

THERMAL ANALYSIS OF COMPOSITES BASED ON CRYSTALLINE POLYMERS AND METALS

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Differential scanning calorimetry (DSC), thermogravimetric analysis (TG) and infrared (IR) spectroscopy have been used to examine the chemical and physical changes (crystallinity, accumulation of oxygen-containing groups, etc.) during thermal oxidation of polyethylene, polypropylene and Penton contained in coatings and metal-filled films, taking into account the thickness of the polymer layer and catalytic activity of the metal.

When polymeric coatings on metals or metal-filled polymeric films undergo thermal oxidation, destruction and cross-linking of macromolecules occur; oxygen-containing groups (carbonyl, ether, etc.) accumulate; the degree of crystallinity varies along with the size and shape of the crystalline formations [1–5].

Polymeric coatings on metals and metal-filled polymeric films are subject to non-uniform oxidation across the depth. The oxidation may take place in the surface layers of polymers or those contiguous to the metal, depending on the catalytic activity of the metal relating to polymer oxidation, the temperature of oxidation, the polymeric film thickness and other factors. However, the peculiarities of polymer contact oxidation have not been studied adequately.

The present paper deals with the study of the thermal contact oxidation of polymers: high-density polyethylene, polypropylene and Penton ($-\text{CH}_2\text{C}(\text{CH}_2\text{Cl})\text{CH}_2\text{O}-$).

Powdered high-density polyethylene, isotactic polypropylene and Penton were tested. The substrates were metallic foils 50 and 100 μm thick, made of iron, aluminium and copper. Disperse metals, namely iron, nickel, lead and copper, with particle size below 50 μm were used as fillers. The compositions of the polymers and fillers were obtained by mechanical mixing of the components. Films of different thicknesses, including those on metals, were prepared from the polymers and their compositions by hot moulding. The moulding regimes were: 413 K for polyethylene; 453 K for polypropylene; 473 K for Penton; time: 60 sec; pressure: 10.0 MPa. The polymeric films on metals were oxidized in air in thermal cabinets at temperatures above those of polymer melting. Thermal analyses were carried out with an OD-102 derivatograph (MOM, Hungary), using a platinum pan-like specimen holder. The heating rate of the specimens was 2.5°/min. The structural changes in the polymeric films oxidized on metals

under isothermal conditions were evaluated by means of DSC using a DSM-2 instrument at a scanning rate of $12.5^\circ/\text{min}$. The chemical changes in the polymers during oxidation were studied by IR spectroscopy using a UR-20 spectrophotometer (Karl-Zeiss, DDR). The oxidation was evaluated via the variations of the coefficient of band absorption damping of the carbonyl $\text{C}=\text{O}$ ($\nu = 1710\text{--}1720\text{ cm}^{-1}$) and ether $\text{C}-\text{O}-\text{C}$ ($\nu = 1170\text{ cm}^{-1}$) groups.

Figures 1 and 2 show the IR spectroscopy results of distribution of the optical density values corresponding to the absorption bands of the carbonyl groups and ether bonds, and values of thicknesses of polyethylene and Penton coatings oxidized on iron, aluminium or copper. Iron and copper, unlike aluminium, are catalytically active metals during thermal oxidation of polyethylene [6]. When polyethylene was oxidized on aluminium, the oxidation process occurred mostly in the surface layer (Fig. 1, curves 2 and 6); on iron or copper the oxidation occurred in the surface layer and at the metal-polymer interface; the inner layer remained unoxidized for a long time (Fig. 1, curves 1, 3–5 and 7–11). The thicker the coating, the less oxidized the inner layer was for polyethylene coatings on iron. Similar results were characteristic of Penton coatings as well (Fig. 2).

Owing to the oxidation of polymeric coatings, considerable variations were observed in their crystallinity. Figure 3 presents data on the variations of the relative area of the polymer melting peak for the surface layers and those contiguous to steel for polyethylene coatings $10\text{ }\mu\text{m}$ thick and Penton coatings of different thicknesses, obtained by differential scanning calorimetry. In the layer

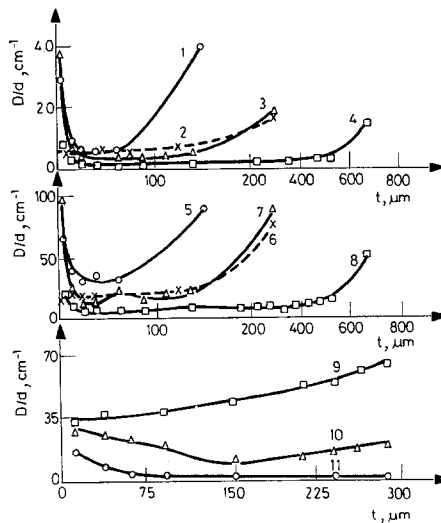


Fig. 1. Distribution across the depth t of ether (1–4) and carbonyl (5–11) groups for polyethylene coatings $200\text{ }\mu\text{m}$ thick (1, 5), $300\text{ }\mu\text{m}$ thick (2, 3, 6, 7, 9–11) and $800\text{ }\mu\text{m}$ thick (4, 8), oxidized at 453 K (1–8) and 413 K (9–11) during 1.8 ksec (11), 3.6 ksec (1–8), 4.2 ksec (10) and 9.0 ksec (9) on aluminium (2, 6), iron (1, 3, 4, 5, 7, 8) and copper (9–11)

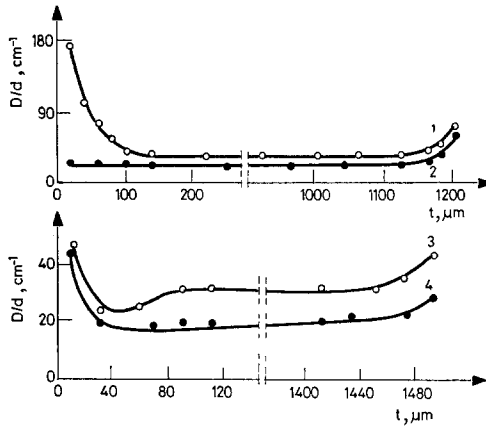


Fig. 2. Distribution across the depth t of carbonyl groups for Penton coatings 1200 μm thick (1, 2) and 1500 μm thick (3, 4), oxidized at 503 K (1, 2) and 473 K (3, 4) during 7.2 ksec (1, 2, 4) and 18.2 ksec (3) on iron (1), aluminium (2) and copper (3, 4)

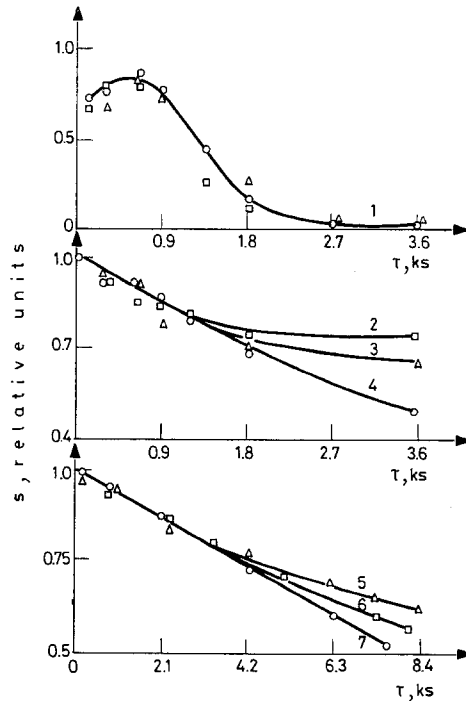


Fig. 3. Influence of the oxidation period τ at 453 K (1-4) and 503 K (5-7) on the variation of the melting peak area S in the surface layer (1) and that conjugate to the iron (2-7) having a thickness of 10 μm , of polyethylene (1-4) or Penton (5-7). Coating thicknesses: 200 μm (1, 4); 300 μm (7); 500 μm (1, 3, 6); 800 μm (1, 2); 1300 μm (5). \circ 200 μm , Δ 500 μm , \square 800 μm

of polymeric coating conjugate to the catalytically active metal, the crystallinity was found to decrease. In the early period of oxidation the coating thickness, in fact, did not influence the decrease of crystallinity in the layer conjugate to the metal. After durable oxidation the degree of crystallinity in that layer was the lower, the thinner the coating (Fig. 3, curves 2–7). The coating thickness (200–800 μm) did not influence the variation of the crystallinity of the polymer surface layer despite the period of oxidation. Here, in the early stage of oxidation an increase of the crystallinity was observed; with further oxidation the crystallinity decreased almost to zero, i.e. the surface layer of the coating became amorphous (Fig. 3, curve 1). The authors believe, that the differences in the variations of crystallinity of the polymer surface layer and that conjugate to the metal are associated with the peculiarities of the destruction and cross-linking of macromolecules in those layers. After prolonged oxidation of the coatings from cross-linking polymers, including polyethylene, autoinhibition of the oxidation process was observed in the surface layer, probably associated with strong macromolecular cross-linkage under autocatalytic oxidation [4].

Figure 4 presents data on the influence of the thickness of the polymer coatings on aluminium, iron or copper on the absolute and specific increments of their weight after oxidation, as obtained by non-isothermal thermogravimetric analysis.

For coatings on the catalytically inactive substrate (aluminium) [7], a drop in the specific (per unit of coating thickness) increment of the weight was observed with the increase of the coating thickness. This is due to the oxidation occurring within a comparatively thin surface layer of the coating [7, 8]. For the coatings on catalytically active substrates (iron and copper), such a regularity was found only with large thicknesses (above 300 μm), when the effect of the substrate on the coating oxidation could be neglected. The thinner the coating and the higher the catalytic activity of the metal, the lower the specific increment of the weight.

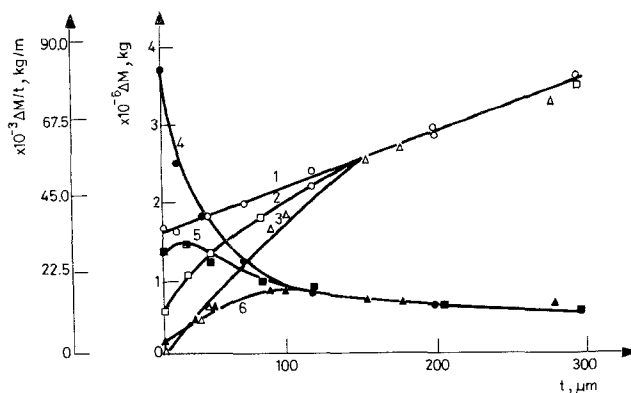


Fig. 4. Influence of thickness t of polyethylene coatings on aluminium (1, 4), iron (2, 5) and copper (3, 6) on the weight increment ΔM (1–3) and the specific weight increment $\Delta M/t$ (4–6) as obtained with TG when polyethylene coatings were oxidized under non-isothermal conditions. Surface area of samples: 23.5 cm^2

For thin coatings this is associated with metal migration into the polymer (in the form of carboxylic acid salts) and, correspondingly, with the transition of the heterogeneous catalysis of oxidation to a homogeneous one. Low molecular weight carboxylic acids are the major products of the oxidative destruction of polymers [3]. Because of this, the rate of oxidation of thin polyethylene films (up to 200 μm) on iron, copper, lead or other catalytically active metals is higher;

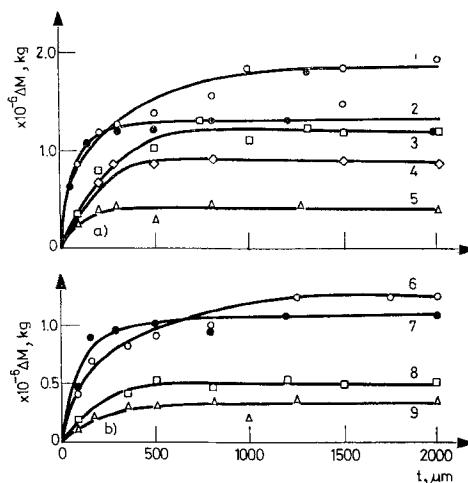


Fig. 5. Dependence of the weight increment ΔM obtained with TG on the thickness of polyethylene (a) and polypropylene (b) films. 1, 6 — unfilled polymers; 2—5, 7—9 — polymers filled with 5.0 vol. % nickel (2, 7); iron (3); lead (4, 8) and copper (5, 9). Surface area of samples: 11.75 cm^2

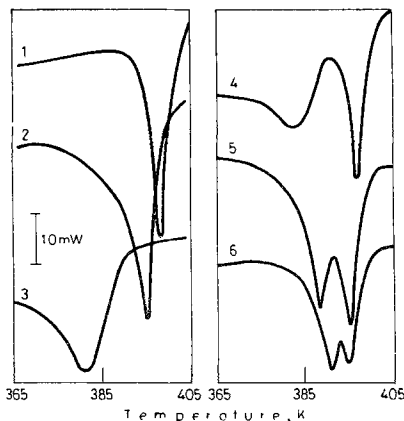


Fig. 6. DSC curves of unoxidized (1) and oxidized (2) polyethylene films; surface layer $10 \mu\text{m}$ thick (3) of film oxidized at 453 K during 0.9 ksec; mixtures of the oxidized surface layer and unoxidized polyethylene (4); of chemically cross-linked and pure polyethylene (5); oxidized polyethylene containing 5.0 vol. % lead (6)

autoinhibition may be reached earlier than on inert substrates [4, 7]. Similarly, the fillers influence the oxidation of polyethylene and polypropylene films (Fig. 5). The more active the filler is for polymer oxidation and the higher its concentration, the lower the total amount of oxidation of the polymer films and their weight increment at oxidation.

With macromolecular cross-linking due to polymer oxidation or the incorporation of cross-linking agents, etc., the melting temperature decreases (Fig. 6, curves 1, 3 and 5) which is probably associated with the crystal imperfection. Owing to this, the melting temperature of the surface-oxidized layers of polymeric coatings is considerably lower than the melting temperature of the unoxidized polymer or oxidized polymeric coating. Non-uniform oxidation of the polymeric coatings across the depth, and the dependence of the melting temperature on the degree of polymer oxidation, give widened melting peaks in the thermograms of the oxidized polymeric coatings (Fig. 6, curves 1 and 2); in some instances multiplet peaks were observed. Multiplet peaks may occur with a distinct non-uniformity of oxidation, for instance with lead powder-filled polyethylene (Fig. 6, curve 6). A similar effect of the peak multiplicity was observed for the mixtures of oxidized and unoxidized polymers (Fig. 6, curve 4) and mixtures of chemically cross-linked (with peroxide compounds, for instance) and non-cross-linked polymers (Fig. 6, curve 5). Similarly, the oxidation affects the melting temperature intervals and crystallization of polymers at the spherulite level, as found with the optical polarizing microscopy [9].

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ZUSAMMENFASSUNG — DSC, thermogravimetrische Analyse (TG) und infrarot (IR) Spektroskopie wurden zur Untersuchung der während der thermischen Oxidation von in Belägen und metallgefüllten Filmen enthaltenem Polyäthylen, Polypropylen und Penton stattfindenden chemischen und physikalischen Veränderungen (Kristallinität, Anhäufung stickstoffhaltiger Gruppen usw.) eingesetzt. Hierbei wurden die Stärke der Polymerschicht und die katalytische Aktivität des Metalls in Betracht genommen.

Резюме — Методами дифференциальной сканирующей калориметрии, термогравиметрического анализа и инфракрасной спектроскопии изучены химические и физические изменения (кристалличность, накопление кислородсодержащих групп и др.) при термическом окислении полиэтилена, полипропилена и пентона в покрытиях и наполненных металлами пленках с учетом толщины слоя полимера и каталитической активности металла.