Stabilization of Alternating Carbon Monoxide–Ethylene Copolymer

S. SHKOLNIK, E. D. WEIL

The Herman S. Mark Polymer Research Institute, Polytechnic University, Brooklyn, New York 11201

ABSTRACT: The alternating copolymer of ethylene and carbon monoxide (POK) has properties that suggest possible utility for fibers. However, in order to be melt spinnable, the copolymer should be stable somewhat above its melt temperature for some minutes. Research to improve the stability of POK was carried out by (1) preparation of hydrogen-bonded polymer blends; and (2) addition of plausible stabilizers, individually or in combinations. To study thermal stability above the polymer melting range, FTIR, TGA, and DSC measurements were used. These studies allowed us to distinguish DSC as an effective method for evaluation of melt-spinning capability. Four DSC evaluation criteria, best suited for selection of stabilizer candidates, were determined for use in the present study but may have broader applicability. In approach (1), phenol-formaldehyde oligomers or poly(4-vinylphenol) showed only a small benefit in crystallinity retention. Most of the effort was put into approach (2). The IR and TGA studies pointed to furan ring formation as an important decomposition mode, and we considered this reaction likely to be catalyzed by acid. Catalyst residues and traces of metals, introduced during processing, were also believed likely to cause degradation. Classes of stabilizer candidates explored comprised acid scavengers, ligands, antioxidants, selected inorganic compounds, and derivatives of cellulose. The best results were found with aromatic carbodiimides, mono- and polyepoxy compounds; beta-diketones and cellulose ethers, and especially combinations of the preceding compounds with calcium hydroxyapatite. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 1691–1704, 1998

Key words: carbon monoxide–ethylene copolymer; melt spinnability; thermal stability evaluation; hydrogen-bonded blends; acid scavengers; ligands; antioxidants

INTRODUCTION

Carbon monoxide–olefin copolymers are relatively new, and are synthesized from plentiful and low cost monomers. However, despite the potential importance of these polymers because of their useful physical and mechanical properties, the literature contains very little on their chemical properties, stability characteristics, and stabilization.

In 1971, a random carbon monoxide–ethylene copolymer (RCE) was proposed to use in blends with poly(vinyl chloride) (PVC) to decrease its melt viscosity.[1] A carbon monoxide–ethylene–vinyl acetate terpolymer[2] (CEV) provided one solution to the problem of processability of PVC with this polymer, and indeed more than 30 patents were noted dealing with blends of PVC with CEV and with various additives (to DuPont, Mitsui, Nippon Unicar, Sekisui, and others). The stabilization of such blends is likely to reflect the specific requirements of PVC compositions. It is noteworthy that PVC-CEV mixtures show a single T_g over the entire composition range[3] evidencing true

miscibility. However, in the absence of the vinyl acetate comonomer, the processing of carbon monoxide–olefin copolymers, especially carbon monoxide–ethylene copolymers, is a more challenging task.

One successful approach to improve the processability of carbon monoxide–ethylene copolymers has been to synthesize an alternating carbon monoxide–ethylene–propylene terpolymer (CEP). Extensive work has been carried out by Shell Oil Co. Since 1988, many patents have issued to Shell, on stabilized CEP and its blends with other polymers, the aim of which was to improve the melt processability, melt stability, creep, and/or other properties of this polymer. According to the patents, almost all of these blends were not truly miscible. As an exception, the mixture of CEP with poly(vinylphenol) may be mentioned[4]; this blend is miscible and has improved impact strength and creep. In several patents, it is claimed that CEP blended with 5–20% of poly-(alpha-olefin),[5] poly(vinylidene fluoride),[6] poly-(tetrafluoroethylene),[7] thermoplastic polyester,[8] or a hydroxyl-terminated poly(alkylene oxide)[9] is suitable for shaping into sheets, films, fibers, etc., owing to improved processability and melt strength.

The literature describes use of RCE for preparing photodegradable and biodegradable compositions.[10] Patents on blends of RCE and random ethylene–vinyl alcohol copolymers describe them as useful for packaging films because of their low oxygen permeability and good processability.[11] A recent review of the alternating carbon monoxide–olefin copolymers discusses mainly the palladium-based catalytic system used to prepare them[11a] and many patents describe further details of their preparation and properties. One patent relates to melt spinning of an alternating carbon monoxide–ethylene copolymer (C/E) with a molecular weight of at least 2000.[12] However, all the examples deal with CEP, which was melt spun, and its tensile strength compared with that of commercial fiber grades of nylon 6 and polypropylene; they were equal to 1,400, 950, and 750 MPa, respectively. Another recent patent application[13] discusses C/E fibers spun from solutions in organic solvents such as mixtures of ethylene carbonate or propylene carbonate and aromatic alcohols. The fibers are said to be very strong and colorless. We may surmise that the hydroxyl groups that are present as a result of enolization of some of the keto groups form hydrogen bonds and may be responsible for some of the high

strength of C/E, although dipole–dipole interactions are another possibility. We presume that melt spinning, a more economical and less hazardous mode of fiber production, cannot be performed on C/E because of instability at the stated melting range of 260–280°C. Details of melt spinning are proprietary, but we believe that polymer stability of a few minutes, not seconds or hours, is appropriate.

In the present study, attempts were made to assure the stability of C/E at melt temperatures. The research made use of two approaches, as follows: (1) preparation of hydrogen-bonded blends. The ketone groups of C/E make it an obvious hydrogen-bond acceptor. A suitable polymeric or oligomeric proton donor could be expected to form hydrogen bonds and perhaps a high-modulus ladder structure. Because the formation of hydrogen bonds is thermally reversible, it was supposed that the melting range of C/E might be somewhat decreased, while the hydrogen bonding might aid crystallinity retention and lead to an increased modulus. (2) Stabilization by nonpolymeric or oligomeric additives. We considered it necessary to develop a rationale for the selection of stabilizer candidates. A study of the thermal behavior of C/E using FTIR (including thermal FTIR with a special heatable cell) along with TGA and DSC measurements was used as a guide to the selection of plausible stabilizing additives from several classes of candidate materials.

EXPERIMENTAL

Materials

Samples of alternating carbon monoxide–ethylene copolymer, synthesized and purified under different conditions, were supplied by the Akzo (now Akzo Nobel) Research Laboratory, Dobbs Ferry, NY. They were white powders. Both were produced by processes differing in proprietary details but similar to the processes disclosed by Hanna and Cheron.[11b,c,d] They are designated as POK-I and POK-II. POK-I was estimated to have a molecular weight of 100,000–150,000 (which had been controlled by hydrogen as in refs. 11a,b) and POK-II, which appeared to be partially cross-linked and had a molecular weight in excess of 300,000.

As a second polymer to be used in the preparation of blends with POK, a novolac (SD-1731, a phenol-formaldehyde condensate of m.wt. $\sim$ 800) and

poly(4-vinylphenol) (Polysciences, MW 1500–7000) were selected as typical polyhydric aromatic polymers.

Some initial observations pointed to acidity as one cause of degradation. Catalyst residues containing metal ions coming from manufacture of POK and traces of metals entering during processing were also believed likely to cause degradation. Therefore, it was decided to try as additives (a) acid scavengers and (b) ligands to trap metal ions; (c) antioxidants (sterically hindered phenols, secondary arylamines, phosphites); and (d) finely divided inorganic solids likely to be scavengers for acids or metal ions. The list of additives tested is given in the appendix; they were used without further purification. The quantity of additive used in the primary testing was 2% unless noted otherwise.

Blending Methods

Compositions for testing were produced by either dry or wet blending of the copolymer with the additives.

Dry blending was done particularly when the components were of comparible hardness or when the additive was an insoluble material, using a "Wig-l-bug" Model LP-602E, Crescent Co. vibratory mixer. This device is a common one used in dental laboratories for intimate mixing of dental repair polymers and cements, in which a hard metal ball is vigorously vibrated back and forth in a stainless capsule containing the sample to be mixed. Mixing conditions of 2 min at the medium vibratory speed were ascertained to be adequate by running preliminary tests in which three small random samples out of each mix were checked for similarity by DSC; visual observation also indicated uniformity. With this short mixing time, the sample did not become warmed substantially beyond ambient temperature.

Wet blending was done, especially with those additives that were viscous liquids or organically soluble resins. To the weighed mixture, acetone was added and the contents mixed with a magnetic stirrer. The mixture was then allowed to age in a closed vessel for 5–18 h and then the acetone was removed by evaporation at ambient temperature. The almost dry samples were then vacuum dried at ambient temperature. This procedure was found to give uniform additive distribution throughout the polymer. No separation of impurities present in the initial polymers was seen in this wet-blending operation.

Infrared Spectroscopy

Fourier transform infrared (FTIR) measurements were made using a Digilab FTS-60 FTIR spectrophotometer. A total of 64 scans at a resolution of 2 cm^{-1} were signal averaged and stored. The temperature of the sample chamber was controlled to within 1°C. Infrared spectra were recorded at different temperature intervals after the preselected temperature was maintained for 15 min.

Attempts were made to coat polished KBr plates with solutions of POK containing additives for infrared measurements. However, the films obtained after evaporation of the POK-novolac solution in hexafluoroisopropanol or benzyl alcohol or mixtures thereof with propylene carbonate were opaque and did not adhere to the KBr plate. Therefore, KBr pellets were prepared for these measurements.

Thermal Analysis

The thermal behavior of POK, with and without additives, was studied in sealed pans on a Perkin-Elmer DSC 7 differential scanning calorimeter (DSC). The pan and its contents were heated and cooled at controlled rates, typically heating at 20°/min until about 20°C above the melting point, and then cooling at 10°/min until 10–25°C was reached. The full test cycle included the following steps: (1) heating to 275°C, (2) cooling to room temperature, (3) heating again to 275°C, (4) isothermal heating at 275°C for 10 min, and (5) finally cooling to room temperature. The first (T_{m_1}) and second (T_{m_2}) melting points, the first (T_{c_1}) and second (T_{c_2}) crystallization temperatures, the corresponding heats of melting (H_1 and H_2) and the heats of crystallization (C_1 and C_2) in J/g were determined from the thermograms.

To evaluate the heat stability of POK formulations, the following criteria were used: (a) crystallinity retention as measured by the crystallinity ratio CR defined as C_2/C_1, (b) shift of the second crystallization temperature ΔT_c defined as $T_{c_1} - T_{c_2}$, (c) second heat of crystallization C_2, and (d) ratio of the height of the second crystallization peak to its width at the middle of the peak height $C_{h/w}$.

The change of color of the polymer after this test was also noted.

The higher the CR, the greater the degree of retention of crystallinity. The lower the ΔT_c and the higher the $C_{h/w}$, the smaller the degradation

of the polymer, and the smaller the changes in the crystallite size distribution. The absolute value of the second heat of crystallizion C_2 is also of significance, because it is proportional to the amount of crystalline phase that survived the isothermal heating. At identical CR values, the sample with the higher C_2 is likely to be the one that has suffered the least degradation. The color change also provides evidence regarding the degree of degradation of the polymer. For a textile fiber, discoloration is generally considered bad for aesthetic reasons, regardless of whether other properties have deteriorated.

We suggest the use of these criteria as tools for selecting stabilizer candidates for further evaluation under actual melt-spinning conditions. Probably priority should be given to those stabilizer candidates that show efficacy by more than one criterion.

A DuPont 1090 Thermal Analyzer, equipped with TGA model 951 was also employed for other thermal stability studies. A heating rate of 20°C/min and a gas (nitrogen or air) flow rate of 50 mL/min were used.

To observe changes in the chemical structure of POK, taking place during thermal degradation, FTIR measurements were carried out. The spectra were recorded at different temperatures starting from room temperature up to 270°C, at intervals of 40°C. The samples were held 15 min at each temperature before recording the spectrum.

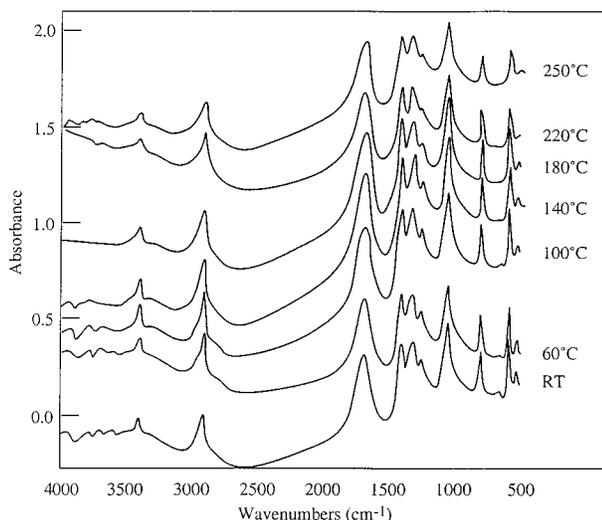To remove possible impurities caused by the

Figure 1 FTIR spectra of the alternating carbon monoxide–ethylene copolymer POK-I recorded at different temperatures, in nitrogen.
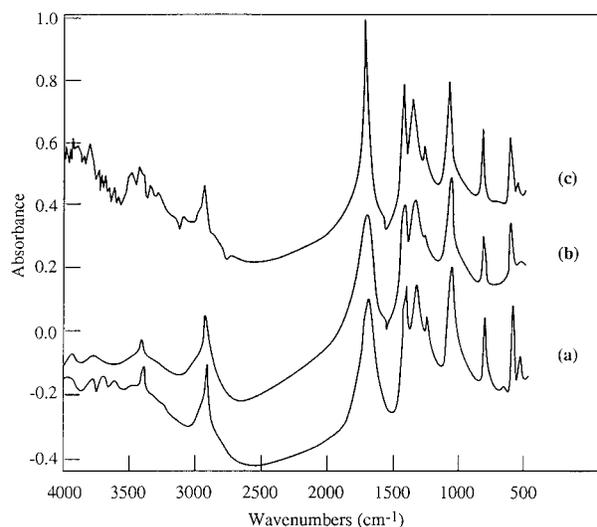

Figure 2 FTIR spectra of POK-I recorded at (a) room temperature, (b) 250°C, and (c) after cooling to room temperature.

acidic catalyst residues, the polymer powder was extracted in a Soxhlet with distilled water. The pH of the water solution was measured with a Orion Model 601A digital Ionalyzer, calibrated with pH 8.0 buffer.

RESULTS AND DISCUSSION

Preliminary Characterization of the Polymer Samples for Selection Purposes

For POK-I and POK-II, samples supplied by Akzo Nobel Research, the pH readings of water extracts from the Soxhlet extraction were 6.54 and 5.98, respectively. The pH of the distilled water used for extraction was 6.50. These measurements showed the presence of some acidic impurities in POK-II.

The recorded FTIR spectra, performed in an inert (nitrogen) atmosphere, are presented in Figures 1–5. For POK-I, no significant differences were observed in the spectra recorded in the temperature range of ambient to 250°C. No changes were observed in the intensity either of the strong carbonyl stretching band at 1702 cm^{-1} nor of the overtone from the same group at 3390 cm^{-1}. No changes occur also with the C—H stretching band at 2910 cm^{-1} or the CH$_2$ bending mode at 1409 cm^{-1}. Peak shifts in the investigated vibration range of the spectrum (4000–500 cm^{-1}) were not seen. In Figure 2 the spectrum of POK-I at room temperature, 250°C and back to room temperature, are compared. It can be seen, that no
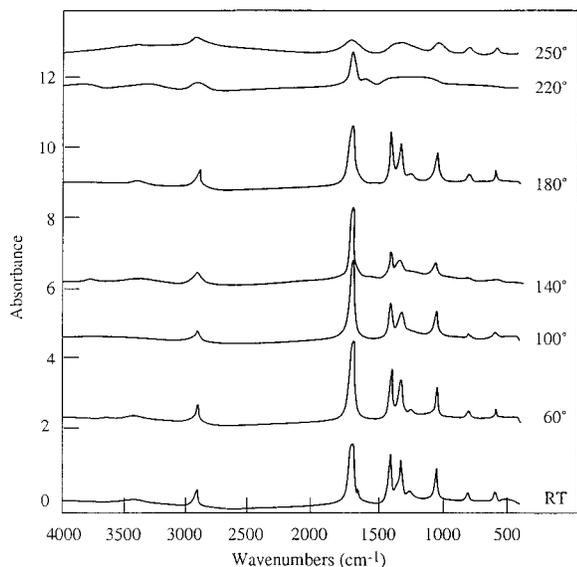
Figure 3 FTIR spectra of POK-II, carried out in conditions as POK-I (see Fig. 1).

changes in the polymer structure were evidenced by the FTIR.

In Figures 3–5, the spectra of the sample POK-II, measured under the same conditions as POK-I, are presented. Already at 220°C, the peaks of the two bands attributed to the C—O stretching have become less intense and broader. In the low-
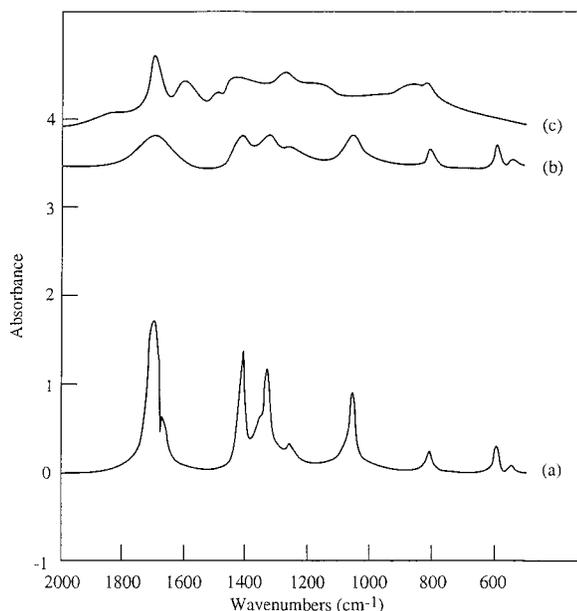

Figure 4 FTIR spectra of POK-II in the 2000–600 cm^{-1} region, carried out in conditions as POK-I; (a–c) as in Figure 2.
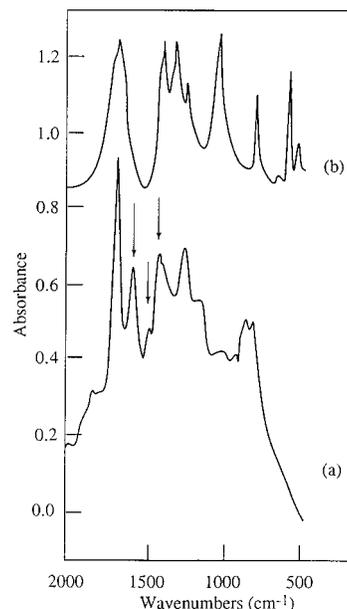

Figure 5 FTIR spectra of POK-II (a) after cooling to room temperature, and (b) at 250°C. The bands marked with arrows at 1600, 1496, and 1403 cm^{-1} are characteristic for 2-substituted furans.

frequency part of the spectrum, bands are also shifted, and some have disappeared. Some of these bands are associated with changes in the olefinic part of the molecule. Also, the presence of new bands in this region was observed. These changes can be seen more clearly in Figure 5. The new bands at 1600, 1496, and 1403 cm^{-1} are characteristic of 2-substituted furans.[14] Their appearance can be explained by the formation of furan rings by intramolecular cyclizations, as might be expected from the acid catalyzed dehydration of 1,4-diketone structures as the temperature is elevated:
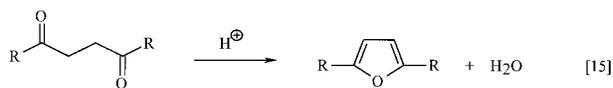
Based on the spectra of the samples investigated, POK-I is stable for at least 15 min at 250°C, whereas POK-II already starts to degrade at 220°C. In fact, neither product could have been used for melt spinning. Therefore, we must conclude that the FTIR is not sensitive enough to be used for heat stability evaluations of POK.

Another method that we tried to use to evaluate the thermal stability of POK was thermogravimetric analysis (TGA). In the present study, the TGA tests were performed in atmospheres of ei-
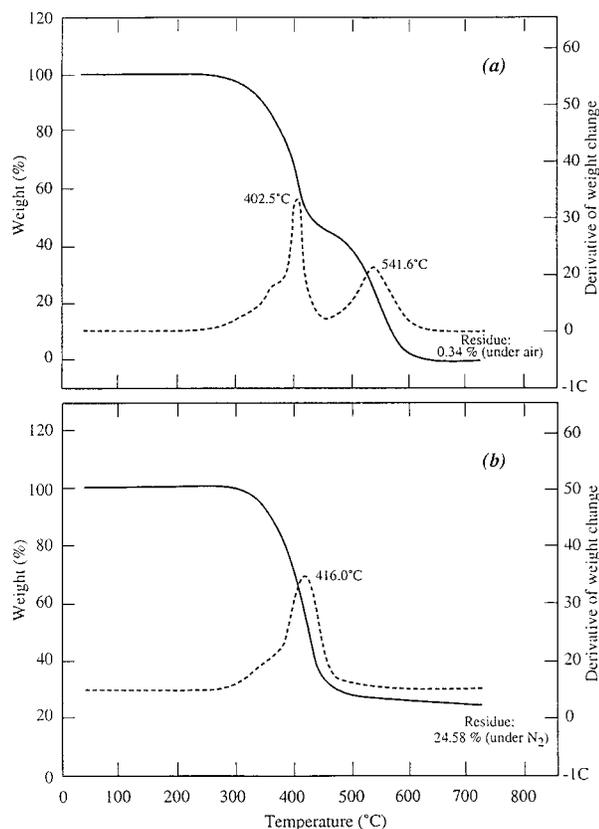
Figure 6 TGA curves of POK at a heating rate of 20°C/min in (a) air and (b) nitrogen.

ther nitrogen or air. The thermograms of POK-I are shown in Figure 6; the data on all the samples tested is summarized in Table I. The TGA curves of POK-II are not given in Figure 6 because their shape is identical to that of POK-I. From Table I, we can see that the weight loss of all samples started in nitrogen at 260°C and in air at 250°C.

At about 400°, the maximum weight loss in air occurs. Between this temperature and approximately 550°, the weight loss per 1°C significantly decreases and a second peak on the derivative curve appears. These phenomena obviously take place because in this temperature interval, in the presence of oxygen, the char formed in the degradation process of the polymer itself begins to degrade or become oxidized until it arrives at the maximum marked by the second peak on the derivative curve at about 550° [Fig. 6(a)]. At 650°, the temperature curves leveled off and at about 750° all tests were stopped. Residues were about 0.3% for POK-I and 2.5% for POK-II. The relatively high residue left by POK-II in pyrolysis under air suggested inorganic components, which was confirmed by the supplier of the samples.

On the derivative curve of the TGA run under nitrogen [Fig. 6(b)], only one peak was observed. All of the samples pyrolyzed under nitrogen left a residue of about 25% (Table I).

The infrared data pointed to furan ring formation, and this suggested that acid-catalyzed dehydration was occurring. A subsidiary piece of evidence is that the char residue (ChR) of POK in TGA under nitrogen corresponds closely to the calculated char yield for the hypothetical polyfuran resulting from every two ketone groups cyclizing dehydratively, as computed by the char prediction formula of van Krevelen[16]:

$$\text{ChR} = 1200 \left\{ \sum_{i} (\text{CFT})_i \right\} / M$$

where CFT is the char-forming tendency for each structural feature i in the structural unit of the polymer and M is the molecular weight per struc-

Table I TGA Data on POK Samples Studied

| POK Sample | Temp. at Which Maximum Weight Loss Occurs (°C) | | | Residue (%) | | Temp. at Which Decrease in Weight Started (°C) | |
| | In N$_2$ | In Air | | In N$_2$ | In Air | In N$_2$ | In Air |
		1st Peak	2nd Peak				
I	416 (24.7)	403 (45.9)	452 (54.3)	24.58	0.34	260	245
II	420 (21.5)	397 (37.9)	584 (64.3)	21.50	2.35	260	250

Figures in parentheses are total percent weight losses observed at the indicated temperatures.
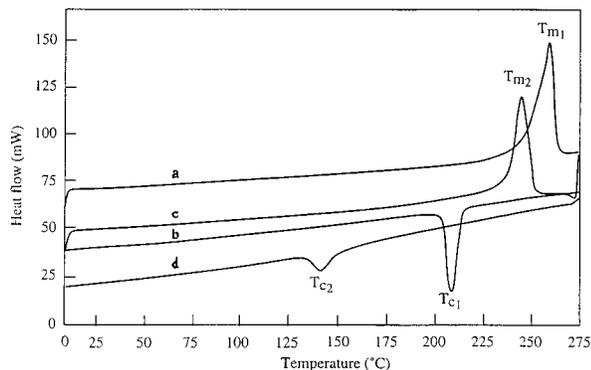
Figure 7 DSC thermograms of POK. The full test cycle includes the following steps: (a) heating to 275°C, (b) cooling to room temperature, (c) heating again to 275°C, and (d) cooling to room temperature. The second cooling step is carried out after an isothermal heating at 275°C for 10 min. T_{m_1} and T_{m_2} are the first and second melting points, T_{c_1} and T_{c_2} are the first and second crystallization temperatures.

Figure 8 The (a) first and (b) second cooling steps of the DSC thermogram from Figure 7, used for calculation of the heat-stability criteria (CR, ΔT_c, C_2, and $C_{h/w}$).

tural unit. Assuming the CFT of furan and benzene rings are similar and that the CFT of the furan ring and the —CH$_2$CH$_2$— group are 4 and −2, respectively, then ChR = 1200 × 2/94 = 25%.

The TGA test results show that, although this method gives interesting information about the weight loss as a function of temperature and ambient atmosphere, it cannot be reliably used as a criterion of melt spinnability of POK.

The thermal behavior of POK was also studied by DSC. A typical DSC-thermogram of an as-supplied POK-I sample, which includes the two heating and two cooling runs, as well as the two scaled-up crystallization (cooling) cycles, which we consider the best evaluation method for heat stability with reference to melt spinnability, are shown in Figures 7 and 8, respectively.

As was mentioned in the Experimental section, the crystallinity retention appeared to be a very important factor, but not the only one, for determination of the melt spinnability of POK. Thus, for instance, POK-II with a crystallinity retention of 58% (Table II) was found to be crosslinked after FTIR tests at elevated temperatures. On the other hand, POK-I did not undergo crosslinking during heating, although its molecular order was more impaired by the thermal treatment (CR = 0.36). Evidence of this phenomenon was the insolubility of the POK-II sample in hexafluoroisopropanol after the FTIR test; the film prepared in a Carver press at about 200°, swelled rapidly, but did not dissolve in this good solvent for POK. From the data in Table II, it can be seen that water extrac-
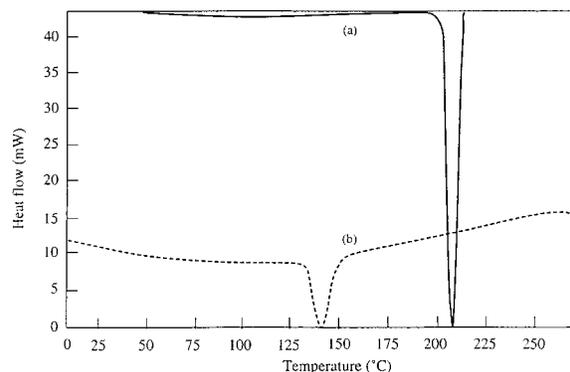
tion improved the heat stability of POK-I by about 30% while the heat stability of POK-II become impaired. As was mentioned above, the water-soluble extract of POK-II was slightly acidic. Therefore, it was decided to use POK-I as the test polymer in the search for heat stability improvement additives. It was used as received and designated as POK (for simplification).

Two general approaches were taken as follows: (1) admixture of hydrogen bonding polymers, and (2) admixture of acid-scavengers and/or other nonpolymeric additives, which should act as heat stabilizers.

The Hydrogen-Bonding Polymer Approach

We selected as a second polymer to use in preparing blends with POK a phenol-formaldehyde novolac (PFR) and poly(4-vinylphenol) (PVP). Their molecular weights were about 800 and 1500–7000, respectively. It was postulated that the hydrogen-bonded copolymer will have a lower melting range, which will lead to an increased

Table II Heat Stability Criteria of Virgin and Water-Extracted POK Samples as Measured by DSC

Sample	CR	ΔT_c, (°C)	C_2 (J/g)
POK-I virgin	0.36	66.7	−37.3
POK-I extracted	0.47	45.2	−48.1
POK-II virgin	0.58	33.7	−42.9
POK-II extracted	0.23	80.2	−16.1

The samples marked "extracted" were Soxhlet extracted 24 h with distilled water.
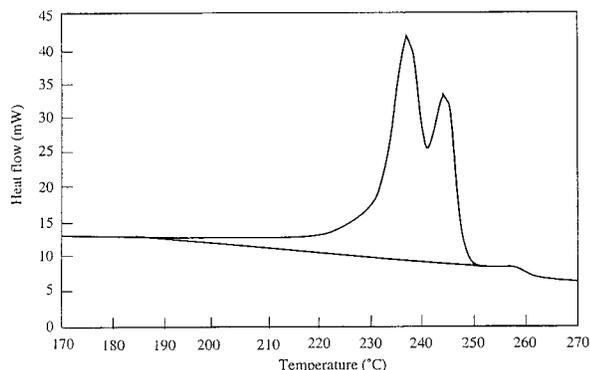
Figure 9 DSC thermogram of POK-10% PVP blend: the second heating run.

stability of POK as a melt. Samples of POK-PFR blends with a content of 5–30% PFR were prepared, and DSC thermal stability tests were carried out. It is interesting to note that the peak in the second heating thermogram of the POK samples blended with PFR and PVP became split (Fig. 9). The higher the amount of the second polymer, the bigger the difference between the newly appearing melting points. The difference became equal to 7, 11, and 17° for blends with 10, 20, and 30% of the added polymer, respectively. This phenomenon might be explained, obviously, by the presence of a hydrogen-bonded polymer of different crystal structure, obtained during the first heating cycle of the polymer mixture. The DSC tests showed also that T_{m_1} of POK was equal to 260°; the addition of 5 and 30% PFR diminished it to 256 and 241°C, respectively. The glass transition temperatures (T_g) of the polymer blends with a content of 0, 10, 20, and 30% of PFR were found to be 53, 46, 46, and 40°C. These data are in a good agreement with the well-known ratio T_g/T_m = 0.6 for high crystalline polymers.

At contents of 10 and 20%, the novolac was found to produce an increase in crystallinity retention of 30 and 50%, respectively, which was deemed encouraging. However, the downward shift of the temperature at which the sample had solidified a second time was quite high (ΔT_c was 45 and 36°, respectively); also the second heat of crystallization was low (see Table III).

Addition of 0.5% of a blend of hindered phenols as antioxidants did not influence the behavior of the copolymer in its melting range. Also, poly(4-vinylphenol) in a blend with POK had no influence on its heat stability.

It should be noted that the range of commercially available proton-donor polymers is quite

limited. Therefore, after these initial experiments, we decided to concentrate our research on the stabilizer additive approach.

The Stabilizer Approach

Some initial observations, as mentioned above, pointed to acidity as one cause of degradation (cyclization, crosslinking) of the copolymer. Water extracts of POK-II, which was noted to be crosslinked after the thermal FTIR tests, were slightly acidic. The infrared and TGA data pointed to furan ring formation, and thus suggested that acid-catalyzed degradation was occurring. Catalyst residues containing metal ions coming from the manufacture of POK and traces of metals getting into the polymer during processing were also suspected of causing degradation. It was also noticed in TGA that air accelerated the degradation somewhat, so there was probably some oxidative involvement also. Therefore, it was decided to try as additives the following: (a) acid scavengers, (b) ligands to trap metal ions, (c) antioxidants (sterically hindered phenols, secondary arylamines, phosphites), and (d) finely divided inorganic solid adsorbents likely to scavenge acids and other destabilizing impurities.

Eleven inorganic compounds (see Appendix, Nos. 1–11) were tested. These were selected based on their frequent utilization as polymer additives, their chemical variety, and their toxicological and color acceptability. We did not consider

Table III Heat Stability Criteria of POK Blended with a Phenol-Formaldehyde Resin or with Poly(4-vinylphenol), Calculated from DSC Thermograms

Additive	CR	ΔT_c, (°C)	C_2 (J/g)
—	0.36	66.7	−37.3
5% PFR	0.38	58.0	−34.7
10% PFR	0.46	45.4	−45.5
20% PFR	0.54	36.4	−43.3
30% PFR	0.42	46.5	−23.9
5% PFR + 0.5% D + Irg.	0.40	53.3	−36.5
30% PFR + 0.5% D + Irg.	0.42	34.5	−23.6
0.5% D + Irg.	0.37	60.0	−36.7
10% PVP	0.37	63.6	−33.6

PFR is Borden SD-1731 novolac, MW ∼ 800. PVP is poly(4-vinylphenol), MW 1500–7000. D is 2,6-di-*tert*-butyl-*p*-cresol. Irg. is *n*-octadecyl ester of 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propanoic acid (Irganox 1076).

Table IV   The Influence of Various Inorganic Additives on the Heat Stability of POK

Additive[a]	CR	ΔT_c, (°C)	C_2 (J/g)	$C_{h/w}$	Remarks[d]
—	0.36	66.7	−37.2	0.89	fd
Calcium silicate	0.29	74	−21	—	fd
Aluminum hydroxide	0.65	14.4	−69	—	vld
CaHA[b]	0.81	4.8	−91	4.97	nd
CaHA[c]	0.84	4.7	−86	—	nd
CaHA + zinc borate	0.81	5.0	−88.3	—	nd

[a] Added at 2% each.
[b] CaHA is calcium hydroxyapatite.
[c] CaHA was added to POK, which had been Soxhlet extracted with water.
[d] Evaluation of copolymer degradation according to color change, ratings as follows: fd—full degradation (from dark brown to almost black); vld—very low degradation (beige); nd—no degradation, color remains (light green olive).

that POK and polyolefins had enough similarity for our selection to be guided by considerations of polyolefin nucleating agents. The results of the DSC measurements showed that calcium silicate, talc, and calcium carbonate actually impaired the structure of the polymer; the crystallinity retention dropped by about 20% in comparison with untreated POK; also, the second heat of crystallization was still very low (−21 J/g, see Table IV). Antimony pentoxide, contaminated with sodium antimonate (a basic compound), calcium stearate, and calcium lactate led to severe degradation already after the second heating step. In the presence of calcium hydroxide and barium nonylphenolate, POK shows catastrophic degradation already during the first heating run.

These results showed that compounds that are even slightly basic, such as salts of strong bases and weak acids, all led to severe degradation of the copolymer. Only the amphoteric aluminum hydroxide and especially the neutral calcium hydroxyapatite (CaHA), improved the heat stability of POK, which is consistent with some patent publications.[17,18] As can be seen from the data of Table IV and Figure 10, the crystallinity retention of the sample that contains CaHA is 2.25 times higher than that of the untreated copolymer, the shift of T_{c_2} is only about 5°C, and only small changes in the crystallite size distribution occurred ($C_{h/w}$ was approximately 5). The presence of zinc borate does not enhance the activity of CaHA (Table IV).

Three ligands, dibenzoylmethane (Rhone-Poulenc R83), benzoylstearoylmethane (Rhone-Poulenc R50) and hydroquinone bis(diphenyl phosphate) (HDP) (Appendix, Nos. 12–14) were tested as single additives and in combinations with CaHA. All of these compounds deteriorated

the heat stability of POK (see Table V). The combination of the diketones R83 or R50 with CaHA, however, results in a sharp improvement in the thermal stability of the copolymer, and it becomes stable in the tested conditions. It must be noted that these two ligands together with CaHA impart the lowest ΔT_c (Fig. 11). The combination HDP-CaHA demonstrates less efficacy—all calculated values of the heat-stability criteria showed low influence of the salt in the presence of HDP. This behavior can obviously be explained by the formation of additional acidic products, although the hydrolysis of phosphoric esters occurs usually in severe conditions.

Two aromatic carbodiimides, Stabaxol I and Stabaxol P (Bayer) (Appendix, Nos. 15–16) were tested because it was known that the carbodiimides can act as acid scavengers[19] by undergoing addition reactions. In Table V are given the heat stability criteria, calculated from the DSC thermograms of the samples containing these additives. It can be seen that both carbodiimides
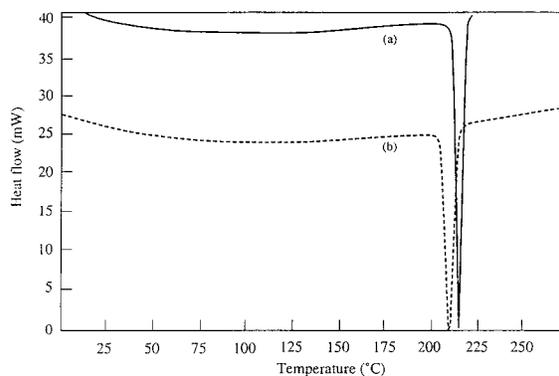

Figure 10 The (a) first and (b) second cooling steps of the DSC thermogram of POK+2% of CaHA.

Table V   The Influence of Some Ligands and Acid-Scavengers on the Heat Stability of POK

Additive[a]	CR	ΔT_c, (°C)	C_2 (J/g)	$C_{h/w}$	Remarks[c]
R83	0.19	86.1	−16.7	0.2	fd
R83 + CaHA	0.77	0	−80.9	3.0	nd
R50	0.31	75.2	−27.8	0.63	fd
R50 + CaHA	0.80	1.3	−85.7	6.79	nd
HDP	0.33	63.6	−30.0	—	fd
HDP + CaHA	0.56	18.5	−45.9	—	ld
Stabaxol I	0.39	51.9	−37.7	—	d
Stabaxol P	0.38	53.0	−37.3	—	d
Stabaxol P + CaHA	0.88	5.1	−94.7	—	nd
Stabaxol P + CaHA[b]	0.87	4.4	−102.4	5.72	nd

[a] As in Table IV.

[b] Added at 1% each.

[c] Evaluation of copolymer degradation according to color change, ratings as follows: ld—low degradation (light brown); d—degradation (brown); fd and nd—as in Table IV.

slightly increase the CR of POK from 0.36 to 0.38–0.39. However, with Stabaxol P at 1–2% in combination with 1–2% CaHA, the samples become very stable under these test conditions.

It is known that epoxy compounds readily esterify acids by a ring-opening reaction. Therefore, it was reasonable to try them in the mode of acid scavengers for stabilization of POK. A variety of epoxy compounds was evaluated (see Appendix, Nos. 17–26). Relatively good results were obtained with the monofunctional epoxy compounds Vikoflex 7010 (an epoxidized soy oil) and two epoxidized terpenes, limonene monoxide and alpha-pinene oxide. However, Vikoflex acts also as a plasticizer and decreases the height of the crystallization peaks; also, the color of the sample after the DSC test showed evidence of some degradation. The other four monofunctional epoxides (Appendix, Nos. 19–22) increased the crystallinity

Figure 11   The (a) first and (b) second cooling steps of the DSC thermogram of POK + 2% R50 + 2% CaHA.

retention only to 0.56–0.65, the ΔT_c was above 20°C and the color indicated degradation.

Polyfunctional epoxy compounds of the cyclohexene epoxide type, namely ERL 4221 and DEN 444, were also tested. The data in Table VI show that these epoxides impart higher thermal stability than the monoepoxides. It was found, however, that when ERL 4221 was used as a single additive, it actually acted as a prodegradant, but gave good results in the presence of Irganox B215 as a background stabilizer. On the other hand, Irganox B215, which is a blend of Irganox 1010 (a hindered phenol, Appendix, No. 36) and Irgafos 168 (a phosphite; Appendix, No. 34) degraded POK in the absence of any acid scavenger. The effect of the two additives on POK, resembling synergism, was used by testing of other epoxies: 1% of Irganox B215 was added to all of them. The third tested polyfunctional epoxy compound, Epon 1007E gave insignificant improvement of the thermal stability of POK (see Table VI).

Some secondary amines are known as efficient antioxidants, especially when used in combination with phenolic stabilizers. Phenolics are also effective in the presence of organophosphites. Nevertheless, we decided to test each of those chosen as heat stabilizers of POK by themselves (see Appendix, Nos. 27–36).

From the three secondary amines tested (Appendix, Nos. 27–29) Aranox degraded POK already in the second heating run, and no crystallinity peak appeared on the second cooling curve. Possibly the sulfonamide functional group in Aranox was detrimental. Aminox, on the other hand, had practically no influence on the thermal stability of POK. Naug-
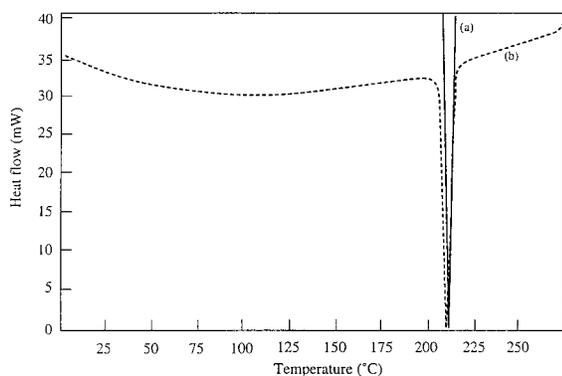
Table VI   Heat Stability of POK in the Presence of Various Epoxy Compounds

Additive[a]	CR	ΔT_c, (°C)	C_2 (J/g)	$C_{h/w}$	Remarks[b]
Vikoflex 7010	0.68	18.1	−59.4	—	ld
Limonene monoxide	0.68	14.1	−74.2	0.91	nd
Alpha-pinene oxide	0.68	15.8	−69.9	1.28	vld
DEN 444	0.71	13.2	−78.9	2.15	nd
ERL 4221	0.70	10.7	−71.3	1.75	nd
EPON 1007F	0.61	22.8	−66.3	1.29	ld

[a] Each sample besides 2% of the epoxy additive also contained 1% Irganox B215.
[b] Evaluation of copolymer degradation according to the color change as in Tables IV and V.

ard 445, an alkylated diphenylamine, showed some positive action on the copolymer—its heat stability by the criteria of CR, ΔT_c and C_2 were 0.48, 41.2°C and −47.9 J/g, respectively.

The multifunctional hindered phenol antioxidants (Appendix, Nos. 30–32 and 36) do not affect the thermal stability of POK. One of the two tested phosphites (Appendix, Nos. 33–34), the Ultranox 626 had a very damaging effect on POK after the second heating run. Irganfos 168 diminished CR and C_2 of the sample to 0.22 and −19.7 J/g, respectively, and increased ΔT_c to almost 110°C. Only Irganox 1425 (Appendix, No. 35), a calcium phosphonate of a hindered phenol, increased the heat stability of POK, but not enough to avoid some deterioration (CR = 0.51). The reason of the deterioration of POK in the presence of the above-mentioned phosphites is probably because they are very readily hydrolyzed to acidic products.

It should be noted that the addition of 1–2% of CaHA along with some of the otherwise damaging or ineffectual antioxidants made the copolymer thermally resistant. Some results are given in Table VII. These data show that CaHA added along with the secondary amine Naugard 445 or the hindered phenol Ethanox 330 sharply improved the

thermal properties of POK: the copolymer after the full DSC sequence, retained more than 80% of its original crystallinity. Moreover, the presence of the antioxidants makes it stable against other unforeseen environmental conditions. On the other hand, phosphorus-containing additives (phosphites, phosphonates) even in combination with CaHA show only a very small increase in thermal stability of POK.

In addition to the four groups of chemical additives, some derivatives of cellulose were also evaluated as thermal stablizers for POK. This was done taking note of a patent[20] that showed that the melt stability and apparent crystallinity retention of polyketone terpolymers was improved by finely divided cellulose itself. We hypothesized that some cellulose ethers might be more miscible and might perform even better than cellulose (Appendix, Nos. 37–40). The data in Table VII summarizes the results obtained. Vacuum-dried cellulose is seen to be better than undried cellulose. Hydroxypropylcellulose and ethylcellulose also had a beneficial stability effect. Ethylcellulose was further improved by the presence of Irganox B215, but hydroxypropylcellulose was not. The Irganox did not influence the activity of cellulose itself.

Table VII   The Influence of Various Antioxidants Individually and in Combination with CaHA on the Heat Stability of POK

Additive[a]	CR	ΔT_c, (°C)	C_2 (J/g)	Remarks[b]
Naugard 445	0.48	41.2	−47.9	d
Naugard 445 + CaHA	0.82	7.0	−91.6	nd
Ethanox 330	0.35	64.4	−33.6	fd
Ethanox 330 + CaHA	0.83	7.3	−92.4	nd
Irganox 1425	0.51	38.4	−50.4	d
Irganox 1425 + CaHA	0.57	25.2	−62.8	ld

[a] The additives were at 2% each.
[b] See note b in previous table.

Table VIII The Influence of Cellulose and Its Ethers on Thermal Stability of POK

Additive[a]	CR	ΔT_c, (°C)	C_2 (J/g)	$C_{h/w}$	Remarks[c]
None	0.36	66.7	−37.3	—	fd
Cellulose	0.39	51.6	−39.9	0.45	fd
Cellulose[b]	0.54	28.1	−56.7	0.63	d
Cellulose + 1% Irganox					
B215	0.40	49.5	−40.8	0.54	fd
Ethylcellulose	0.51	30.6	−52.3	—	d
1% Ethylcellulose + 1%					
Irganox B215	0.62	19.7	−67.6	2.07	vld
Hydroxyethylcellulose	0.02	89.9	−1.3	—	fd
1% Hydroxypropylcellulose	0.60	23.8	−60.0	0.48	vld
1% Hydroxypropylcellulose					
+ 1% Irganox B215	0.62	21.0	−65.1	1.75	vld

[a] As in Table IV if not otherwise marked.
[b] Vacuum dried.
[c] As in previous tables.

Curiously, hydroxyethylcellulose had a prodegradant effect, but we found by pH testing that the sample was strongly alkaline, probably the result of the use of alkali in its production.

SUMMARY

Attempts were made to assure the stability of POK at its melting range. The research began

with two approaches: (1) preparation of hydrogen-bonded polymer blends, and (2) addition of plausible stabilizers, singly or in combination with already known stabilizers.

FTIR, TGA, and DSC measurements showed that the DSC method can be used for sensitive evaluation of POK stability in the melt-spinning temperature range. Four criteria, obtainable from the thermograms, were selected for this purpose,

Table IX Summary of the Most Favorable Results

Sample No.	Additive	CR	ΔT_c, (°C)	C_2 (J/g)	$C_{h/w}$
1	1% Stabaxol P	0.73	12.1	−77	3.2
2	2% Stabaxol P + 2% CaHA	0.88	5.1	−95	5.7
3	1% Stabaxol P + 1% CaHA + 1% R50	0.85	2.7	−98	5.6
4	2% R50 + 2% CaHA	0.81	1.3	−92	7.7
5	2% R83 + 2% CaHA	0.77	−1.2	−81	3.0
6	2% ERL 4221	0.70	10.7	−72	1.8
7	1% ERL 4221 + 1% CaHA + 1% R50	0.77	3.3	−86	6.7
8	1% ERL 4221 + 1% CaHA + 1% R83	0.75	5.7	−84	4.1
9	1% ERL 4221 + 1% Naugard 445	0.71	14.0	−68	1.0
10	2% DEN 444	0.71	13.2	−79	2.2
11	2% Limonene monoxide	0.68	14.0	−74	1.0
12	1% Ethylcellulose	0.62	19.0	−68	2.1
13	1% Hydroxypropylcellulose	0.62	21.0	−65	1.8

[a] To all blends except samples 2, 4, and 5, Irganox B215 was added at 1%, as a background stabilizer.
[b] No change of color, after the DSC tests, of any of the listed samples was seen except for slight change with samples 12 and 13.

namely: the crystallinity retention CR, the shift of the second (cycle) crystallization temperature ΔT_c, the second heat of crystallization C_2, and the ratio of the height of the second crysallization peak to its width at the middle of the peak height $C_{h/w}$. These four DSC criteria represent an effective selection tool. Also, the change of color of the polymer after the DSC test can be taken into consideration.

In approach (1), phenol-formaldehyde oligomer and poly(4-vinylpyridine) showed only small increments of C_2 and ΔT_c. Taking into account that few suitable blending polymers for this purpose are commercially available, most of our effort was put into approach (2). Based on the IR, TGA, and also some pH measurements on POK samples, the classes of stabilizer candidates explored were acid scavengers, ligands, antioxidants, some possible buffering-type inorganic compounds, and cellulose ethers. The best results obtained under our experimental conditions (Table IX) were with combinations of hydroxyapatite with a polymeric carbodiimide and/or with a metal chelant. A hindered phenol antioxidant may have also contributed stabilization in some combinations. A cycloaliphatic epoxide (presumed acid acceptor) was moderely active by itself but better in combination with hydroxyapatite and a metal chelant. All of the results in which no (or very little) change of color was seen on DSC testing are given in Table IX. They show that if CR 0.70, ΔT_c 14°C and C_2 -70 J/g, no deterioration of POK (as evidenced by color change in the DSC sequence) was observed. At CR 0.75, $C_{h/w}$ was always higher than 3.00.

These additive systems are reasonable selections for trial in melt-spinning tests.

APPENDIX

List of Additives Evaluated as Stabilizers in POK

1. Calcium hydroxyapatite, Aldrich.
2. Calcium silicate, synthetic, Micro-Gel.
3. Talc, RX-3441, Pfizer, $Mg_3H_2(SiO_3)_4$.
4. Calcium carbonate, Albaglos, Pfizer.
5. Calcium hydroxide, Fisher Scientific, CP grade.
6. Colloidal antimony pentoxide, cont. $\sim$ 4% sodium antimonite, Nyacol, PQ Corp.
7. Aluminum hydroxide, OL, 104LE, Lonza.
8. Zinc borate, anhydrous, XPI, 187, U.S. Borax.
9. Calcium stearate (Mallincrodt).
10. Barium nonylphenolate (Interstab).
11. Calcium lactate, Pationic 1230, Pationic Polymer Additives.
12. Dibenzoylmethane, Rhodiastab 83, Rhône-Poulenc.
13. Benzoylstearoylmethane, Rhodiastab 50, Rhône-Poulenc.
14. Hydroquinone bis(diphenyl phosphate), Akzo Nobel experimental sample.
15. Aromatic carbodiimide, 2,2′,6,6′-tetraisopropyldiphenylcarbodiimide, Stabaxol I, Rhein Chemie Corp. (Bayer).
16. Aromatic polycarbodiimide, Stabaxol P, Rhein Chemie Corp. (Bayer).
17. Epoxynovolac, DEN 444, Dow.
18. Cycloaliphatic diepoxide, ERL 4221, Union Carbide.
19. Styrene oxide (phenyl oxirane), Union Carbide.
20. Vinyl cyclohexene monoxide (1,2-epoxy-4-vinylcyclohexane), Union Carbide.
21. Alpha-olefin epoxide C16 (1,2-epoxyhexadecane), Union Carbide.
22. Oligomeric epoxyalkane, Permethyl 100 Epoxide, Permethyl Co.
23. Methyl epoxy soyate, Vikoflex 7010, Elf Atochem.
24. Limonene monoxide, Elf Atochem.
25. Alpha-pinene oxide, Elf Atochem.
26. Bisphenol-A-based epoxy resin, EPON 1007F, Shell Chemical Co.
27. p-(p-Toluenesulfonamido)diphenylamine, Aranox, Uniroyal Chemical.
28. Diphenylamine-acetone reaction product, Aminox, Uniroyal Chemical.
29. Alkylated diphenylamine, Naugard 445, Uniroyal Chemical.
30. 1,2-Bis(3,5-di-t-butyl-hydroxyhydrocinnamoyl)hydrazine, Irganox MD 1024, Ciba Geigy.
31. Tris-(3,5-di-t-butyl-4-hydroxybenzyl)isocyanurate, Irganox 3114, Ciba-Geigy.
32. 1,2,3-Trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl)benzene, Ethanox 330, Ethyl Corp.

33. Bis(2,4-di-*t*-butylphenyl)pentaerythritol diphosphite, Ultranox 626, GE.
34. Tris(2,4-di-*t*-butylphenyl)phosphite, Irgafos 168, Ciba-Geigy.
35. Calcium bis[monoethyl(3,5-di-*t*-butyl-4-hydroxybenzyl)phosphonate], Irganox 1425, Ciba–Geigy.
36. Tetrakis[methylene(3,5-di-*t*-butyl-4-hydroxyhydrocinnamate)]methane, Irganox 1010, Ciba-Geigy.
37. Ethylcellulose, Type No.50, Aqualon Co.
38. Hydroxyethylcellulose, Natrosol 250 MR, Aqualon. Co.
39. Hydroxypropylcellulose Klucel M, Aqualon Co.
40. Microcrystalline cellulose, water < 5%, FMC Corp.

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