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THERMAL PROPERTIES OF FILMS OF POLYETHYLENE WITH GRAFT POLYACRYLIC ACID

A. P. Polikarpov, L. P. Krul, I. F. Osipenko* and *N. R. Prokopchuk*

INSTITUTE OF PHYSICAL ORGANIC CHEMISTRY OF THE BYELORUSSIAN
ACADEMY OF SCIENCES, MINSK, 220603, U.S.S.R.
*SCIENTIFIC RESEARCH INSTITUTE OF PHYSICAL AND CHEMICAL PROBLEMS
OF THE BYELORUSSIAN LENIN STATE UNIVERSITY, MINSK, 220080, U.S.S.R.

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The processes of thermal and thermal-oxidative degradation taking place in polyethylene (PE) films modified by graft polyacrylic acid (PAA) have been studied by TG and DTA. The mutual influence of the components on the degradation of the macromolecules present in the graft copolymer has been revealed. The increase in thermal stability of PE in the graft copolymers is explained by the decrease in the molecular mobility in PE amorphous regions containing microphase particles of graft PAA.

Acrylic acid (AA) graft polymerization is an effective method of PE modification and permits improvements in the mechanical, adhesion, and sorption-diffusion properties, and also dyeability, cation-exchange properties and water-receptivity [1–8]. Graft polymerization may be performed in PE granules prior to their conversion into goods. Thus it is important to know the thermal properties of graft copolymers, because the optimal conditions of good moulding may be determined by taking into account the thermal and thermal-oxidative degradation of copolymer macromolecules. Data on the thermal stability of PE graft copolymers with AA are limited [7–11]. Little attention has previously been paid to the mutual influence of the PE and PAA in a copolymer on its thermal stability. The question of the cause of the thermal stability change remains to be classified.

The aim of the present paper is to investigate the mutual influence of the components on the thermal stability of PE films modified by AA grafting.

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Experimental

PE low-density films of 90 ± 5 mkm thickness with a molecular mass of 2.10^4 were used in the experiments. AA grafting was performed from toluene solutions by a known method [6]. PE films modified by graft polyacrylonitrile (PAN), polystyrene (PS) [9] and polyacrylic acid (PAA) isolated as a by-product in the experiments on graft polymerization, the initial PE, and blends of PE with PAA were studied for comparison. The content of the second component in the graft copolymers and blends with PE is expressed in mass fraction (x).

The thermal analysis of the polymers was performed in air and in an argon atmosphere on a Paulik, Paulik, Erdey derivatograph (type OD–103): the heating rate was 5 deg·min^{-1}.

Results

It is useful to compare the results of the thermal analysis of graft copolymers and the corresponding homopolymers (Figs 1 and 2) to estimate the mutual influence of

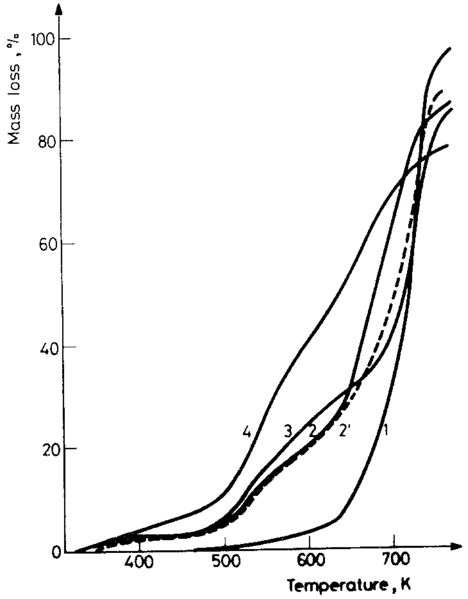

Fig. 1 TG curves of PE (1), PAA (4), PE and PAA blend (2, 2′) and PE and AA graft copolymer (3) with $x = 0.42$ in air atmosphere. Curves 1–4: experimental ones, curve 2′: calculated from curves 1 and 4 according to the additivity equation

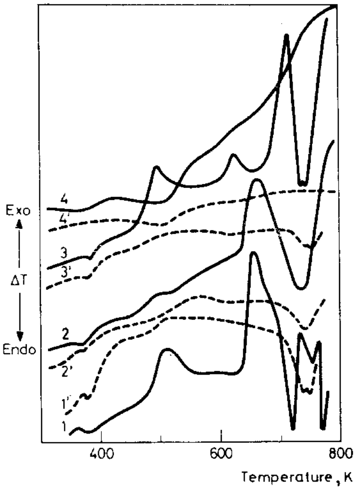

Fig. 2 DTA curves of PE (1, 1'), PAA (4, 4'), PE and PAA blend (2, 2') and PE and AA graft copolymer (3, 3') with $x = 0.42$ in an air (1–4, solid lines) and in an argon atmosphere (1–4', dushed lines)

the macromolecules present in the copolymer on the degradation of the sample as a whole. The homopolymers (PE and PAA) differ substantially in thermal stability.

The starting temperatures of PE (T_s^{PE}) and PAA (T_s^{PAA}) decomposition obtained by comparing the TG and DTG curves are 628 and 483 K in air, and 673 and 483 K in an argon atmosphere, respectively (Table 1). The mass loss (Δm) of PAA is substantially higher than that of PE in the temperature range 473–733 K. The relatively low PAA thermal stability is caused by macromolecule decarboxylation during heating [12]. A comparison of the TG and DTA curves of PE and PAA in air and argon atmospheres shows that the presence of oxygen accelerates PE decomposition while it only affects the PAA decomposition rate.

In the TG curves of the graft copolymer and the blend of PE and PAA there are two temperature regions in which a sharp increase of the decomposition rate is observed. Since the beginning of these temperature regions is close to the starting temperatures of the individual PE and PAA decompositions, the assumption may be made that they are characteristic of the beginnings of the PAA and PE decompositions in the composition. The values of T_s^{PE} and T_s^{PAA} for the PE and PAA blend and those for the corresponding homopolymers coincide. In the case of the graft copolymer ($x = 0.42$), the T_s^{PE} value is 35 deg (air) and 20 deg (argon) higher, while T_s^{PAA} value is 20 deg (air or argon) lower than those for the corresponding homopolymers (Table 1). The Δm values for the graft copolymer are slightly higher than those for the PE and PAA blend up to 635 K, and higher temperatures they are lower.

Table 1 Thermal stability characteristics of PE blends with PAA and graft copolymers of PE and AA

x	T_s^{PE}	$(T_m^{\mathrm{PE}})_{\mathrm{I}}$	$(T_m^{\mathrm{PE}})_{\mathrm{II}}$	T_s^{PAA}	T_m^{PAA}
	Temperature, K				
			Homopolymers		
0	628 (673)	653 (723)	733 (743)	—	—
1	—	—	—	483 (483)	548 (548)
			PEE–PAA blends		
0.24	623	658	733.	483	548
0.42	623	658	703	483	548
0.50	623	658	703	483	543
0.56	623	658	703	483	548
			Graft copolymers		
0.09	637	668	723	483	548
0.24	653 (683)	693 (723)	733 (743)	483 (483)	543 (548)
0.42	663 (693)	703 (733)	733 (743)	463 (463)	523 (523)
0.50	668	713	733	463	523
0.56	673 (703)	703 (733)	733 (748)	463 (463)	518 (518)

Values obtained in an argon atmosphere are given in parentheses.

A comparison of the experimental TG curve of the PE and PAA blend with that calculated via the additivity equation

$$\Delta m_T^b = (1-x)\Delta m_T^{\mathrm{PE}} + x\Delta m_T^{\mathrm{PAA}}$$

where Δm_T^b, Δm_T^{PE} and $\Delta m_T^{\mathrm{PAA}}$ are the values of Δm at temperature T for the blend, PEE and PAA, respectively, shows that up to T_s^{PE} these curves coincide, while at higher temperatures the experimental curve has higher Δm values. The TG curve of the graft copolymer in the above temperature region has lower Δm vlues, as compared with the experimental one for the blend and with the curve calculated via the additivity equation. Therefore, AA grafting to PE retards PE decomposition.

The thermal stability of graft copolymers depends primarily on the graft PAA content. The values of Δm for graft copolymers increase as the degree of grafting increases at temperatures lower than T_s^{PE} (Fig. 3). The values of T_s^{PE} for graft copolymers, and also the temperature of the PE maximum decomposition rate for the first stage of the process $(T_m^{\mathrm{PE}})_{\mathrm{I}}$, increase with increase of x, while the temperature of the PE maximum decomposition rate in the second stage $(T_m^{\mathrm{PE}})_{\mathrm{II}}$ is practically unchanged as compared with that of the initial PE (Table 1). The values of T_s^{PAA} in the graft copolymers are lower than those in the PAA homopolymer and

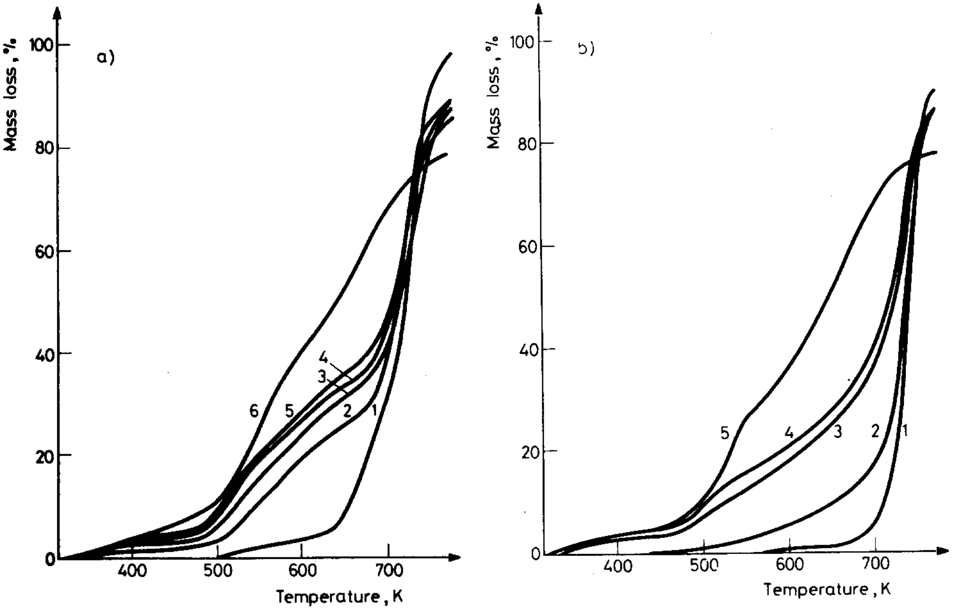

Fig. 3 TG curves of PE (1), PE and AA graft copolymers with x = 0.24 (2), 0.42 (3), 0.50 (4), 0.56 (5) and PAA (6) in an air (a) and in an argon (b) atmosphere

depend slightly on x, the temperature of the PAA maximum decomposition rate (T_m^{PAA}) decreasing from 543 to 518 K as x increases from 0.09 to 0.56. The parameters T_s^{PE} and $(T_m^{\mathrm{PE}})_{\mathrm{I}}$ for the graft samples in air are lower than in argon, while T_s^{PAA} and T_m^{PAA} are independent of the medium composition.

The thermal stabilities of the PE and AA graft copolymers depend not only on the degree of grafting, but also on the conditions of graft polymerization. Graft copolymers obtained from 30% solutions of AA in toluene have higher T_s^{PE} values than those grafted from 15% AA solutions (Fig. 4). Graft PAA decreases the molecular mobility of macromolecules in PE amorphous regions. Grafting conditions which influence the concentration and the microphase size, as well as the graft PAA distribution in the PE bulk, affect the degree of decrease of PE molecular mobility [11], and seem to affect the PE thermal stability in the graft copolymer.

A value of activation energy of degradation (E_d) may be determined from the results of dynamic TG [13]. It is an important characteristic of the thermal stability of the material and a parameter permitting the determination of a value of the intermolecular interaction energy in amorphous regions of the polymer from the results of mechanical testing [14]. The reaction order of PE and PAA decomposition is close to unity [12, 13], so the log-log method may be used to obtain the value of E_d

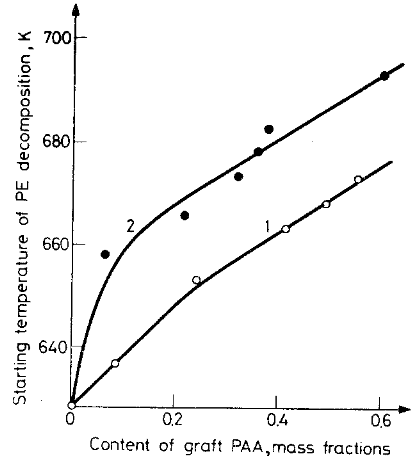

Fig. 4 Dependence of the starting temperature of PE decomposition on the content of graft PAA in films obtained by grafting from 15% (1) and 30% (2) solutions of AA in toluene

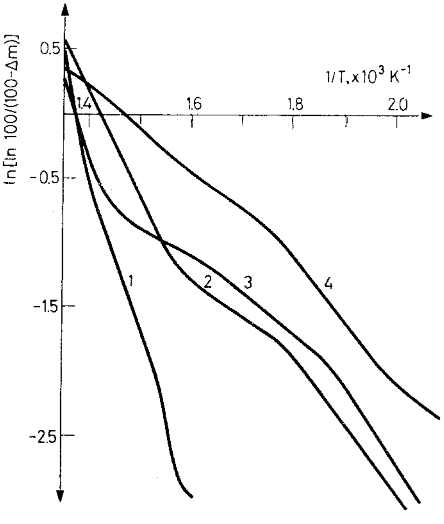

Fig. 5 Ln-ln value of a relative loss of mass of PE (1), PAA (4), PE and PAA blend (2) and PE and graft copolymer (3) with $x = 0.42$ in an air vs. reciprocal temperature

[13]. There are linear parts in the plot of $\ln\left(\ln\dfrac{100}{100-\Delta m}\right)$ *vs.* $1/T$ (Fig. 5). For the initial PE (curve 1) there is a linear part in the temperature region from 648 to 708 K. The beginning of this region is close to $(T_m^{PE})_I$. In this temperature region, Δm is about 35%. In the case of PAA (curve 4), there is also a linear part in the region from 508 to 565 K (close to T_m^{PAA}). The value of Δm for PAA in this region is

about 30%. Linear parts are found in curve 2 (for the PE and PAA blend) in the same temperature regions as in the homopolymer curves. Thus, the linear part of curve 2 in the temperature range 503–565 K is used to calculate, the PAA E_d values (E_d^{PAA}), while the linear part in the range 648–705 K is used to obtain the PE E_d (E_d^{PE}) values for the PE and PAA blend. The temperature regions used for the E_d^{PAA} calculations for the graft copolymers are shifted in accordance with the change in thermal stability of macromolecules present in the graft copolymer composition (Table 2).

The values of E_d^{PAA} for the graft copolymer and the PE and PAA blend are close, while E_d^{PE} for the former is higher than for the latter, especially in the tests carried out in air.

An increase in the thermal stability of the PE macromolecules is characteristic not only of PE with graft PAA, but also of other thermally stable polymers [9, 15].

Table 2 Dependence of the value of activation energy of PE and PAA blends and PE and AA graft copolymers on their composition

x	Thermal range of PE decomposition, K	E_d, kJ/mol	Thermal range of PAA decomposition, K	E_d, kJ/mol
		Homopolymers		
0	648–708 (703–743)	92 (271)	—	—
1	—	—	503–543 (498–548)	37 (46)
		PE–PAA blends		
0.24	648–673 633–703 (708–730)	68 64 (112)	473–523 473–573 (498–548)	43 43 (41)
0.42	648–673 633–703 (708–730)	71 48 (78)	483–553 473–573 (498–548)	45 36 (42)
0.50	663–678 633–703 (708–730)	72 44 (67)	483–553 473–573 (498–548)	44 33 (41)
0.56	648–673 633–703 (708–730)	58 41 (57)	483–553 473–573 (498–548)	44 35 (41)
		Graft copolymers		
0.24	688–718 (723–743)	109 (200)	473–543 (513–573)	56 (59)
0.42	703–723 (733–753)	87 (117)	473–533 (473–548)	49 (28)
0.50	693–733	83	473–533	46
0.56	703–723 (733–753)	88 (125)	473–533 (473–533)	45 (33)

Values obtained in an argon atmosphere are given in parentheses; values calculated from the TG experimental data for blends are in the numerator, those from TG curves calculated by additivity equation are in the denominator.

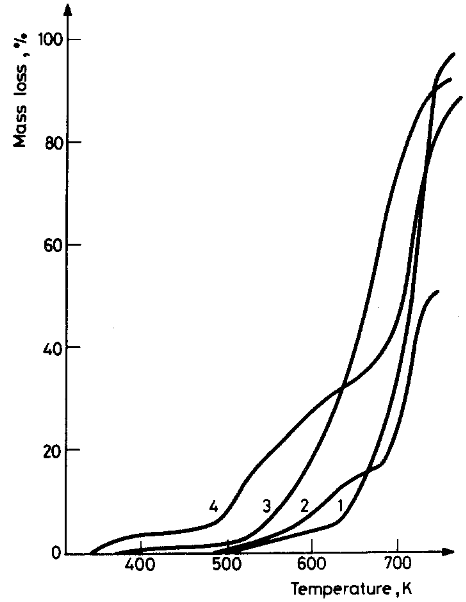

Fig. 6 TG curves of PE (1), PE graft copolymers with AN (2), styrene (3) and AA (4) in an air atmosphere; $x = 0.49$ (2), 0.51 (3), 0.50 (4)

In contrast to those of PE with graft PS, the TG curves of PE samples with graft PAA and PAN are shifted to higher temperatures in the region of strong PE decomposition (Fig. 6). The T_s^{PE} value for PE with graft PAA and PAN increases by 50–65 deg, compared with that of the initial PE, while that for PE with graft PS remains unchanged. The values of E_a^{PE} with graft PAA ($x = 0.50$), PAN ($x = 0.49$) and PS ($x = 0.51$) are 83, 101 and 75 kJ/mol, respectively.

It should be noted that PAA, PAN and PS differ in their thermal stabilities. Styrene grafting to PE does not substantially affect the molecular mobility of PE. This is evidenced by analysis of the thermal mechanical properties of graft copolymers [9] and by NMR broad line spectroscopy [16]. At the same time, AA and AN grafting lead to an increase in the energy of the intermolecular interaction in the PE amorphous region [15]. As a result of this the molecular mobility of PE decreases [9, 16]. An increase in the intermolecular interaction energy and a decrease in the molecular mobility in the PE amorphous regions are caused by the presence of graft polymer particles (graft structures) in these PE regions [15]. A comparison of the modes of influence of different graft polymers and grafting conditions on the thermal stability and molecular mobility of PE [9, 11] permits the supposition that the increase in PE thermal stability as a result of grafting is due to a decrease in the mobility of the PE chains fixed by graft structures, if the graft structures do not soften at the temperatures at which degradation of the initial PE creates PE thermal stability increases. In the case of destruction of the graft structures (PE and graft PS) at these temperatures, on heating the thermal stability of PE remains unchanged.

Thus, the phenomenon of increasing PE thermal stability in graft copolymers is based on a decrease in molecular mobility in PE amorphous regions caused by the formation of thermally stable particles of graft polymer microphase. An increase in the concentration of these particles leads to an increase in the effect of enhancing PE thermal stability.

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Zusammenfassung — Die bei der thermischen und thermisch-oxydativen Zersetzung in durch pfropfpolymerisierte Polyacrylsäure (PAA) verstärkten Polyethylen (PE)-Filmen verlaufenden Prozesse wurden mittels TG und DTA untersucht. Es wurde ein gegenseitiger Einfluß der Komponenten auf den Abbau der Pfropfpolymere bildenden Makromoleküle festgestellt. Die Erhöhung der thermischen Stabilität von PE in Pfropfpolymeren wird durch die Abnahme der molekularen Beweglichkeit in Mikrophasenpartikeln von Pfropf-PAA aufweisenden amorphen Bereichen des PE erklärt.

Резюме — С помощью ТГ и ДТА изучены процессы термоокислительного распада, протекающего в полиэтиленовых (ПЭ) пленках, видоизменных привитой полиакриловой кислотой. Было выявлено совместное влияние компонентов на распад макромолекул, имеющихся в привитом сополимере. Увеличение термоустойчивости ПЭ в привитых сополимерах объяснено уменьшением молекулярной подвижности в аморфных участках ПЭ, содержащих микрофазы привитой полиакриловой кислоты.