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GAS AND GEL PERMEATION CHROMATOGRAPHIC INVESTIGATION OF POLYETHYLENE MODIFICATION IN MODEL CHEMICAL REACTIONS

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SUMMARY

The modification of polyethylene for application in the cable industry, consisting in cross-linking with dicumyl peroxide in the presence of vinyl tri(2-methoxyethoxy)silane and the reaction of the silane with aluminium hydroxide, were investigated by use of model reactions. The reaction components were analysed by high-performance gas and gel permeation chromatography. From the results it was assumed that radical polymerization of the silane occurs preferentially by addition of formed radicals to the vinyl groups and polycondensation by water evolved from aluminium hydroxide at higher temperatures.

INTRODUCTION

Extensive fires have often been caused by the failure of electric cables and insulators. An effective prevention is the use of flame-resistant materials. Most of them, however, liberate toxic and corrosive products on burning. Aluminium hydroxide, from which at higher temperatures only water is endothermically evolved, resulting in flame cooling, has therefore recently gained popularity as a fire retardant for polyethylene (PE)[1]. In the cable industry, to improve the thermo-mechanical properties of PE insulations, PE[2] cross-linked by various methods is preferred. A relatively high proportion of $Al(OH)_3$ to PE is needed to obtain the desired degree of flame resistance, which unfavourably influences the mechanical, electrical and thermal properties of the final products. This undesirable effect can be decreased by the use of an interface between the polymer and the filler particles[3]. For this purpose the unsaturated trialkoxysilanes were proposed.

The bimodal character of olefinic alkoxysilanes permits them to react both in radical (cross-linking) and in polycondensation (creating the interface) reactions. This work was undertaken to study the radical reactions of dicumyl peroxide (DCP) and vinyl tri(2-methoxyethoxy) silane (VMES) in *n*-heptane as model hydrocarbon substrate, the condensation reactions of VMES and $Al(OH)_3$ in toluene, as well as the evolution of water from $Al(OH)_3$ when heated. Analysis of the reaction components in model reactions was used as an investigation method.

The analysis of DCP decomposition products in hydrocarbons, acetophenone

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(AP) and 2-phenyl-2-propanol (cumyl alcohol, CA), has already been described. For that purpose, spectroscopic methods (infrared[4–6], ultraviolet[4] and mass spectrometric[7] and especially gas chromatographic (GC) methods[8–11] were used. Also the GC–thermogravimetric (TG) estimation of water evolution from polybasic acids was elaborated[12]. In this paper, for the analysis of reaction products, high-performance chromatographic methods, GC on a fused-silica wall-coated open tubular (WCOT) capillary column and gel permeation chromatography (GPC) on high-efficiency micro-styragel columns were used. GC–TG was also applied for the estimation of water evolution from $Al(OH)_3$.

EXPERIMENTAL

Apparatus

For GC analysis a Hewlett-Packard (U.S.A.) Model 5840A gas chromatograph was used, equipped with flame ionization detector, capillary inlet system (HP-18835B) and 12 m × 0.2 mm I.D. fused-silica WCOT capillary column (HP-19091-60010) with methylsilicone fluid SP-2100. For the analysis of the decomposition products of DCP, VMES and *n*-heptane dimers the column temperature was 110°C. For the determination of the 2-methoxyethanol (ME) formed and unreacted VMES, the column temperature was held for 2 min at 80°C and then programmed to 160°C at a rate of 10°C/min. The injector and detector temperatures were 220°C and 250°C respectively. The flow-rate of nitrogen carrier gas was 1 ml/min and the splitting ratio was 1:30.

For GC–TG, the gas chromatograph described above was modified by replacing the chromatographic column by a short glass tube (10 cm × 4 mm I.D.) packed with about 100 mg of the material to be tested, accurately weighed. A thermal conductivity detector with helium as carrier gas (10 ml/min) was used in this case. The temperature of the oven containing the sample was programmed from 40°C to 120°C at rate of 10°C/min and then to 260°C at a rate of 1°C/min. The detector signal was continually plotted and 5-min area slices were integrated and quantified by calibration with a water–ethanol standard or reweighing the remaining material.

For GPC analysis of VMES monomer/polymer a Waters Assoc. (U.S.A.) liquid chromatograph Model ALC/GPC 301 was used, equipped with a differential refractometer (RI detector) and ultraviolet (UV) detector (254 nm) and U6K valve injector. The chromatographic system consisted of five 300 × 7.8 mm I.D. stainless-steel columns packed with fully porous highly cross-linked styrene–divinylbenzene copolymers (μStyragel, Waters Assoc.). The porosities of the columns used were: 100 nm (one), 50 nm (two) and 10 nm (two), respectively. The eluent was tetrahydrofuran at room temperature.

Materials

Aluminium hydroxide (Martinal) was obtained from Martinswerk (F.R.G.) in two batches, A and E, with the following specifications: mean particle diameters 0.5 and 6.5 μm; surface areas (BET) 4–6 and 0.14 m^2/g; humidities 0.19 and 0.045% (w/w) respectively. Dicumyl peroxide (Dicup R) was obtained from Hercules Powder (U.K.), and was twice recrystallized from ethanol. Vinyl tri(2-methoxyethoxy)silane (A-172) was obtained from Union Carbide (U.S.A.). Toluene and *n*-heptane, obtained from Lachema (Czechoslovakia) were reagent grade. They were used without purification.

Procedures

For the reaction of DCP and VMES in *n*-heptane a stock solution of each reagent (5%, w/w) was prepared. Various weighed volumes (0–80 μl) were injected with Hamilton microsyringes into glass ampoules (7 × 0.4 cm I.D.) and diluted in *n*-heptane to the desired concentrations listed in Table I. The ampoules were cooled with solid CO_2 and a nitrogen atmosphere was provided, alternated by evacuation (100 Pa). The sealed ampoules were heated at 145 ± 1°C for 5 h to complete the decomposition of DCP. For GC analysis, 50 μl of *n*-heptane enriched with naphthalene (NP) as internal standard (10 mg naphthalene in 10 mg *n*-heptane) were added to each solution. Appropriate volumes were injected for GC and GPC analysis.

For the reaction of VMES and $Al(OH)_3$ in toluene, 330 mg of $Al(OH)_3$ were weighed in glass ampoules (6 × 1 cm I.D.). Then 1.5 ml of a stock solution of VMES (2.20 g VMES in 100 ml dry toluene) were added. The ampoules were sealed, fixed in the frame of a mixing apparatus, dipped in a silicone oil-bath controlled by an ultrathermostat to 70–170 ± 0.5°C. After some time (20–140 min) the individual ampoules were cooled and centrifuged. For GC analysis, 50 μl of the clear solution were injected into other ampoules (4 × 0.4 cm I.D.) and 50 μl of toluene enriched with NP (0.102 g NP in 10 ml toluene) were added. For GPC analysis, partially

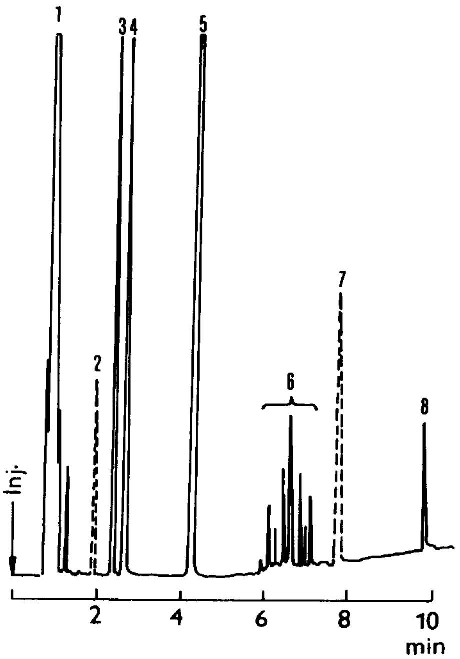

Fig. 1. GC separation of the reaction mixture of DCP and VMES in *n*-heptane. For conditions see the text. Peaks: 1 = *n*-heptane; 2 = α-methylstyrene; 3 = acetophenone; 4 = cumylalcohol; 5 = naphthalene; 6 = *n*-heptane dimers; 7 = *n*-tetradecane; 8 = VMES. Dashed lines represent standards.

evaporated solutes were used. Appropriate volumes were injected for GC and GPC analysis.

RESULTS AND DISCUSSION

Gas chromatography

By using the chromatographic column and conditions described above, we achieved the baseline separation of all components of the reaction mixture of DCP and VMES in *n*-heptane (Fig. 1). *n*-Tetradecane (standard for *n*-heptane dimers) and α-methylstyrene, added to the calibration mixture (dashed lines in the chromatogram) were not found in the reaction products. The absence of methylstyrene demonstrates that the thermolysis of CA[13,14] does not occur under the described conditions. The inertness and high efficiency of the chromatographic column led to a relative error of the determination in the range of ±2–3%.

Gas chromatography–thermogravimetry

GC–TG is a sensitive method for the determination by weight of the losses of water at various temperatures in the absence of other volatile products. The method exceeds the sensitivity of TG alone by more than one order of magnitude. The plots obtained from two different samples of $Al(OH)_3$ are shown in Fig. 2. It is evident that the evolution of water is not a monotonic process, but is characterized by some maxima probably due to the various kinds of bonding present in the tested materials.

Gel permeation chromatography

The GPC analysis of VMES and its polymeric products was achieved by the use of tetrahydrofuran as eluent and a UV and RI detector. The column combination used allowed a comparison of the products of the examined reactions over a large range of molecular weights. The approximate molecular weights of the polymeric products were estimated with the aid of polystyrene and polypropylene glycol calibration standards (Waters Assoc.).

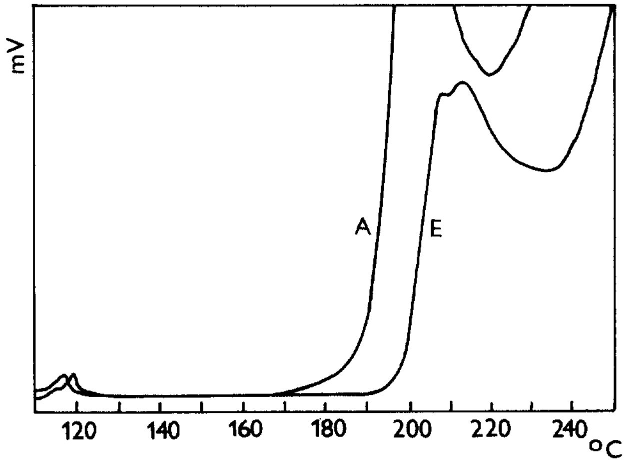

Fig. 2. GC–TG of $Al(OH)_3$. Curves: A, Martinal A; E, Martinal E.

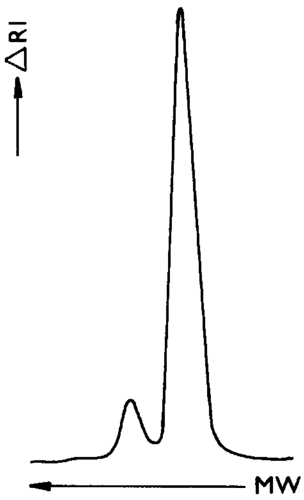

Fig. 3. GPC separation of parent VMES at an elution rate of 2 ml/min.

The GPC elution curve of VMES (Fig. 3) demonstrates that about 5% of higher-molecular-weight compounds, probably dimers, are present in the raw material.

Radical-induced reactions

It is well known[8–11] that DCP when heated in our hydrocarbon substrate undergoes homolytic cleavage to form cumyloxy radicals by a monomolecular reaction. The radicals then either abstract hydrogen atoms from the substrate forming CA and hydrocarbon radicals, or decompose to methyl radicals and AP. Methyl radicals also act as a hydrogen abstracting agent, generating hydrocarbon radicals, which form hydrocarbon dimers or oligomers by recombination. The cross-linking of PE is accomplished in this way. The ratio of concentrations of CA to AP formed is a measure of the reactivity of the substrate in relation to cumyloxy radicals.

TABLE I

GC ANALYSIS OF COMPONENTS (IN mol/kg OF *n*-HEPTANE) OF THE REACTION DCP AND VMES IN *n*-HEPTANE

Added		*Measured*				
DCP	*VMES*	*AP*	*CA*	*Dimers*	*VMES*	*DCP**
0.104	–	0.101	0.111	0.034	–	0.103
0.105	0.075	0.099	0.109	0.028	0.001	0.104
0.103	0.099	0.096	0.105	0.028	0.002	0.100
0.111	0.219	0.100	0.112	0.024	0.004	0.106
0.114	0.337	0.095	0.109	0.022	0.006	0.101
0.115	0.461	0.093	0.105	0.019	0.009	0.099
0.118	0.585	0.085	0.097	0.016	0.011	0.091

* DCP calculated from (AP + CA)/2.

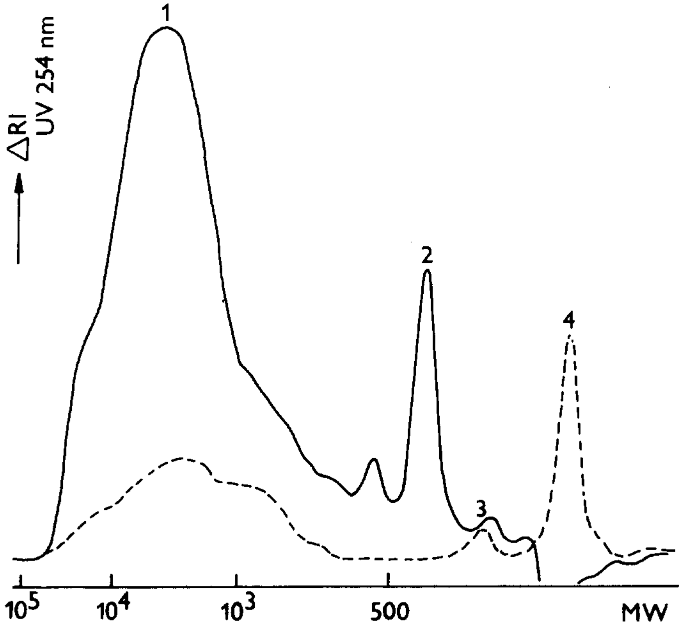

Fig. 4. GPC separation of VMES polymeric products of the radical induced reaction (5 h at 145°C). Peaks: 1 = VMES polymer; 2 = VMES; 3 = cumylalcohol; 4 = acetophenone. Solid line, RI signal; dashed line, UV signal.

In the presence of VMES further reactions with the radicals could occur: (1) abstraction of hydrogen atoms from the hydrocarbon part of the silane and (2) addition to the vinyl groups. The formation of dimers and oligomers of VMES, the bonding of the hydrocarbon used to the silane and the homopolymerization of VMES are accomplished in this way. The occurrence of such reactions, especially with cumyloxy radicals, is evident (Table I) from the rapid decrease in the amount of VMES monomer and the consumption of DCP. The addition of cumyloxy radicals to the VMES is evident also from the UV detector signal for the polymeric products, as shown in Fig. 4.

From the CA/AP ratio the relative rates of the main reactions could be calculated. From the values in Table I it was established that the rate of addition of cumyloxy radicals to the vinyl groups of VMES is two orders of magnitude higher than the dehydrogenation of *n*-heptane and VMES by cumyloxy radicals, and the abstraction of hydrogen atoms from *n*-heptane is twice as fast as that from VMES[15].

In the chromatogram in Fig. 1 the distribution of *n*-heptane dimers is remarkable. Almost all possible isomers of the C_{14} hydrocarbon (except *n*-tetradecane) are formed, but in irregular proportions. The total amounts of the dimers formed represent only one third of the theoretical value, even in the absence of VMES. It could be concluded that only one third of the DCP originally present is consumed in crosslinking reactions, in good agreement with published data[16].

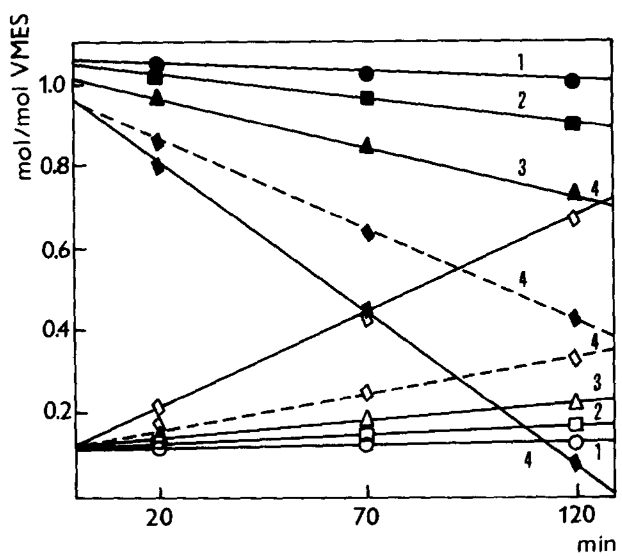

Fig. 5. Kinetics of formation of 2-methoxyethanol (open symbols) and consumption of VMES (filled symbols). Solid lines, Martinal A; dashed lines, Martinal E. Curves: 1 = 70°C; 2 = 120°C; 3 = 145°C; 4 = 170°C.

Condensation reactions

For the reaction of aminopropyltriethoxysilane with $Al(OH)_3$ the following steps were proposed[17]:

(1) Hydrolysis of silane alkoxy groups with water present, to form silanols and liberation of the corresponding alcohol

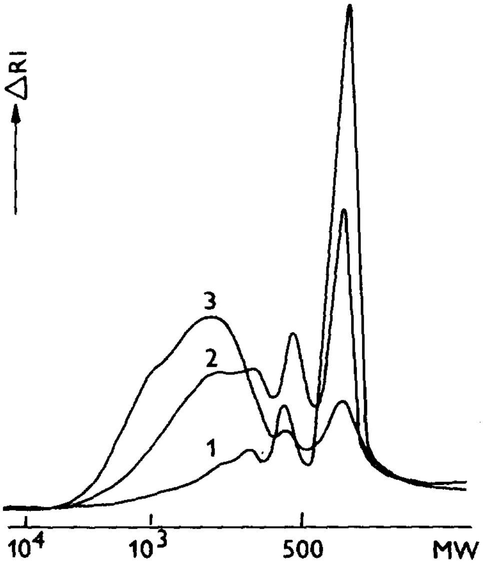

Fig. 6. GPC separation of VMES polycondensates formed in toluene at 170°C in the presence of Martinal A. Curves: 1 = 20 min; 2 = 70 min; 3 = 120 min.

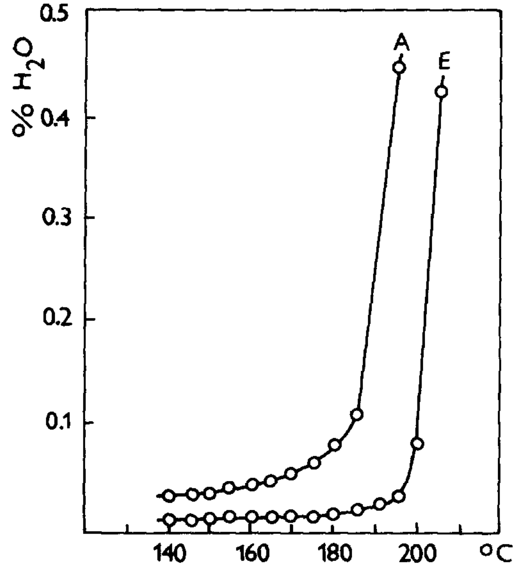

Fig. 7. GC–TG of Al(OH)$_3$ expressed as the dependence of the weight loss of water on temperature. Curves: A = Martinal A; E = Martinal E.

(2) Condensation of these silanols with hydroxyl groups of Al(OH)$_3$

(3) Condensation of alkoxy groups with each other

Al(OH)$_3$ is known to liberate up to 34% of water when heated; it was also found by TG and DTA that water evolution starts at 200°C[18].

We studied the reactions described in the system of Al(OH)$_3$ and VMES in toluene at various temperatures (70–170°C) by GC determination of the increase in ME formed, GC and GPC estimation of the decrease in VMES and GPC determination of the total amount of VMES as monomer and polymer. The results of the GC and GPC analyses are plotted in Fig. 5 as the dependence of compound concentration on reaction time. It is evident that at 70–145°C the reaction is very slow, but that above 145°C a higher reaction rate is observed. The reaction rates are also dependent on the surface area of the material tested. This is in good agreement with the GPC results (Fig. 6), which demonstrated that in the presence of Martinal E (surface area 0.14 m^2/g) at 170°C during 120 min there was a 55% conversion of the monomer into polymer, while with Martinal A (4–6 m^2/g) a 95% conversion was obtained.

Quantitative interpretation of GPC chromatograms (Fig. 6) showed that the total amounts of VMES as monomer and polymer remain almost constant during the reaction, from which it can be concluded that only a negligible part of VMES is chemically bonded to Al(OH)$_3$.

The irregular temperature dependence of the described reactions (non-linearity of Arrhenius plot) and the GPC observations required further explanation. GC–TG, due to its higher sensitivity (Fig. 7), indicated that small amounts of water (desorption of free water and formation of reaction water) are liberated at lower temperatures than the spontaneous evolution found by routine TG[18]. From the good agreement of the temperature dependence of water evolution with the VMES consumption, the ME formation and the results of GPC analysis, it can be concluded that the main condensation reaction is the homopolycondensation of VMES caused by the water evolved from $Al(OH)_3$ when heated.

CONCLUSIONS

The described GC and GPC methods were applied to an investigation of the radical and condensation reactions of VMES with DCP and $Al(OH)_3$ in hydrocarbon substrates.

The ratio of CA to AP and refractometer to UV detector signals, the amounts of dimers of *n*-heptane formed and the total amounts of VMES as monomer and polymer hint at the preferential addition of DCP radicals to the vinyl groups of VMES. The bonding and the subsequent cross-linking of the hydrocarbon substrate is thus facilitated.

On the basis of the constant amounts of the sum of VMES as monomer and polymer, the rates of decrease of VMES and increase of ME and the temperature dependence corresponding to the formation of water from $Al(OH)_3$, it was assumed that the condensation of VMES with $Al(OH)_3$ is negligible. A substantial part of VMES is converted into the polymer by polymerization with DCP and condensation with water evolved from $Al(OH)_3$ when heated. The critical temperature of water evolution is dependent on the physical properties of the tested material.

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