаємодію кремнійорганічних сполук і кополімерів етилену з вінілацетатом та малеїновим ангідридом. Встановлено, що відбувається збагачення поверхневих шарів полімерів силоксановою фазою, що може бути використано при формуванні хімічної структури адгезійних матеріалів різноманітного призначення.*

Ключові слова: *ІЧ-спектроскопія, хімічна взаємодія, кополімери етилену, кремнійорганічні сполуки..*