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# THERMAL ANALYSIS OF POLYETHYLENE GRAFT COPOLYMERS

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## ABSTRACT

The thermal and heat stabilities of graft copolymer macromolecules of polyethylene (PE), polyacrylonitrile (PAN), polyacrylic acid (PAA), polyvinylidene chloride (PVDC), polymethylmethacrylate (PMMA) and polystyrene (PS) have been investigated by thermogravimetric, differential thermal analysis and thermo-mechanical methods. The increase in the thermal and heat stabilities of PE, resulting from PAN, PAA and PVDC grafting, was explained in terms of the increase in the intermolecular interaction energy in the amorphous phase of PE caused by the formation of microphase particles of the graft polymer. These particles ( ~ 100 Å across) serve as multiplet points of a space network. Thermal properties of PE graft copolymers obtained by the inhibited graft polymerization method have also been considered.

## INTRODUCTION

Thermal analysis methods provide information on physical and chemical processes taking place on heating macromolecules and submicroscopic structures. Using thermal analysis, distinctions can be found between physicochemical properties of separate components of graft polymer materials and those of the corresponding homopolymers and also, new information can be obtained on the structure and properties of graft polymer materials [1]. This report contains results of the thermal analysis of graft copolymers of PE with PAN, PAA, PVDC, PMMA and PS.

## EXPERIMENTAL

Graft films of PE obtained by radiation-induced gas-phase post-polymerization and direct irradiation of PE in a liquid monomer or its solution [2] were studied. Blends of corresponding homopolymers were prepared for comparison. The content of the second component is expressed as a percentage of the initial mass of PE. The dynamic thermogravimetric and differential thermal analyses were performed on MOM derivatographs (type

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OD-103 and Q-derivatograph, Hungary). Thermo-mechanical contraction curves were obtained on the UIP-70 apparatus, with a sample loading of 0.6 MPa. Thermo-mechanical stretching curves of the non-oriented samples and diagrams of isothermal heating of the oriented samples characterizing their macromolecular heat stability were obtained on the UMIV-3 apparatus. The heating rate during both the thermo-mechanical study and the thermal stability investigation of the samples was 5°C $\text{min}^{-1}$.

## RESULTS AND DISCUSSION

The temperatures characterizing PE thermal stability ($T_d$, starting temperature of PE decomposition; $T_{max}$, temperature of maximum PE macromolecular degradation rate; $T_s$, starting temperature of endothermic band caused by PE decomposition) were found by comparing the integral and differential thermogravimetry and differential thermal analysis curves.

The characteristic influence of the graft polymer on the thermal stability of PE is determined, first, by its chemical nature (Table 1). Thus, PAN, PAA and PVDC grafting, in contrast to PMMA and PS grafting, results in a substantial increase in PE thermal stability. For example, at $\Delta P = 20$–$50\%$,

TABLE 1

Thermal stability characteristics [a] of PE graft copolymers and PE blends with corresponding homopolymers

| Sample composition | $\Delta P$ (%) | Grafting technique | Thermal stability characteristics (K) | | |
|---|---|---|---|---|---|
| | | | $T_d$ | $T_{max}$ | $T_s$ |
| | | | Initial PE | | |
| PE | 0 | – | 628 (673) | 653 (723) | 658 (693) |
| | | | Graft copolymers | | |
| PE–PMMA | 32.8 | [b] | 628 | 653 | 675 |
| PE–PVDC | 29.0 | [b] | 673 | 708 | 718 |
| PE–PAN | 48.0 | [b] | 691 | 743 | 715 |
| PE–PAN | 58.7 | [c] | 655 | 686 | 671 |
| PE–PAA | 32.3 | [c] | 653 (673) | 693 (723) | 693 |
| PE–PS | 50.2 | [c] | 633 | 653 | 663 |
| | | | Blends | | |
| PE–PMMA | 32.8 | – | 613 | – | 653 |
| PE–PVDC | 29.0 | – | 623 | – | 663 |
| PE–PAN | 48.0 | – | 623 | – | 685 |
| PE–PAN | 58.7 | – | 618 | – | 658 |
| PE–PAA | 32.3 | – | 623 | 658 | 663 |
| PE–PS | 50.2 | – | 613 | 653 | 663 |

[a] Values obtained in an argon atmosphere are given in parentheses.

[b] Gas-phase polymerization.

[c] Direct irradiation in a monomer solution or in a liquid monomer.

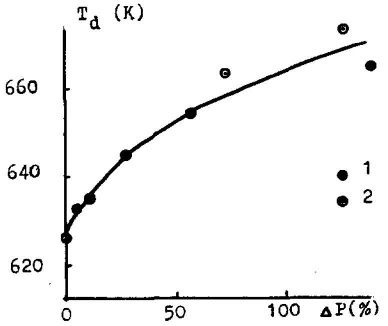

Fig. 1. Starting temperature of decomposition of PE in graft copolymers of PE and PAN (1), PE and PAA (2) versus graft polymer content.

$T_d$ and $T_{max}$ increase by 50–60°C as compared with those of the initial PE sample. This increased PE thermal stability is observed in graft copolymers only. In blends of PE with the corresponding homopolymers this effect is absent, and is qualitatively the same in both inert and oxygen atmospheres. The thermal stability of PE in graft copolymers increases with increasing graft polymer content (Fig. 1).

The thermal stability of the grafted PE film was estimated from the results of thermo-mechanical analysis. The thermo-mechanical contraction curves shown in Fig. 2 give evidence for a difference in the thermo-mechanical properties of PE modified by grafting with PAA, PAN and PS. Thus, a frictional flow in PE with PS graft begins at the same temperature as in the initial PE sample, while in the PE samples with PAA and PAN grafts, this only occurs at 673–703 K.

The thermo-mechanical stretching curve and isometric heating diagram of the initial PE and that with PAA, PAN, PVDC and PMMA grafts have shown that the heat resistance of PE increases with PAN, PAA and PVDC grafting and does not change with PS and PMMA grafting. When comparing the thermal stability and thermo-mechanical properties of PE graft copolymers, an increasing thermal stability is observed on polymer grafting which

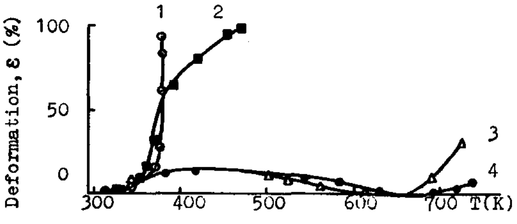

Fig. 2. Thermo-mechanical contraction curves of the initial PE (1) and PE modified by styrene (2), acrylic acid (3) and acrylonitrile (4) grafting. $\Delta P = 102.8$ (2), 98.0 (3) and 91.4% (4).

increases the heat stability of PE. This gives evidence for the common mechanism on which both effects are based.

The results of X-ray and electron microscopy studies [2] show the PE graft copolymers to have a microheterogeneous structure: in a sample of the initial polymer, particles ( ~ 100 Å across), formed by the graft polymer chains (graft structures), are dispersed throughout its mass. These particles are localized in PE amorphous micro-ranges (Fig. 3) and, as shown previously [3,4], increase the intermolecular interaction energy in the system, simultaneously decreasing the macromolecular mobility of PE.

The microphase particles of the graft polymer (with melting or flow temperatures above the PE melting temperature) serve as points in a space network which hinder the development of frictional flow in PE. The increase in thermal stability of PE is due to the decreasing molecular mobility of PE chains fixed by the graft structures. If the graft structures are stable enough, i.e., they do not transform into the frictional flow state at the starting temperatures of degradation of the initial PE, the thermal stability of PE increases. When multiplet points of a space network of physical bonds are

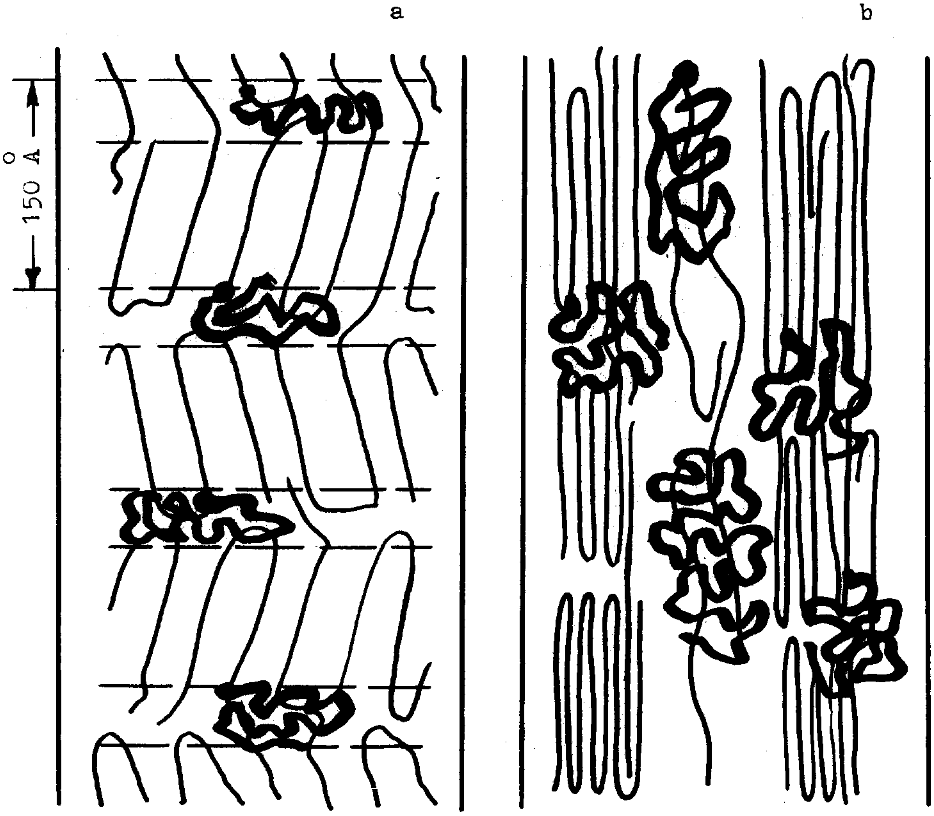

Fig. 3. PE graft copolymer structure. (a) Extruded films; (b) oriented films.

destroyed by heating (as in PE samples with PS and PMMA grafts) the thermal stability of PE remains unchanged.

Thus, the phenomenon of increasing thermal stability of PE due to grafting is based on an increase in intermolecular interactions in the amorphous PE region, caused by microheterogeneous graft structure formation, and a decrease in molecular mobility of PE chains related to it.

By thermal analysis of PE and PAN graft copolymers obtained by the inhibited graft polymerization method [5] one can prove that introduction of inhibiting additives in a reaction system during grafting provides a substantial increase in PE macromolecular thermal stability due to the stabilizing effect of the molecular fragments of the inhibitor being chemically attached to PE chains by PAN macromolecules.

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