Investigation of Destruction of Polymers Modified by Nitrogen and Phosphorus Containing Silicon-Organical Compounds

KURBANOVA M. A, ISMAILOV I.I., DJALILOV A.T., TILLAEV A.T., VALEEVA N.G.

Department of Chemistry, Tashkent State Technical University named after Beruni, Uzbekistan

Abstract

In this article thermal destruction of polyethylene modified silicon-organica antipyrine AP-1 and AP-1A (products of reaction metasilicate of sodium with adduct of urea with starinic acid) was investigated. For more precise definition of mechanism of action of stabilizers on the base silicates the kinetically parameters, loss of mass of polyethylene samples, their decomposition at different temperatures were determined. Results by investigation of influence of content of silicon-organica compounds in polymer on its thermo-oxized destruction are presented. Destruction was investigated by methods of differential thermal analysis (DTA) and thermo-gravimetrical analysis (TGA).

Key words: polyethylene, destruction, exploitation, polymeric materials, thermo-stability, silicon-organic polymers, thermo-oxidation, antipirene, sodium metasilicate, adducte, dermatographic curve.

Introduction

Owing to development of production and wide using of polymeric products it is necessary to value their behavior at different heat influences.

It is known that polymers can destructed under action of different agents presented in environment. Very often at exploitation of polymeric materials conditions can arise when duration of heating to temperature of beginning of their destruction can present parts of second. Obtain of thermo-stable silicon-organic polymers was a great success in field of polymer chemistry. At present time numerous investigations have been carried out by synthesis compounds containing silicon atoms bonding in different combinations with other different elements.

Materials and Methods

With aim of increasing of affectivity and thermo-oxidized stability of polymers a silicon-organic oligomers AP-1, AP-1A on the base of silicate has been synthesized which were introduced in different rations in polymer with aim of increasing of its thermo-stability. Polyethylene (PE) of low density of mark P-Y-342 was used as polymer.

Thermal stability is determined by temperature limit at which thermal or thermo-oxidized destruction of polymer sample accompanied by isolation of volatile products is begined. At destruction the loss of mass of investigation sample of polymer was observed and this fact has become of the base of thermo-gravimetric analysis of polymer (TGA).

Results of investigation of influence of silicon-organic oligomers content in PE on its thermo-oxized destruction are presented (methods TGA and DTA were used). More high thermo oxidezed stability of polymer modified by silicon-organic oligomers AP-1; AP-1A has been shown. It is recommended to use these oligomers as antipirene at production of PE.

Methods of Thermo-gravimetric Analysis

Result and Discussion

Theoretical aspects of destruction silicon-organic polymers are presented in [1,7]. For determination of mechanism of oxidation of compositions on the base of polyolefines it is necessary to investigate some physic-chemical transformations carrying out in multicomponent system under action of high temperatures. There are works [1,2] devoted to investigation of mechanism and kinetics of polyolefines and their compositions destruction in different conditions.

This investigation is devoted to dermatographic investigation of initial PE of low density (PELD) of mark P-Y-342 ShGGK (Shurtan gas-chemical complex) and also it`s samples modified by synthesized silicon-organic oligomers.

Thermal proper ties of samples were investigated on the derivatograph of system F.Paulik, I.Paulik and L.Erdej's in dynamical conditions at rate of temperature increasing 10% /min in open quartz crucibles in atmospheric air (Al_2O_3 was used as standard).

By data of DTGA stability of PE to action of high temperatures in air has increased at introduction in it antipyrine (AP). It is known that at 270 ^{o}C silicon-organic oligomers can be used during of prolonged time but at higher temperatures (370 ^{o}C and above) they are sufferers to reorganization with formation of low-molecular cyclic compounds. Thermal stability of silicon-organic oligomers is determined by stability of Si-O bond and modification of its electronic character can to carry out to increasing its thermo stability. Displacement of some bonds Si-O on bonds Si-R (where R-N or P) can carried out to increasing of thermal stability of silicon-organic oligomers.

Appearance in PE of silicon-organic groups has provide an increasing of critical temperature of beginning of its decomposition from 260 to 370 ^{o}C what is correlated with results of DTA according to which the first exothermal peak in range 355 ^{o}C at stabilized samples of PE has disappeared [3].

It was interested to investigate influence of AP on the base of silicate on kinetics of PE thermal destruction with aim of determination of some kinetics parameters of its decomposition and more precise of mechanism of action of stabilizes on the base of silicon.

Analysis of investigation of dependence of quantity of volatile products from time of PE pyrolysis (fig.1.) and kinetics of thermo-oxidized destruction of initial and modified PE containing 0,5-2 % AP (fig.2.) has shown that process of destruction was begined through definite time. This can be caused by regrouping of

structural elements and their condensation [3]. Time of intensive of gases isolation was equaled 15-65 min in dependence on of pyrolysis temperature. With increasing of time of samples exposure at given temperature before 6 h. at the intensivity of destruction of microspheres didn`t changed. At increasing of temperature process of destruction is unstable and characterized by additional isolation of volatile products before maximal level at this temperature. Then destruction process again has stabilized. Thus behavior of polymers at their destruction in isothermal conditions can be explained by limited mobility of intsecting segments of polymer net [4]. In result of thermal destruction accumulation of more stable, structural elements has carried out namely some compounds with silicon.

On the fig.1 integral curves of dependence on quantity of volatile compounds and logogriph of product remainder (dotted lines) from time of thermo-oxidizing destruction of   PE are presented which reflect almost ideal case of PE destruction by reaction of first order. By the inclination by dotted lines values of rate constant have been calculated. Rate of thermo-oxidizing destruction of PE was investigated   at temperatures 613, 643 and 633, 653 K.
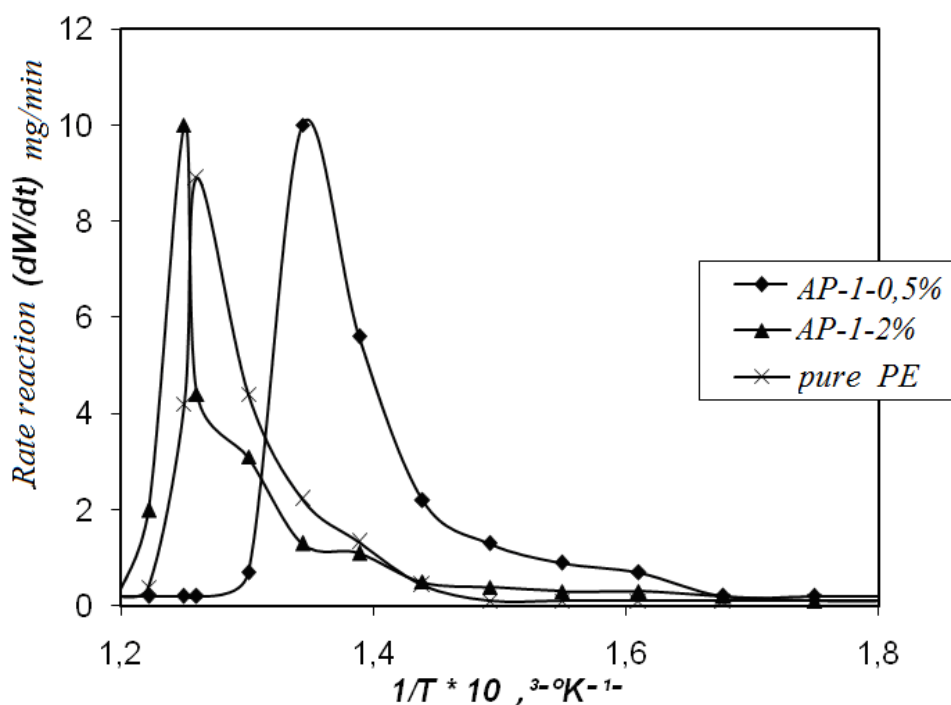

Fig.1. Destruction of PE in vacuum. The derivative of curve is prezented
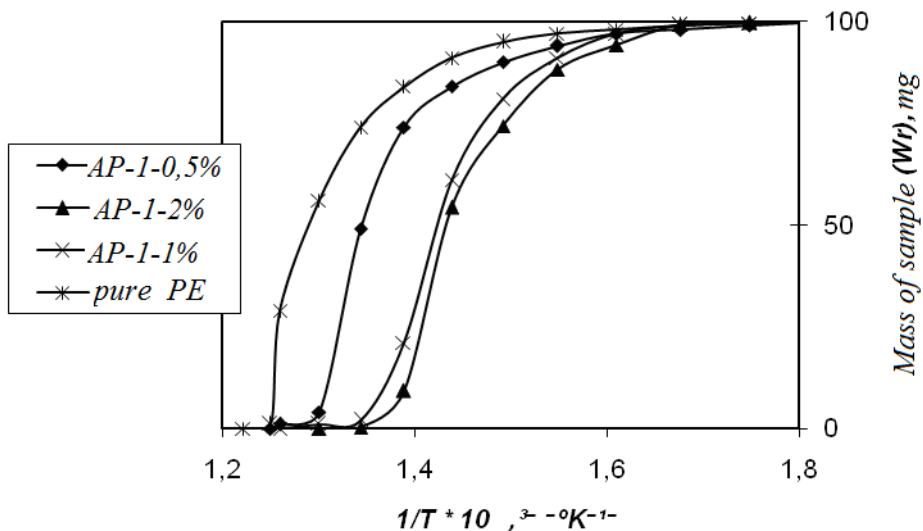as function of absolute temperature.

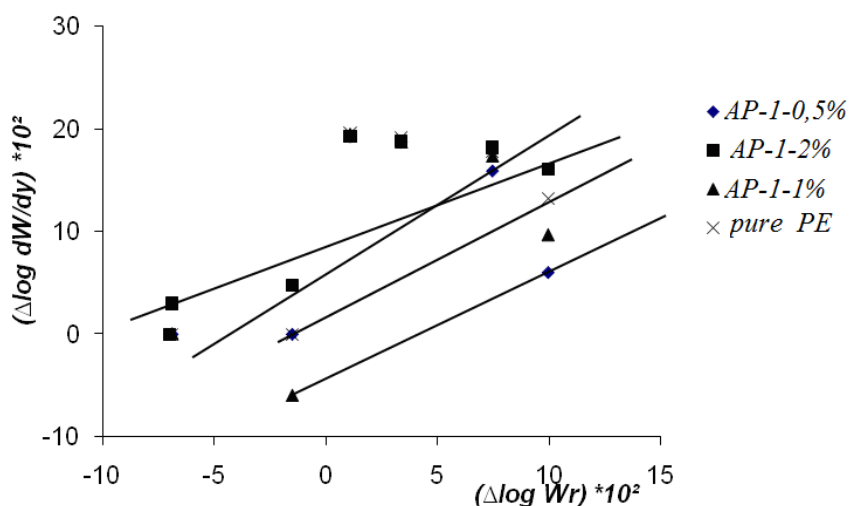Fig.2. loss of mass PE sample as function of 1/T

Fig.3. Kinetics parameters of thermodestruction of PE in vacuum (by data of fig. 1 and 2)

By these data the rates of isolation of volatile compounds were calculated and also curves of dependence of destruction of PE from quantity of volatile products were constructed (fig.2). On the base of these curves the rate of destruction was calculated; it`s dependence on depth of destruction is presented on fig.3. At first destruction has carried out with high rate but after loss about 10% mass rate decreased and then it increased more smoothly and dependence is presented almost right lines which were extrapolated to zero at 100% conversion.

Then thermal destruction was investigated in vacuum. Integral loss of mass in tests carrying out on spring balance in temperature interval 613-653 K is presented on fig.3 as complete curves by which it is possible

to judge about stabilization of destruction process which was begined after loss about 30-80 % mass of initial PE when all curves of rates are brought nearer to axis of abscess that is to zero values of rate.

On the base of these data the dependence of reaction rate from quantity of volatile products was determined (fig.4); at this obtained curves have affected almost ideal case of PE destruction by reaction of first order. Integral curves of mass and also curves of destruction rates have begined in the beginning of coordinates. The curves of rate have carried out through maximums at the conversion degree from 30 to 60% and rate of thermal destruction is in right dependence from temperature.
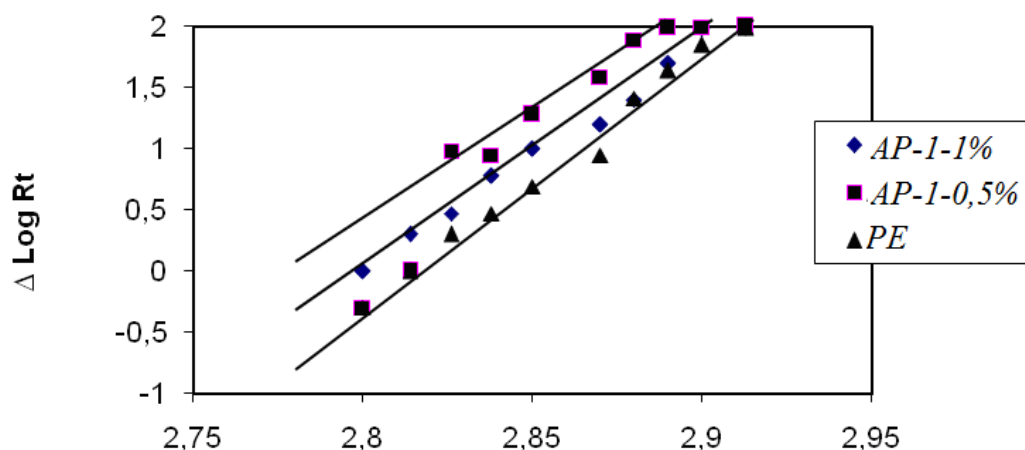

Fig.4. $\Delta log\ R_\tau$ as function of $\Delta log\ W_r$ for thermo destruction of PE in vacuum (by data of fig.1,2)

After carrying out of maximums curves straighten and at these segments of straights can be continued to axis of abscess (zero rate of reaction) and they intersect with it in points corresponding 100% conversion. Points of intersection of segments of straights with axis of ordinate can be considered as reactions rates (seeming initial rate).

On the base of determined regularities the order of destruction reaction of initial PE and it`s compositions was determined in isothermal conditions. Fractional order of destruction reaction of initial PE is caused by diffusion from it forming volatile gaseous products. Breaking of bonds and formation of new bonds at action of high temperatures are carried out sufficiently quickly in comparison with diffusion of products of oxidation and don`t introduce essential contribution in rate of destruction process.

Thermo stability is determined by temperature limit at which thermal or thermo-oxidized destruction of polymer begin with isolation of volatile products. Owing to this there is loss of mass of investigated sample of polymer. Temperature at which decreasing of polymer mass carried out has characterizes it`s thermo stability [6].

Thermo stability of polymers comprehensively is characterized by curves of TGA. But data obtained from curves of TGA it is necessary to express in some figures indexes. For this figures values characterizing different points of TGA are used. In table values of indexes using for characteristics of thermo stability of number of polymers are presented. They were obtained by method of TGA.

Table 1 Thermo-stable parameters of modified sample of PELP by data of TGA

Samples of polymers	Temperature of destruction, K				Loss of mass at definite	
	T_0	T_{10}	T_{20}	T_{50}	B_{673}	B_{783}
PELP –without stabilizers	613	683	703	733	9	-
PELP +AP-1 (0,5%)	643	703	733	753	6,8	37,9
PELP +AP-1 (1,0%)	653	723	753	763	3,0	34,0
PELP +AP-1 (2,0%)	633	693	733	783	4,1	38,2
PELP +AP-1A (1,0%)	653	723	753	773	4,0	32,3

N o t e : kinetic parameters by data TGA were calculated by method of Frimen-Kerol.

The data of corresponding temperatures which are used for characteristics of thermo-stability of polymers by characteristically points of gravimetrical curve of mass loss at temperature of destruction on the different stages: (T_0, T_{10}-10%, T_{20}-20% and so on). Thermostability also can be characterized by mass loss (B) in isothermal conditions at one definite temperature [7]. Authors [8] for estimation of thermo stability of polymers have proposed to use term "temperature of destruction" corresponding to temperature of beginning of mass loss at heating. Results of carrying investigation have shown that the least loss of mass and highest temperature of destruction have corresponded in all cases to optimal content of modification - 1,0 %. Obtained results are presented in table1.

Conclusions

Thus data presented on fig.1-4 have proved that PE containing modificators (AP-1; AP-1A) containing in their composition Si, N and P have shown more stability effect in comparison with pure PE. On the base of above mentioned data it is possible to maintain that synthesized nitrogen- and phosphorus-containing silicon-organic oligomers have increased the thermo stability of olefins and can be used as modificators in particular for PE.

References

[1] Andrianov K.A. Polymer with inorganic main chains of molecules. M, Publishing house an of the USSR, 1962, - p.7.

[2] Fraser A.G. Heat-resistant polymers. Publishing house "Chemistry", M, 1971.-p.30.

[3]   Shlyapnykov J. A. Anti-oxidizing stabilisation of polymers. Successes of chemistry, 1981, т.50, №6, - With. 1105-1140.

[4]   Shljapnikov J.A., Kirjushkin of this year, Maryin A.P. Ant oxidizing stabilisation of polymers. M: Chemistry. 1986, - With. p.256.

[5]   Beknazarov H.S., Djalilov A.T. Studying of ant oxidizing properties of derivatives gossypol at thermo oxidizing destruction PE. //Materials of the International scientific and technical conference «the Science, formation, manufacture in the decision of environmental problems» (Ecology-2006), Ufa-2006. T.2, pp.21-23.

[6]   Korshak V. V. Heat-resistant polymers. Publishing house "Science". M, 1969, - p.45.

[7]   Veliev M. G, Chalabieva L.Z., Ishchenko N.J., Askerov O.V. Issledovanie of modifying properties of some functional silicon-organic of connections. //J.Plasticheskie massa, №10, 2005.-p.24-25.

[8]   Horowitz E., Perros T.P., Inorg J. Nuclear Chem., 26, 1959, p.139.