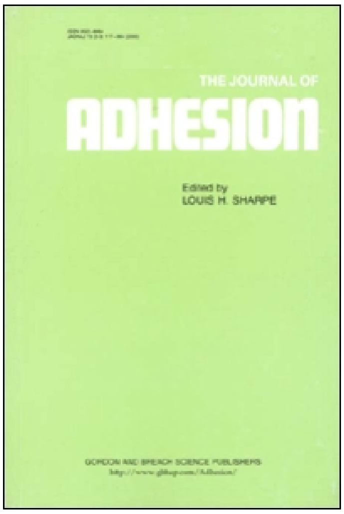

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Study of Oxidation and Adhesion of Filled Stabilized Polyethylene

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The degree of oxidation and adhesion has been studied for polyethylene coatings containing antioxidant (2,2′-Bis[1-oxy-4-methyl-6-(α-methylbenzyl)]-monosulphide) and a filler (aluminium oxide). It has been shown that the induction period of oxidation corresponds to the conventional induction period of adhesion. On increasing the antioxidant concentration, the conventional induction period of adhesion increases. Incorporation of the filler into polyethylene containing antioxidant, decreases the induction period of oxidation and conventional induction period of polyethylene adhesion. The latter is associated with antioxidant decay under the influence of the filler.

INTRODUCTION

A great number of papers have been devoted to investigations into the adhesion of polyethylene to hard surfaces, including metals.[1-15] However, there is a lack of common opinion on the nature of adhesive bonds for polyethylene and hard surfaces. Several investigators believe that the dispersion forces are quite enough for obtaining strong adhesive joints of polyethylene-metal.[1, 2] Other investigators state that satisfactory adhesion between polyethylene and metals is provided only by incorporating polar functional groups into polyethylene macromolecules (e.g. by thermal, liquid-phase, or radiation oxidation of polyethylene).[3-6] A third group of investigators[1, 7] while denying a large contribution of oxidation or giving a secondary meaning to it, believe that polyethylene adhesion to metals is due to physical or chemical[7] adsorption of macromolecules. Several investigators[8] are of the opinion that polyethylene adhesion to metals (e.g. to anodized aluminium) being chemical and is associated with melt penetration into micropores of metal oxide films.

Apparently, adhesion of polyethylene to metals in adhesive joints obtained under various conditions is due to different types of bonds. Urgent is the problem of defining the exact types of adhesive bonds between polyethylene and hard surfaces, and conditions under which these occur.

It was shown experimentally [3, 6, 9-14] that polyethylene oxidation causes an increase in its adhesiveness to metals, glass, and polar polymers. Adhesion of polyethylene to metals decreases on incorporating antioxidants into polyethylene, as well as on increasing the extent of air rarefaction (formation medium).

When coatings on glass and metal-polyethylene-metal systems (adhints) are formed in air from polyethylene containing an antioxidant, there is a formation period of time when adhesion is negligibly weak (actually there is no adhesion). It was suggested to call this formation period[15] "induction period of adhesion". The induction period of adhesion increases with percentage of antioxidant and with lowering the temperature of adhints formation.[15] Experiments show the adhesion being negligible not for all substrates; this applies to several metals as well. Consequently it is reasonable to use the expression "conventional induction period of adhesion".

Comparison of values of the conventional induction period of adhesion and induction period of oxidation is of interest when determining the nature of the conventional induction period of adhesion and the role of oxidation in polyethylene adhesion to hard surfaces.

Fillers cause a considerable effect on polyethylene adhesion to hard surfaces.[16-18] It is known,[17] that by incorporating inorganic fillers (e.g. aluminium oxide, talc oxide, kaolin oxide) it is possible in certain cases to increase several times polyethylene adhesion to metals. Here polyethylene strength either decreases or slightly increases; intrinsic stresses, hardness and elastic modulus increase.[16, 19] It is believed,[4] that increase in polyethylene adhesion to metals on incorporating inorganic fillers is due to acceleration in oxidation on the interface of the adhesive contact. However, there is no data on comparison between rates of oxidation and changes in adhesion in case of filled polyethylene.

The purpose of the present work was to study relations between oxidation and adhesion for stabilized polyethylene coatings on introducing inorganic fillers into the polymers.

EXPERIMENTAL PROCEDURE

Powdered unstabilized high density polyethylene with melt index 7 (g/10 min), particle size ≤250 μm; powdered aluminium oxide of particle size ≤50–70 μm (chemically pure); aluminium foil of 100 μm in thickness, and sheet inorganic window glass were used in the experiments. To stabilize polyethylene, antioxidant 2,2'-Bis-[1-oxy-4-methyl-6-(α-methylbenzyl)]-monosulphide has been used as incorporated by treating the polymer powder in solution of antioxidant in acetone with subsequent drying of the material to a constant weight (mass). Powdered aluminium oxide was introduced into powdered polyethylene by agitation. From the composition films were pressed 100 μm thick between polytetrafluoroethylene films at 423°K (during 30 sec). Polyethylene films were placed on substrate surfaces (aluminium or glass) and exposed to temperature 423°K in air. Aluminium surfaces had been cleaned mechanically (by abrasive paper) and rinsed in ethyl alcohol; glass surfaces had been cleaned only by ethyl alcohol. After thermal treatment the coatings were cooled in air at room temperature. The adhesion of polyethylene to metals was estimated by peeling metal foil from polymer; and that to glass by peeling polyethylene films from glass. The peeling was done at 180° angle. The peeling rate was about 0.3 mm/sec. After oxidation polyethylene films become brittle and break on peeling. Because of that, glass-filled polyethylene films were used for estimating polyethylene adhesion to glass. The adhesion was represented by the peeling stress. Polyethylene oxidation was recorded with a spectrophotometer, UR-20 (Karl Zeiss, Jena, DDR). The degree of oxidation was represented by optical density "D" of the band, corresponding to vibrations of carbonyl groups at 1720 cm^{-1}.

The effect of the filler on polyethylene oxidation was observed by differential thermal analysis (DTA) with derivatograph OD–102 (MOM, Budapest, Hungary), when determining the temperature of severe oxidation by the point of bending of the thermogram before the exothermal peak.

EXPERIMENTAL RESULTS AND THEIR DISCUSSION

Induction period of oxidation for unstabilized polyethylene at 423°K and higher is not observed. The adhesion of coatings with increase in the degree of oxidation for unstabilized polyethylene is represented by a curve with a maximum (Figure 1; curves 1, 4). On incorporating the antioxidant into polyethylene there occurs an induction period of oxidation which increases with percentage of the antioxidant (Figure 1; curves 4–6). A conventional induction period of adhesion also occurs (Figure 1; curves 1–3). Numerical values of induction periods of oxidation and adhesion actually coincide (Figure 2; curve 1). In contrast to adhesion of coatings to glass (Figure 3), their adhesion to aluminium (Figure 1) during the induction period of oxidation, is relatively strong and in a short time becomes constant (about 0.6 kN/m). After the induction period of oxidation has elapsed, the adhesion of coatings to aluminium and glass for stabilized polyethylene grows rapidly, reaches a maximum and then drops, i.e. varies similar to variations in the adhesion of unstabilized polyethylene coatings. Irrespective of the nature of the substrate, maximum adhesion is reached for stabilized and unstabilized polyethylene at low degree of oxidation (0.1 D and lower).

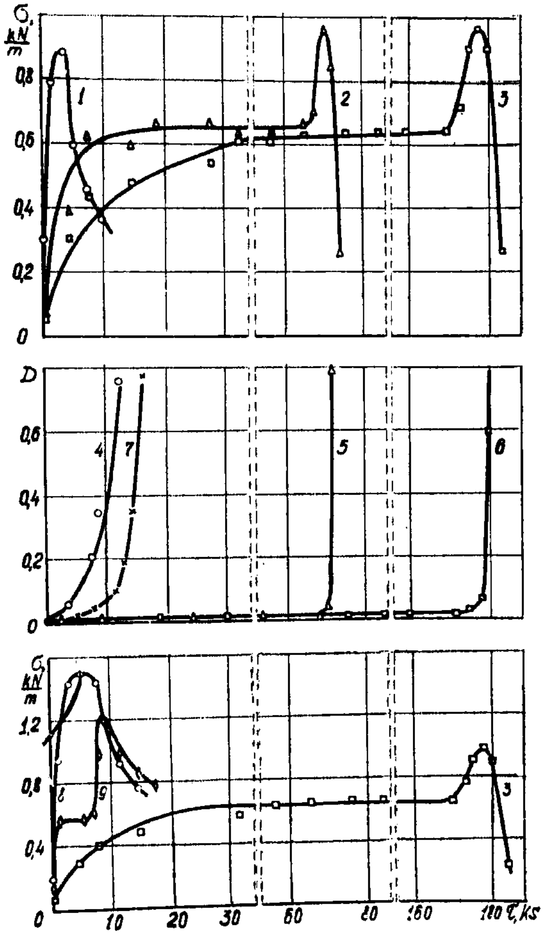

FIGURE 1 Variations in adhesion σ (1–3, 8, 9) and oxidation degree D (4–7) for unstabilized (1, 4) and stabilized (2, 5) with 0.01%-mass and (3, 6–9) with 0.05%-mass of 2,2′-Bis-[1-oxy-4-methyl-6-(α-methylbenzyl)]-monosulphide polyethylene to aluminium *versus* time of thermal treatment τ for unfilled polyethylene coatings (1–6) and polyethylene containing 1%-vol. (7, 9) and 10%-vol. (8) of aluminium oxide.

In contrast to coatings (polyethylene–foil), the adhesion of unstabilized polyethylene to aluminium in adhints (foil–polyethylene–foil) reaches constant values and later is actually independent of the period of heat treatment (Figure 4; curves 1, 2). Adhesion of unstabilized polyethylene

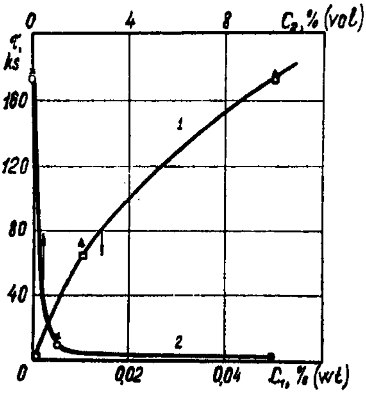

FIGURE 2 Effect of antioxidant percentage C_1 on the induction period τ of oxidation (Δ) and adhesion to aluminium (□) for unfilled polyethylene (I) and also the filler percentage C_2 on induction period τ of oxidation (×) and adhesion to aluminium (○) of polyethylene containing 0.05 %-mass of the antioxidant (2).

to aluminium in adhints varies with thermal treatment similarly to the adhesion of stabilized polyethylene coatings during the induction period of oxidation. From data of infrared spectroscopy, oxidation is not observed in adhints (except the peripheral areas) (Figure 4; curve 3). The peripheral

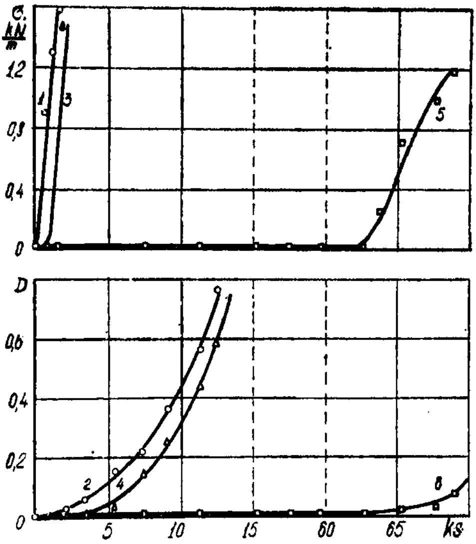

FIGURE 3 Effect of time of thermal treatment on the adhesion to glass σ (1, 3, 5) and degree of oxidation D (2, 4, 6) for coatings of unstabilized (1, 2) and stabilized with 0.01 %-mass of 2,2′-Bis-[1-oxy-4-methyl-6-(α-methylbenzyl)]-monosulphide (3–6) unfilled (1, 2, 5, 6) and filled with 5 %-vol. of aluminium oxide polyethylene (3, 4).

areas were cut off after adhints formation and were not used in the experiments on estimating the adhesion. On peeling the foil from one side of the adhint, oxidation starts in polyethylene (Figure 4; curve 6) and simultaneously a sharp increase in polyethylene adhesion to aluminium is observed (Figure 4; curve 5). The period of steady state adhesion in these experiments had been termed as "forced" conventional induction period of adhesion, associated with the fact that the supply of oxygen from the environment to the interface of the adhesive contact for foil–polyethylene–foil systems systems is hindered. Somewhat higher values of adhesion for unstabilized polyethylene in adhints (0.7 kN/m) than those for stabilized polyethylene coatings during the induction period of oxidation (0.6 kN/m) are due to two possible factors. Firstly, unstabilized polyethylene in adhints can be slightly (beyond the sensitivity limits of infrared spectrum) oxidized by oxygen, dissolved in the polymer and adsorbed by the substrate surface or entrapped by polymer melt in the microflaws of the substrate surfaces. Secondly, the antioxidant in the stabilized polyethylene can be adsorbed by the substrate surface decreasing its free surface energy, or it can form a layer with lower cohesive strength at the interface of the adhesive contact.

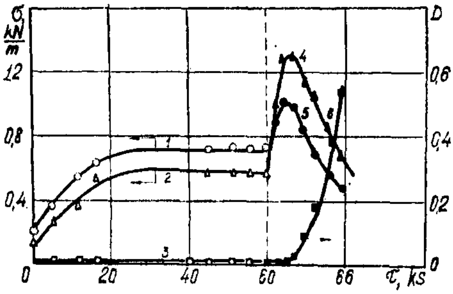

FIGURE 4 Effect of time of thermal treatment τ on adhesion to aluminium σ (1, 2, 4, 5) and degree of oxidation D (3, 6) for unfilled (1, 3, 5, 6) and filled with 5%-vol. of aluminium oxide (2, 4) polyethylene in foil-polyethylene (4–6) and foil-polyethylene-foil systems (1–3).

On incorporating a filler into unstabilized polyethylene the adhesion between polyethylene and aluminium decreases for foil–polyethylene–foil systems. Apparently, this is associated with decrease in the actual (real) contact area in the adhesive contact due to either decrease in the melt viscosity (Figure 5) or decrease in the rate of gas dissolution in the melt,[21] the gas which had been entrapped in the microflaws at the interface of the adhesive contact. The less the area of the molecular contact, the less the strength of the adhesive joint. On peeling the foil from one side of the adhint there starts oxidation of filled polyethylene; the adhesion grows and becomes higher than that of the unfilled polyethylene (Figure 4; curves 4, 5).

Incorporation of a filler into stabilized polyethylene decreases the conventional induction period of adhesion for polyethylene coatings on aluminium (Figure 1; curves 3, 8, 9; Figure 2; curves 2) and on glass (Figure 3; curves 3, 5). Correspondingly, the induction period of oxidation decreases for stabilized polyethylene (Figure 1; curves 6, 7 and Figure 3; curves 2, 4, 6). When 10%-volume of aluminium oxide had been incorporated into polyethylene containing 0.05%-mass of antioxidant the induction period of oxidation and conventional induction period of adhesion for coatings are not observed (Figure 1; curve 8), i.e. filled stabilized polyethylene behaves like unstabilized one.

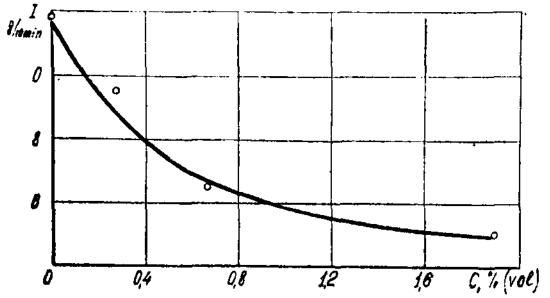

FIGURE 5 Effect of aluminium oxide percentage C on the melt index I of polyethylene.

Data on the acceleration of oxidation obtained by infrared spectroscopy for stabilized polyethylene with incorporated filler, is supported by the data obtained by differential thermal analysis (Figure 6). Three factors may cause acceleration in the oxidation of stabilized polyethylene on filling: first, direct acceleration in oxidation of polyethylene macromolecules by the filler; second, decay of antioxidant under the effect of the filler; third, adsorption of the antioxidant by the filler which causes decrease in the content of the antioxidant in the bulk polymer. All these factors can act simultaneously. It is known, however, that aluminium and aluminium oxide surfaces do not cause any significant effect on the oxidation rates of unstabilized polyethylene films. For instance, at 423°K the oxidation rates of polyethylene films on aluminium, polytetrafluoroethylene and window glass surfaces are almost identical.[20] It is also known that incorporation of aluminium oxide into unstabilized polyethylene[21] increases resistance of polyethylene and adhints on its basis[18] to thermal oxidation. Experiments showed that aluminium oxide accelerates antioxidant decay. On the thermograms for antioxidant with aluminium oxide, the beginning of the severe oxidation shifts to the region of lower temperatures (Figure 7). Apparently, the filler adsorbs the antioxidant as on incorporation of aluminium oxide into stabilized polyethylene there occurs a slight decrease in the optical density of the adsorption band 3450 cm^{-1} in the infrared spectrum (valence vibrations of —OH groups in the antioxidant).

Thus, an increase in the adhesion for stabilized polyethylene on incorporating inorganic fillers may be due to accelerated oxidation associated with decrease in the induction period of oxidation as the result of decay or adsorption of the antioxidant by the filler. In this case an increase in the adhesion is observed both for the metal (aluminium) and nonmetal (glass) on filling.

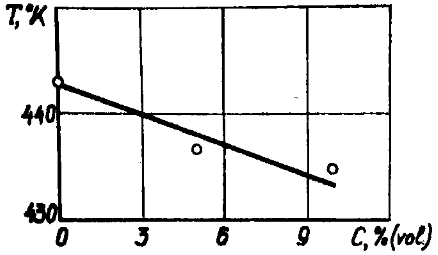

FIGURE 6 Effect of aluminium oxide percentage C on the temperature of the beginning of severe oxidation T for polyethylene containing 0.05 %-mass of the antioxidant (according to DTA).

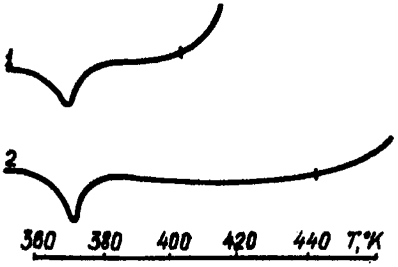

FIGURE 7 Thermograms for the antioxidant (2) and that containing 70%-mass of aluminium oxide (1).

It should be noted that an increase in the percentage of antioxidant in polyethylene causes a slight decrease in the ultimate values of the adhesion for coatings on aluminium during the induction period of oxidation (Figure 1; curves 2, 3). This can be related to the fact that substrate surfaces adsorb the antioxidant or a weak layer (boundary one) is formed of the antioxidant on the interface of the adhesive joint.

The data obtained show that between oxidation and adhesion for filled polyethylene there exists a direct relationship. Here, the oxidation can increase as well as decrease the adhesion. However, with certain substrates (e.g. aluminium) a satisfactory adhesion can be achieved without oxidation.

The increase in adhesion of polyethylene to hard surfaces on oxidation can be due not only to the adsorptionally active functional groups in its macromolecules, but to other consequences of the oxidative reactions. The following factors can contribute in the increase of adhesion on polyethylene oxidation: (a) decrease in its crystallinity caused by irregularities in the structure of the oxidized macromolecules; (b) increase in the ability of polyethylene to dissolve polar low molecular compounds which form weak boundary layers (including those of the antioxidant); (c) decrease in the melt viscosity associated with the oxidative destruction of macromolecules, etc. All these factors can act simultaneously and at present it seems impossible to define the contribution of each in increasing the adhesion of polyethylene to hard surfaces.

References

1. J. J. Bikerman, *J. Appl. Polym. Sci.* **2**, 216 (1959).
2. A. A. Berlin and V. E. Basin, *Fundamentals of Polymer Adhesion*, 2nd edn. (Khimia, Moscow, 1974), Chap. 8, pp. 288–320.
3. F. J. Bockhoff, E. T. McDonel and J. Rutzler, *Ind. Eng. Chem.* **50**, 904 (1958).
4. M. M. Kalnin', E. O. Metnietse and B. P. Karlivan, *Vysokomolek. Soyedineniya.* **A13**, 38 (1971).
5. D. A. Kardashov, *Synthetic Adhesives*, 2nd edn. (Khimia, Moscow, 1968). Chap. 3, pp. 255–319.
6. Yu. E. Lobanov, *Mekhanika Polimerov.* no. 5, 932 (1970).
7. A. T. Sanzharovsky and L. B. Kovarskaya, *Dokl. Akad. Nauk SSSR* **203**, 409 (1960).
8. K. Bright, B. W. Malpass and D. E. Packhann, *British Polymer J.* **3**, 205 (1971).
9. H. A. Arbit, E. E. Greisser and W. A. Haine, *TAPPI* **40**, 161 (1957).
10. N. I. Egorenkov, D. G. Lin and V. A. Bely, *Dokl. Akad. Nauk SSSR* **210**, 1148 (1973).
11. N. I. Egorenkov, V. L. Mlynsky and V. A. Bely, *Dokl. Akad. Nauk BSSR* **17**, 329 (1973).
12. N. I. Egorenkov and V. A. Bely, in *Macromolecules at the Interface* (Navukova Dumka, Kiev, 1971). P. 194.
13. N. I. Egorenkov, in *New Adhesives and Technology of Gluing* (MDNTP, Moscow, 1973). Part I, p. 24.
14. F. J. Lasak, *US Patent* 2, 697, 058.
15. M. M. Kalnin', R. R. Brakere and F. V. Rekner, *Vysokomolek. Soyedineniya.* **B14**, 747 (1972).
16. N. I. Egorenkov and V. A. Bely, *Dokl. Akad. Nauk BSSR* **15**, 790 (1971).
17. M. M. Kalnin', V. P. Karlivan and R. R. Brakere, *Vysokomolek. Soyedineniya.* **A1X**, 2178 (1967).
18. N. I. Egorenkov and V. A. Bely, in *Reliability and Durability of Polymer Materials and Their Products* (MDNTP, Moscow, 1969). P. 172.
19. M. M. Kalnin', *et al.*, in *Modifications of Polymer Materials* (RPI, Riga, 1969). P. 20.
20. V. A. Bely, N. I. Egorenkov and D. G. Lin, *Plasticheskie Massy.* no. 1, 44 (1973).
21. V. A. Bely, N. I. Egorenkov and Yu. M. Pleskachevsky, *Adhesion of Polymers to Metals* (Nauka i Tekhnika, Minsk, 1971). Chap. 3, pp. 134–232.