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X-RAY STRUCTURAL ANALYSIS OF A POLYMER MIXTURE OF ISOTACT POLYPROPYLENE AND ETHYLENE-PROPYLENE COPOLYMER

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ABSTRACT: The reliable functioning of the electrical-technical facilities basically depends on their electrical isolation in working conditions. This entails the use of high-quality isolation materials with suitable electrical-physical properties. The evaluation of these properties is conducted by applying certain electrical-physical methods of research. In this work the method of X-ray structural analysis has been employed to study the structural changes of homo-polymer polypropylene, in whose matrix high-molecule additives are inserted in definite quantity ratio. The modification of propylene allows its wider application as electrical isolation.

KEYWORDS: polypropylene, butadiene-stirene, ethylene-propylene, structure modifying, thermo stimulation current

INTRODUCTION

The development of polymer chemical synthesis has brought about the implementation of different types of synthetic high-molecule compounds. One of the most widely applied methods of physical modification of polymers is their mechanical mixing which results in polymer mixtures with valuable physic-mechanical qualities [1;2].

The present work is a continuation of a series of scientific researches [3,4] connected with the implementation of polymer mixtures of polypropylene (PP) with different kinds of polymers: amorphous; semi-crystal or block – and statistical co-polymers.

The aim is to examine the super-molecule structure of organization with the use of the structural method of the x-ray structural analysis.

The PP homo-polymer used of the BUPLIN 6531 make produced in LUKOIL BULGARIA Corp. in the city of Bourgas. Ethylene propylene co-polymer has the commercial brand name NOVOLEN 1200 NX of the German BASF Company.

To the polymer mixture is added a high-melting additive Hydrotalcite-like Compound DHT-4A, hydrate of magnesium-aluminum hydroxyl carbonate. It is white, non-toxic, finely dispersed powder with size of particles from 0.4 to 4 μ m. It does not dissolve in water and oils. It is a product of the Kyowa Chemical Industry Company – Japan. DHT-4A inactivates through chemical reactions the remaining quantities of substances connected with catalysts of acid type, like those of Cigler-Natta, used in the production of polyenes, of PP [5] in particular. DHT-4A not only substantially reduces, but even eliminates the corrosion activity of the polymer [6].

Scientific literature presents a number of announcements on the influence of DHT-4A on the corrosion activity of PP when processed [7, 8] but there is no data about the influence of the additive on the electrical-physical properties in mixture with PP.

The implemented polymer specimens have the form of circular discs with diameter (50-55) mm and thickness (2,00-2,06)mm.

TEST RESULTS AND THEIR PHYSICAL INTERPRETATION

To implement the x-ray structure analysis of polymer specimens TUR M62 x-ray de-fraction meter has been used. Ferrous selective filter for cobalt x-ray radiation has been employed with a wave length of $\lambda = 1,7909 \text{ \AA} = 0,17909 \text{ nm}$.

The tests have been conducted at room temperature, constant high-voltage tension of the x-ray tube $U = 32 \text{ kV}$ and power of the electric current $I = 12 \text{ mA}$; a stream of $6 \cdot 10^4 \text{ x-ray. imp/min}$; angle velocity of rotation of the goniometer with an installed polymer test specimen of $1^\circ/2 \text{ min}$; registration inductor – proportional counter of the VA-Z-522 type.

Under the given circumstances it follows that: the speeded electrons in the tube have kinetic energy of 32keV and velocity of $1,06 \cdot 10^8$ m/s; the x-ray rays radiated have frequency of $\nu = 1,68 \cdot 10^{18}$ s⁻¹ and energy 6,94keV. The consequent x-ray graphs are typical of PP [2] with clearly formed x-ray reflexes, one of which is double. The formation of the crystal x-ray reflexes and amorphous halo on the x-ray graphs has been conducted by the method of Hermans and Weidinger [9], described in [10]. Defining of the x-ray degree of crystallizing (χ) is performed through correlation (1):

$$\chi(\text{DRC}) = \left[\frac{\sum_{i=1}^k S(\text{RRC})_i}{\sum_{i=1}^k S(\text{RRC})_i + S(\text{HA})} \right]^{-1} \quad (1)$$

To define the inter-molecular spaces (d) within the crystal structures formula (2) of Breg-Wulf has been used, to read the angle (θ), referred to every crystal x-ray reflex

$$d_i = n\lambda (2 \sin \theta_i)^{-1} \quad (2)$$

To define the long period (L_i) of the crystals Sherer's formula (3)

$$L_i = 0.9 \lambda [(\Delta \theta_i) \cos \theta_i]^{-1} \quad (3)$$

where ($\Delta \theta$) is the width of the crystal x-ray reflexes at half its height, the change of ($\Delta \theta$) being in radians (rad).

To read the temperature factor and the difference in the density of the crystal and amorphous phase in the semi-crystal polymers a correction coefficient has been introduced (0,556) in the correlation (1), which assumes appearance (4):

$$\tilde{\chi}(\text{DRC}) = \left[\frac{\sum_{i=1}^k S(\text{RRC})_i}{\sum_{i=1}^k S(\text{RRC})_i + 0.556S(\text{HA})} \right]^{-1} \quad (4)$$

The resulting x-ray graphs are typical of the semi-crystal polymers of the PP [10] type with clearly formed 8 crystal x-ray reflexes. The differentiation of the crystal x-ray reflexes from the amorphous halo on the x-ray graphs has been conducted by the method of Hermans and Weidinger. After defining the angles (θ), corresponding to the respective crystal x-ray reflexes, Breg and Wulf formula (2) has been applied to define the corresponding 8 types of inter-plane spaces (d_i) in the crystallites in the pure PP and in the polymer mixtures of PP and the ethylene-propylene co-polymer (EPC). The following figure values of (d_i) have resulted: 6.23;5.48;5.21; 4.75;4.20;4.07;3.47;3.12 Å. These figure values refer to the pure PP, but they do not change with the polymer mixtures of PP and EPC, which demonstrates the existence of free crystallization of the macro-molecule PP chains, without any substantial influence of the macro-molecule EPC chains in the polymer mixtures, which crystallize as well.

In this case the crystal x-ray reflexes corresponding to (d_i) of pure PP and pure EPC have similar values of (d_i) and therefore no substantial deviations of (d_i) in polymer mixtures have been detected.

Synthesizing of co-polymers of ethylene and propylene provides the opportunity to implement new co-polymer systems with complexes of physic-mechanical qualities which in certain cases have proved much better than those of the corresponding homo-polymers – polypropylene and polyethylene [11]. The improved elasticity and stroke-resistance of the implementation within aggressive environments [11], moisture- and cold-resistance [12], electrical stability, mechanical endurance [13-15], wear-and-tear resistance [16], as well as other important qualities [17] make possible the wide practical application of EPC.

[18] shows correlation (5) between (d_i) and the effective diameter (\tilde{d}_i) of macromolecular chains [19], which is of the type

$$\tilde{d}_i = (d_i)^{1.22} \quad (5)$$

Replacement of the figure values of (d_i) in (5) results in the following figure values of (\tilde{d}_i): 9.32; 7.97; 7.49; 6.69; 5.76; 5.54; 4.56; 4.01 Å, which correspond to the crystal x-ray reflexes of the x-ray graphs of pure PP and of polymer mixtures of PP and EPC.

When reading the chemical composition and structure of the monomer units of PP and polyethylene, it can be assumed that the maximum geometrical diameter ($(d_r)_{\max}$) of macromolecular chains is of the type

$$(d_r)_{\max} = 2[\ell(\text{C}-\text{C}) + \ell(\text{C}-\text{H})] \quad (6)$$

According to [20], the lengths of the chemical links are: $\ell(C-C)=1.5\text{\AA}$ and $\ell(C-H)=1.1\text{\AA}$, from (6) it follows that $(d_r)_{\max}=5.2\text{\AA}$. As far as $(d_r)_{\min}$ is concerned, the figure value is $(d_r)_{\min}=3.7\text{\AA}$. From the point of view of molecular physics, repulsive forces between the molecules arise at the distance of $\ell < 2\text{\AA}$ between them. The effective diameter (\tilde{d}_i) of the macro-molecule chains “reads” the existence of repulsive forces at the formation of the inter-molecular and super-molecular structural organization, which proves the reality of the figure values of (\tilde{d}_i) , resulting from the x-ray structural analysis.

By applying Sherer’s formula the long periods of (L_i) of the crystals have been defined, corresponding to (d_i) and the crystal x-ray from the x-ray graphs. The resulting figure values of (L_i) are presented in table 1, the interval of change being $(120 \div 693)\text{\AA}$ and correspond to literary data that usually for different types of semi-crystal polymers $L = (100 \div 1000)\text{\AA}$ [21].

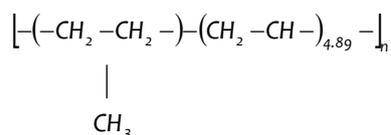
When comparing the x-ray graphs with the resulting crystal x-ray reflexes for the pure PP and its polymer mixtures with EPC disappearance of the seventh (last) crystal x-ray reflex has been detected for the test specimens of polymer mixtures. Consequently this is the only example of certain substantial influence of EPC for the formation of the super-molecular structure of organization in the polymer mixtures.

Table 1.

Nº	specimens	L_1 [Å] L_2	L_3 L_4	L_5 L_6	L_7 L_8	χ $\chi_{\text{correct.}}$	$\tilde{\chi}$ $\tilde{\chi}_{\text{correct.}}$
1	PP	352	446	246	382	76	85
		693	369	234	193	66	78
2	PP+ 15 mass % EPC	373	391	236	319	69	80
		699	313	245	-	57	70
3	PP + 20 mass % EPC	397	392	120	273	68	79
		624	313	273	-	60	73
4	PP + 25 mass % EPC	340	408	236	368	70	81
		624	289	263	-	57	70
5	PP + 30 mass % EPC	359	375	236	347	72	82
		624	303	252	-	59	72

An x-ray degree of crystal purity has been defined as well (χ) and $(\tilde{\chi})$ respectively through correlations (1) and (4). A correction in the amorphous halo in the x-ray graphs has been made, with the definition of $(\chi_{\text{correct.}})$, $(\tilde{\chi}_{\text{correct.}})$ which have been presented in table 1, too. Some insufficient changes have been noted on their figure values within the transition from pure PP to polymer mixtures of PP and EPC.

Verification of the thermodynamic compatibility of the two components of the PP and EPC polymer mixtures has been carried out. For this purpose the method of adaptive additive atom-group admixtures has been employed [22], the perimeter of dissolving being specifically defined (δ_p) by the method of [23]. The following has resulted: $\delta_p(\text{PP})=7.62(\text{cal}/\text{cm}^3)^{1/2}$ and $\delta_p(\text{EPC})=7.69(\text{cal}/\text{cm}^3)^{1/2}$, which shows that the figure values of (δ_p) with the two components are very close and that existence of thermodynamic compatibility should be expected on this basis. Having in mind the massive presence of the two components in EPC PC - 12 mass% E + 88 mass% P the type of the average co-polymer unit has been defined which is of the type



which has a mass $M = 233.83\text{ aem} = 3.88 \cdot 10^{-25}\text{ kg}$ and a volume $V = 273.0\text{ cm}^3/\text{mol} = 4.53 \cdot 10^{-28}\text{ m}^3$.

CONCLUSIONS

8 crystal x-ray reflexes have been implemented of x-ray graphs from the x-ray structural analysis. The addition of EPC in PP and the resulting of the different types of polymers does not change (d) and causes change in (L_i) and (χ_i) . This proves that there is no substantial difference in the processes of crystallization that have occurred in the different test specimens. The close values of (δ_p) of the two components of PP and EPC makes it possible to assume that the necessary thermo-dynamic compatibility is in existence.

The individual influence of 0.05% DHT-4A does not show any change of the electrical-physical properties of pure and modified PP. The use of DHT-4A shows the efficiency of its employment as an anti-corrosion modifier of polypropylene.

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