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**FEATURES OF THERMAL OXIDATIVE DESTRUCTION
OF POLYMER BLENDS OF POLYVINYLCHLORIDE
AND LINEAR COPOLYMER OF POLYETHYLENE
WITH BUTENE - 1**

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Abstract: Features of thermo-oxidative destruction of polymeric mixtures of polyvinylchloride (PVC) and linear copolymer of polyethylene with butene - 1 (LLDPE) are investigated in this paper. Influence of composition of polymeric mixtures of PVC/LLDPE and type of the compatibilizer on thermo-oxidative destruction of the composition is revealed. It is shown that for polymeric mixtures containing a compatibilizer, thermal decomposition is observed in several stages, the number of which grows with the increase in the concentration of LLDPE 's in the mixture. For each stage of thermal decomposition, a grafted copolymer is responsible for the thermal stability of the composition, which is formed by the reaction of recombination of radicals of both PVC and LLDPE. It has been revealed that the use of chlorinated polyethylene as a compatibilizer contributes to the increase of thermal stability of the composition.

Keywords: polyvinylchloride, linear low density polyethylene, polymeric mixtures, chlorinated polyethylene, grafted copolymer, compatibilizer, thermal stability, polyene and carbonyl indexes.

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INTRODUCTION

Despite the wide use of polyvinylchloride (PVC) in different spheres of our life, this polymer has low thermal stability [1].

Degradation of PVC is conditioned by the process of dehydrochlorination, which results in the formation of long

polysacchaged double bonds, i.e. polyene sequences $(-\text{CH}=\text{CH}-)_n$, accompanied by a change in sample color from white to yellow-brown. This process is much faster in the presence of oxygen, forming a carbonyl group. In turn, polyene sequences tend to cross-link and degrade PVC macromolecules [2].

It is known that PVC application areas can be extended by formation of polymeric mixtures, in particular, with polyethylene (PE). For such systems, the researchers' interests were related to the identification of the peculiarities of thermal oxidation degradation, including the presence of various compatibilizers and their impact on operational characteristics. A number of papers [3-6] are devoted to the study of this problem.

The conclusions of these studies can be briefly formulated as follows: experimentally proved the presence of interactions between components due to produced radicals, leading to the formation of grafted and block copolymers, cross-linked structures; at low PE content a decrease in polyene index and glass transition temperature was detected; increase in thermal stability was expressed by an increase in the initial decomposition temperature of PVC; suppression of the process of dehydrochlorination of PVC, a competitive reaction of recombination of the forming macro

This paper presents the results of the thermal behavior of a mixture of PVC with a linear copolymer of polyethylene with butene -1 (LLDPE) in a wide range of ratios of PVC/LLDPE in the presence of two types of compounds - grafted copolymer of PVC-g-LLDPE(and chlorinated polyethylene (CPE), containing 35 wt% chlorine.

EXPERIMENTAL

The synthesis of the grafted PE-PVC copolymer was performed as follows: 300 ml of m-xylene and 20

ml of cyclohexanone were poured into a four-neck flask, 4 g of LLDPE (F - 0320) and 4 g of PVC suspension (C - 70) were added. The flask was heated up to 130°C and stirred until the polymers were completely dissolved in the solvent mixture. Then the temperature of the solution was reduced to ? 90°C and 0.08 g of benzoyl peroxide in xylene solution (~4 ml) was added by drops. After adding benzoyl peroxide, the solution temperature was gradually raised to boiling point (~137°C) and at intensive mixing the reaction continued for 2.5 hours, then the temperature was raised to 139°C and mixing continued for another 15 minutes. After the vaccination reaction the solution remained transparent. After cooling to room temperature, the formed sediment in the form of swollen polymer was separated from the solvent by filtration method. The resulting product (grafted copolymer) was dried at 500°C in a thermal cabinet to remove the residual weight of the solvent.

The obtained grafted copolymer was used as a compiler when obtaining polymeric mixtures.

Polymer-polymeric mixtures were obtained in Plasticorder Brabender OHG DUISBURG (Germany) during 15 min, at 50 rpm and $180 \pm 5^\circ\text{C}$.

In work used: PVC suspension mark C-7059-M. Manufacturer of Bashkir soda company Joint Stock Company Russia, Republic of Bashkortostan and F-0320 LLDPE, $\rho = 0.920 \text{ g/cm}^3$, MFI = 2.5 g/

10min (2.16 kg). Manufacturer - Shurtan gas-chemical complex of Uzbekistan; n-dioctylphthalate (DOP), $M = 390.56$ g/mol; colorless oily liquid; $d_4^{20} = 0.978$ g/cm³;

Thermal analysis of polymeric mixtures was carried out in dynamic mode on the device Q500 [thermogravimetric analysis (TGA) simultaneous thermogravimetric analyzer] (in the air atmosphere) in the temperature range of 20 - 1000 °C, according to the requirements established by the standard ASTM E 1131. The heating rate was 10 °C/min, and the sample weight for analysis was from 2 to 100 mg.

To assess the degree of degradation of PVC, we determined the polished and carbonyl indexes using infrared spectroscopy. Spectroscopic analysis of the studied compositions was carried out on the Thermo Nicolet 6700 ATR/FTIR in the range from 400 to 4000 cm⁻¹. For the analysis the samples were used in the form of films with an average thickness of 80 μm, which were prepared by pressing at 190 °C for 3 min. The carbonyl and polyene indices were calculated according to the method [15] from peaks with three different wave numbers: a) 2920 cm⁻¹ corresponding to the valence oscillations of -CH₂-, (b) 1725 cm⁻¹ for carbonyl groups and (c) 1580 cm⁻¹ for polyene sequences, as shown in equations 1 and 2[15].

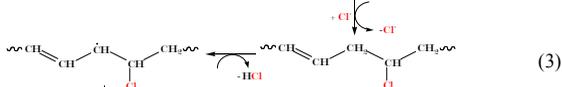
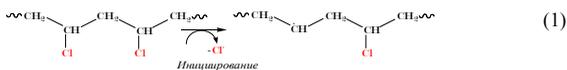
$$\text{Carbonyl index} = \frac{T_B - T_{1725}}{T_B - T_{2920}}$$

$$\text{Polyene index} = \frac{T_B - T_{1580}}{T_B - T_{2920}}$$

The morphology of polymeric mixtures was studied using atomic force (scanning probe microscope Agilent 5500) microscopy at room temperature. Silicon cantilevers with a stiffness of 9.5 N/m and a frequency of 145 kHz were used. The maximum scanning area on AFM on X, Y is 15x15μm², on Z - 1 μm.

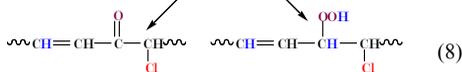
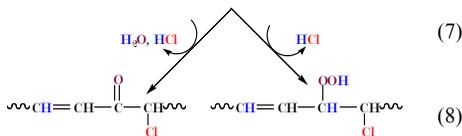
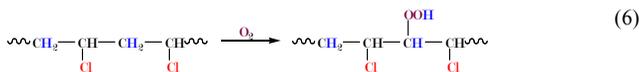
RESULTS AND DISCUSSION

Due to the fact that the composition of the polymeric mixture includes PVC and PE, it is advisable to consider the thermal decomposition of each component separately from the outset. Thus, for thermal dehydrochlorination of PVC, different stages of the radical mechanism are represented by reactions according to Scheme I:



Initiation occurs as a result of separation of the Cl atom from the labile structural group. It is assumed that chlorine atoms mainly react with hydrogen atoms of the neighboring methylene group to form conjugated unsaturated bonds. Chain breakage occurs by the reaction of chlorine atoms recombination [7].

Thermooxidative destruction of PVC (Fig. 1) occurs in two stages. Thus, when the polymer heats up above 100oC (no more than 350oC), HCl (activation energy of 20-39 kcal/mol) and very small (less than 3%) amounts of aromatic hydrocarbons are mainly released at the first stage; at the same time, conjugate bonds -C=C- are formed, which are distributed in different ways in chains [8]. The peculiarities of oxidative decomposition of PVC are obviously connected with heterolytic decomposition of hydroperoxides under the action of HCl at the moment of their formation.

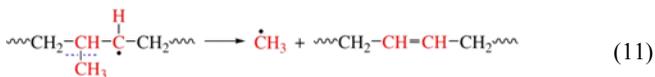
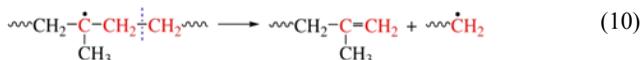


When a certain number of double bonds are reached, the influence of oxygen on the process of HCl elimination is significantly enhanced by the oxidation of unsaturated bonds and the formation of carbonyl, hydroxyl, ether and other oxygen-containing groups.

Transverse bonds in macromolecules are usually formed when PVC is heated for a long time (2-4 hours, at 175oC). In the products of PVC pyrolysis (the second stage of decomposition) (400oC, 30 min), except

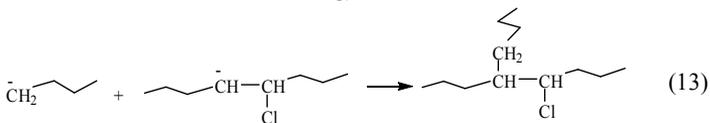
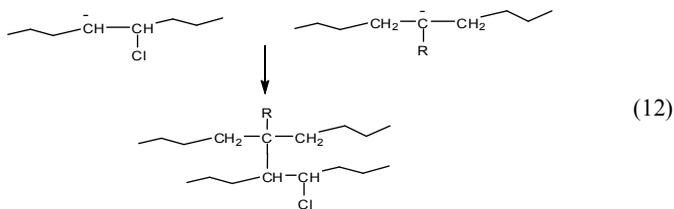
for carbonized and partially graphitized PVC and HCl, hydrocarbons were found [8].

Thermodegradation of PE (Fig.1) (proceeds in one stage) leads to the reduction of molecular weight, formation of oligomers and low-molecular hydrocarbons. At relatively low temperatures, compounds with unsaturated bonds are formed, which are accumulated continuously during the entire process period according to Scheme II:



In the presence of oxygen, oxidation of polyethylene macromolecules, which consist of compounds containing a carbonyl group - ketones and aldehydes - occurs in parallel with these processes. The concentration of these compounds increases at 270°C and decreases at 300°C. At temperatures above 300°C, compounds containing an²-epoxide group are found, the formation of which begins with a hydroperoxide OO-macroradical [9].

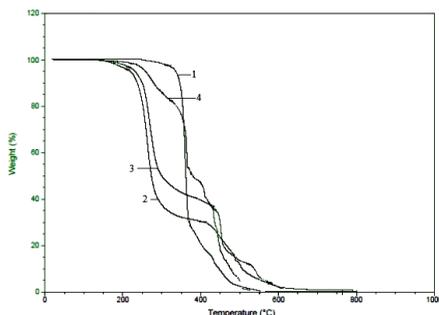
During the process of thermal destruction of PVC/PE mixture components, the recombination of PVC and PE macroradicals is reacted according to scheme III [14]:



As can be seen from the above scheme, the formation of PVC macroradicals in the process of dehydrochlorination is observed, and in PE as a result of dehydrogenation, and, as noted in [13,14], the latter occurs much faster compared to PVC, culminating in the break of long PE chains into short (reactions 9-11). At the initial stage, the competition

between PVC dehydrochlorination, intra-molecular cross-linking of PVC macrochains and the reaction between PVC and PE macroradicals is in favor of the latter, i.e. the reaction with the formation of a grafted copolymer of PVC components leading to increased thermal stability of PVC (reactions 12, 13).

Proceeding from these considerations, let's consider the data of the results of thermal analysis of the polymeric mixtures under study presented in Fig. 1 and Table 1.



Picture 1. TG curves for samples: LLDPE-1, PVC-2, PVC/LLDPE (80/20) -3, LLDPE/PVC (80/20) - 4.

Fig. 1 shows that the decomposition of PVC and LLDPE before the loss of mass of 60-65% occurs in one stage, and as noted above, this process takes place at a high rate in PE. Introduction of LLDPE up to 20% slows down the PVC degradation process.

Table 1.

Name and composition of the sample	Temperature of indicated loss of mass, °C			PI	CI	Dispersion particlesize	
	Onset decomposition temperature T _d , °C (*)	5%	10%				
		T, °C	T, °C				T, °C
PVC-P	222,19 (4,62%)	222,0	244,0	259,8	0,100	0,775	-
PVC-P/LLDPE (80/20)	220,68 (3,06%)	239,56	256,3	270,3	0,028	0,633	2,5-5 μm
PVC-P/LLDPE/CPE (80/20/5)	238,20 (4,24%)	241,8	261,1	275,2	-	-	-
PVC-P/LLDPE/PVC-g-LLDPE(80/20/9)	237,91 (8,77%)	217,6	239,1	256,7	-	-	-
PVC-P/LLDPE (50/50)	206,57 (1,50%)	245,3	261,5	276,9	-	0,329	1,5-μm
PVC-P/LLDPE / PVC-g-LLDPE (50/50/3)	229,02 (2,12%)	252,2	262,2	278,6	-	-	-
LLDPE	316,52 (2,43%)	337,4	345,5	354,5	0,118	-	-
LLDPE / PVC-P (90/10)	235,84 (0,99)	277,2	313,1	365,9	-	0,142	1-1,5 μm
LLDPE / PVC-P (80/20)	229,77 (1,83%)	263,6	281,7	336,3	-	0,276	1,5-2 μm
LLDPE / PVC-P / CPE (80/20/5)	249,48 (2,44%)	265,89	231,7	354,54	-	-	-
LLDPE / PVC-P / PVC-g-LLDPE (80/20/6)	333,58 (3,84%)	336,3	351,3	359,1	-	-	300 μm

Note: PVC-P - PVC plasticized 25 wt% DOP; PI and CI - polyene and carbonyl indexes were determined according to [15]; (*) mass loss, % at T_d, 0C is indicated in brackets.

As it is said above, for PVC-P and LDPE thermal decomposition takes place in 2 stages, and for their polymeric mixtures it is possible to observe several stages with the initial decomposition temperature of 220 0C, inherent in PVC. The temperature position and the number of subsequent transitions are conditioned by the reaction products between PVC and LLDPE macroradicals, which is determined by the initial composition of the mixture.

Due to different decomposition mechanisms of the mixture components, it is reasonable to analyze the data separately for the PVC and PVC matrix composition in the form of a disperse phase in the LLDPE matrix.

Each stage is accompanied by the formation of both PVC and LLDPE radicals, and due to their recombination reaction the formation of grafted copolymers is completed. Thus, at the ratio of PVC-P/LLDPE - 80/20 thermal decomposition is observed in 3 stages. As can be seen from Table 1 in relation to PVC: at the first stage, respectively, an increase in the decomposition temperature is observed, 5%, 10% and 20% (T5, T10 and T20) of the mass loss of the samples; pyrolysis of PVC (carbonization and partial graphitization of PVC) begins with less mass loss; at the second stage, further decomposition of the mixture products is observed at a higher rate; at the third stage, decomposition of degradation products is also observed, but at a lower rate until the complete decomposition of the mixture.

As can be seen from Fig. 1, at the ratio of PVC-P/LLDPE - 50/50 thermal decomposition is observed similar to PVC - in the 2nd stage with a shift (by 20 0C) of the coking stage in the direction of lower mass losses, which is due to the reaction of recombination of the formed macroradicals of PVC and LLDPE. The introduction of the grafted copolymer as a compatibilizer leads to a further shift of the coking stage towards lower mass losses and the appearance of an additional transition in the form of a shoulder with higher mass losses.

At the ratio of PVC-P/LLDPE 20/80 (PVC in the form of a disperse phase) there are already 4 stages of destruction, where each subsequent stage is accompanied by an increase in thermal resistance and a shift in the pyrolysis stage towards lower mass losses (Fig. 1).

As it was noted above, at low LLDPE content (up to 20% weight) PVC thermal stability increases due to the predominant formation of grafted copolymer with short LLDPE chains as compared to the process of dehydrochlorination and intramolecular cross-linking of PVC. In confirmation of this picture, the values of carbonyl and polyene indexes also testify, which for the composition containing 20% LLDPE decrease by 18% and 72% respectively (Table 1).

At equal content of components, coexistence of two continuous phases (Fig.2) is observed, thus (in relation to PVC) Td decreases on 16 0C whereas T5, T10 and T20 increase on 23, 17,7 0C and 17,7 0C accordingly.

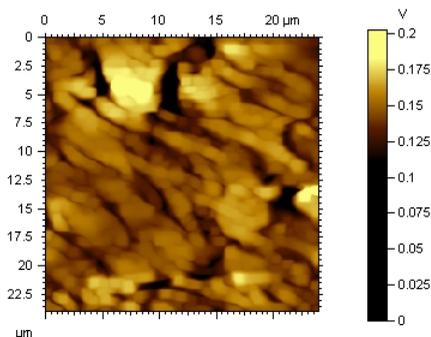


FIG.2 AFM photo micrographs of PVC/LLDPE (50/50)

When PVC/LLDPE polymers are added to the mixture of polymers, the thermal stability in relation to PVC and the initial mixture of polymers increases, and in the case of chlorinated PE it is much more effective. Such effect can be explained as follows in the formation of polymer-polymer mixture the compatibilizer in the form of grafted copolymer in the form of grafted copolymer of PVC and PE goes to the phase interface and, in general, the general picture of thermal decomposition of the mixture components practically does not change. In the case of a composition with a compatibilizer in the form of chlorinated polyethylene, macroradicals formed during the thermal decomposition of the compatibilizer are able to form in the matrix additionally grafted copolymers of both PVC and PE, which contributes to the formation of a larger number of grafted copolymers, and, accordingly, contributes to the thermal stability of the composition. This effect is manifested more with the growth of LLDPE concentration in the mixture (Table 1).

CONCLUSIONS

1. Thermal decomposition in several stages is observed for polymeric mixtures of PVC-P/LLDPE composition. For each stage of thermal decomposition, a grafted copolymer is responsible for the thermal stability of the composition, which is formed by the reaction of recombination of radicals of both PVC and LLDPE.
2. At low LLDPE content (up to 20 wt%) PVC thermal stability increases due to the predominant formation of grafted copolymer with short LLDPE chains as compared to the process of dehydrochlorination and intramolecular cross-linking of PVC
- 3 It has been revealed that the use of chlorinated polyethylene as a compatibilizer contributes to the increase of thermal stability of the composition.

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