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### PERFORMANCE OF PE PIPES UNDER EXTRACTIVE CONDITIONS; EFFECT OF THE ADDITIVE PACKAGE AND PROCESSING

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## ABSTRACT

Polyethylene (PE) compounds were prepared with five primary antioxidants and five application stabilizers, pelletized and extruded to pipes under industrial conditions. The pipes were stored in water at 80 °C for one year. Samples were taken at various intervals and a range of properties were determined from the functional group (methyl, vinyl, *t*-vinylene) content of the polymer to the crack propagation rate of the pipe. The results showed that chemical reactions take place both during extrusion and soaking. The chain structure of the polymer is modified only during processing, but not during storage, at least in the time scale of the study. The direction and extent of changes are determined mainly by the type of the application stabilizer, but primary antioxidants also influence them to some extent. Soaking modifies the physical, but not the chemical structure of the polymer. On the other hand, the chemical reactions of the additives determine color and stabilizer loss thus the residual stability of the pipes. The chemical structure of the polymer has a larger effect on final properties, on the rate of slow crack propagation and failure, than the physical structure of the pipes. As a consequence, the application stabilizer plays an important role in the determination of pipe performance.

**KEYWORDS:** polyethylene, pipe, antioxidant, application stabilizer, crack propagation

## 1. INTRODUCTION

The service life of plastic pipes and the factors influencing it have been the subject of considerable interest for some time. Pipes are used in the most diverse application areas including water, waste water and sewer pipes, floor, wall and ceiling heating systems, warm and hot water solar systems and natural gas supply [1]. Their guaranteed service life is 50 years in most cases. The lifetime of pipes is usually predicted by using internal pressure tests, in which the pipe is subjected to different internal stresses and the time to rupture is measured [2,3]. In accordance with most literature sources, Gedde and Ifwarson [4] claim that chemical processes play a role only in the last stage of lifetime, when the complete consumption of stabilizers leads to brittle fracture. The detailed study of the failure of pipes in a pressure test showed that many different mechanisms contribute to rupture, e.g. the diffusion of additives and oxygen, degradation reactions, etc. [5-8]. These processes depend on the polymer, the additive package, the surrounding environment and other conditions [9-15].

Evaporation, leaching by the surrounding media or chemical reactions result in the loss of stabilizers during the lifetime of the pipes. According to Gedde et al. [16-19] the consumption of stabilizers by chemical reactions can be neglected, the largest loss is usually caused by leaching. Pfahler [20,21] also showed that in the presence of water migration and loss depends on the chemical structure of the stabilizer; the use of additives with smaller molecular mass often leads to shorter lifetimes, because of faster evaporation or leaching [22,23]. Gedde et al. [18,19,24] divided the time dependence of stabilizer loss and chemical degradation into three stages: the precipitation and segregation of the additive, leaching, and the autoxidation of the polymer. Although segregation might occur indeed, Dörner et al. [25] did not find a stepwise decrease in stabilizer content and OIT with time, and Billingham [26] could not prove the existence of additive droplets in the poly-

mer. Nevertheless, it is clear that the hydrolytic and chemical stability, solubility and diffusion of additives are crucial factors determining the lifetime of polyolefin pipes especially when they are in contact with extractive media. At the beginning chemical reactions are not supposed to play any role in the failure of the pipe. However, it is known that oxygen, stabilizers and the polymer always react with each other leading to stabilizer consumption and to the modification of the chain structure of the polymer.

Numerous literature sources including those cited above prove that considerable work has been done on the degradation and failure of polyethylene pipes. Nevertheless, several questions are completely unclear or have not been dealt with at all. For example, only limited attention has been paid to the hydrolytic stability of antioxidants and its possible effect on the lifetime of products in contact with extractive media [27]. Moreover, industrial additive packages used in pipe production contain several components including a primary antioxidant, a processing stabilizer and additives to protect the pipe during its application. These components may have different influences on the lifetime of the pipes and they might even interact with each other resulting in synergistic or antagonistic effects [28,29]. In the framework of a larger project, we prepared polyethylenes with a wide variety of additive packages and extruded pipes from them under industrial conditions. We stored them in water at 80 °C and followed changes in a number of properties including the chemical structure of the polymer, additive loss, color, MFI and slow crack propagation. The goal was to identify the main factors determining the behavior of pipes during their use in the presence of water. The effect and efficiency of the various additive packages are also compared and the role of processing versus soaking in the determination of pipe performance is analyzed in the final section of the paper.

## 2. EXPERIMENTAL

The polymer used in the experiments was the Tipelin PS 380 pipe grade ethylene-1-hexene copolymer of TVK, Hungary. The additive packages contained five phenolic antioxidants and five application stabilizers. Hostanox O10 and Hostanox O3 (both from Clariant) are ester type antioxidants, while Ethanox 330 (Albemarle) and Cyanox 1790 (Cytec Industries) were used for comparison, since they do not contain such groups and should be stable in water. The fifth antioxidant used was Hostanox HO310, which is the 1:1 mixture of Hostanox O3 and O10. The application stabilizers included Hostanox SE4 (Clariant), an organosulphur compound, and Hostavin N30 (Clariant), Tinuvin 622 and Chimasorb 944 (both Ciba Specialty Chemicals), which are relatively large molecular mass hindered amines with various structures. The fifth application stabilizer was Tinuvin 783 (Ciba), which is the 1:1 mixture of Tinuvin 622 and Chimasorb 944. The commercial and chemical names, the supplier, abbreviation and molecular mass of the stabilizers are compiled in Table 1, while their chemical structure is shown in Fig. 1. All five antioxidants were used in combination with the five application stabilizers, thus altogether 25 packages were created. Packages prepared with the SE4 application stabilizer contained 1500 ppm of the antioxidants, while all the other packages 1000 ppm. The amount of the application stabilizer was always 2500 ppm. Additionally, all packages contained also 1500 ppm calcium stearate acid scavenger and 1000 ppm Sandostab PEPQ phosphonite processing stabilizer.

The polymer powder and the additives were homogenized in a Henschel FM 40D/FM 40 AK high speed mixer at 300 rpm for 10 min. The dry-blend was pelletized using a Davo Viscosystem 1.30.02 type single screw extruder at 170-180-185-190-195-200-205 °C zone temperatures and 90 rpm at TVK. The processing stabilization efficiency of the packages was compared by multiple, degradative extrusions. The granules were extruded

using a Rheomex S 3/4" 25 L/D single screw extruder attached to a HAAKE Rheocord EU-10 V driving unit. The extruder was equipped with a screw of constant pitch and 3:1 compression ratio. The die was fitted with a single orifice of 4 mm diameter. The temperature of all zones was set to 260 °C in all extrusion steps. Samples were taken for testing after each extrusion. Pressure pipes with 32 mm outer diameter and 3 mm wall thickness were produced from the pellets by using a Szvogeg SZ-63 extruder at 180-183-183-187 °C barrel and 190-194-195 °C die temperatures and 100 rpm at Pannonpipe Ltd. Pieces of 350 mm length were cut from the extruded pipes and stored in water at 80 °C at TVK. Samples were taken after 0, 3, 5, 7 and 12 months and submitted to various tests.

The functional group content of the polymer was determined by FTIR spectroscopy using a Matson Galaxy 3020 (Unicam) spectrophotometer in the wavelength range of 4000-400  $\text{cm}^{-1}$  at 2  $\text{cm}^{-1}$  resolution with 16 scans. The concentration of methyl [30], vinyl [31,32], trans-vinylene [31,32] and carbonyl groups [33] was determined from the spectra according to the methods described in the respective references. The amount of vinylidene groups could not be determined because their absorbance ( $888 \text{ cm}^{-1}$ ) overlaps with that of the P(V) transformation products of PEPQ ( $890 \text{ cm}^{-1}$ ). The melting and crystallization characteristics of PE were determined using the DSC-30 cell of a Mettler TA 4000 equipment. The measurements were made between -50 and 200 °C on 7-8 mg samples cut from the pipes in two heating and a cooling cycles at 10 °C/min heating and cooling rates. The melt flow index (MFI) of the granules and the pipes was determined according to the ASTM D 1238-79 standard at 190 °C with 2.16 kg load using a Göttfert MPS-D apparatus. Five parallel measurements were carried out on each sample. Residual thermooxidative stability was characterized by the oxygen induction time (OIT) at 200 °C in oxygen atmosphere using a Perkin Elmer DSC 2 equipment. Three parallel measurements were carried out on samples cut from the pipes. All color coordinates, yellowness

(YI) and whiteness (WI) indices and  $\Delta E$  color difference were determined and used to follow color changes. The measurements were carried out using a Hunterlab Colorquest 45/0 apparatus. The rate of slow crack propagation was determined to characterize the resistance of the pipes against mechanical failure. The measurement was carried out according to the ISO 13480:1997 standard on 100 mm long pipes notched to 10 mm length (see Fig. 2) in 5 % polyglycol ether surfactant (NP-10 type Tergitol, Sigma-Aldrich) solution at 80 °C. The rate of crack propagation was followed by daily measurements.

### 3. RESULTS AND DISCUSSION

The results are presented in three sections. First we show the effect of storage in water on various pipe properties and then analyze the influence of granulation and pipe production on the structure of the polymer. General correlations are discussed in a final section including the role of the additive package on the processes taking place during production and storage.

#### 3.1. Soaking

One would expect a number of changes to take place in the physical and chemical structure of PE pipes during their storage in water at 80 °C. The stabilizers may react with dissolved oxygen and water, with each other, and the functional groups of the polymer may also take part in chemical reactions. Soaking leads also to the transformation of crystalline structure, to recrystallization and the perfection of the lamellae. All these changes should appear in the measured properties of the pipes. Rather surprisingly the functional group content of the polymer changed only slightly or practically not at all during one year soaking in water. The limited changes occurring were determined primarily by the application stabilizer, but the primary antioxidant had some effect as well. Vinyl group content is

plotted against soaking time in Fig. 3, as an example, for additive packages containing E330 and the various application stabilizers. The lines drawn in Fig. 3, and in fact in all subsequent figures, are not based on models, but are included to indicate trends and to guide the eye. Vinyl group content seems to decrease slightly at the beginning of soaking in the case of some additive combinations (C944, T783 and N30), while it is constant for the other two additives (T622, SE4). The differences are difficult or impossible to explain, since T783 also contains the Tinuvin 622 stabilizer. The comparison of the effect of the additive packages studied showed that the vinyl group content of the polymer is more or less constant. Similar conclusions can be drawn from the analysis of changes in the concentration of the other functional groups as well, i.e. the chemical structure of the polymer practically does not change during soaking. On the other hand, some migration or leaching of the additives was indicated by the decrease in the intensity of methyl and carbonyl absorptions in the FTIR spectra. As consequence, it is not surprising that the MFI of the polymer does not change much either during soaking. Melt flow index is plotted against soaking time in Fig. 4 for packages containing the C1790 stabilizer. The viscosity of the polymer changes in a very limited extent indeed.

Although soaking time does not have a significant influence on the properties of the polymer, based on Figs. 3 and 4 it is clear that the type of the additives, especially that of the application stabilizers, do. Compounds form groups, and the processing of PE in the presence of the various application stabilizers results in products with quite different properties. The vinyl group content of the polymer is the smallest when packages containing N30 and SE4 are used, while considerably larger in the pipes produced with the other three additives. Melt flow index changes in the opposite direction; the largest MFI is measured in the presence of SE4, N30 and T783, while significantly smaller values are obtained with T622 and C944. Some correlation seems to exist between vinyl content and



MFI, but the relationship is not straightforward shown by the effect and performance of the T783 additive. Although general correlations are clear (groups of additives, relationship between MFI and vinyl) further measurements and analysis are needed to explain small differences and the specific effect of the individual additives satisfactorily.

The results presented above might easily lead to the conclusion that chemical reactions do not take place during soaking or at least they do not influence the properties of the pipes. However, Fig. 5 strongly contradicts this conclusion. The photograph of two sets of pipes is shown in the figure indicating very strong discoloration and different colors. The combination of HO10 and N30 results in strong dark color, whereas yellow color develops gradually during soaking in pipes containing E330 and C944. All pipes show some discoloration, the weakest is observed in the presence of the HO3 antioxidant. A relatively weak yellow color was observed in its combination with all five application stabilizers, but color was always considerably stronger than without any stabilizers. The color developed and the extent of discoloration depended very much on the combination of the primary antioxidant and the application stabilizer also in all other cases changing from very weak to the strong color shown in Fig. 5.

The discoloration of the pipes clearly indicates that chemical reactions take place during their soaking. These reactions do not influence the structure of the polymer, but change the amount of active stabilizer shown by the decrease of oxidation induction time (Fig. 6). The residual stability of the pipes decreases gradually to very small values, at some additive combinations (E330/C944) to zero, in one year. Although loose correlation exists between the discoloration and the decrease of stability, strong deviations can be observed from the general tendency as well (e.g. HO3). The comparison of OIT with carbonyl concentration and yellowness index unambiguously shows that the loss of stability does not result only from chemical reactions including hydrolysis, but also from the leaching of

the stabilizer. Similarly to the functional group content of the polymer and the color of the pipes, residual stability is also strongly affected by the chemical structure of the application stabilizer.

Besides chemical reactions one would expect changes also in the crystalline structure of the polymer as an effect of soaking at 80 °C. Crystallinity is plotted against storage time in Fig. 7 showing an increase, which is relatively fast at the beginning then levels out at the end of storage. Quite unexpectedly, significant differences can be seen also here in the effect of the various additives, especially in that of the application stabilizers. Similarly to other properties, pipes containing C944 and T622 form one group and the remaining three another; the degree of crystallinity is smaller in the presence of the first group and larger when a stabilizer from the second group is used. A possible reason for the different degree of crystallinity might be the grafting of some of the stabilizers (C944, T622) onto the polymer chains that changes their regularity [34]. Mechanical properties and strength are important attributes of pipes. They, including crack propagation, should be determined by the crystalline structure of the polymer. As a consequence, a similar dependence on storage time is expected as in the case of crystallinity. The rate of slow crack propagation is plotted against soaking time in Fig. 8. Contrary to the expectation crack propagation rate changes only slightly as a function of time, and definitely not according to the function as crystallinity. The lack of close correlation between the two parameters (compare Figs. 7 and 8) indicates that not crystallinity, but some other factor determines the fracture resistance of the pipes (see section 3.3). The different effect of the two groups of application stabilizers is clearly visible in this case too. Some of the primary antioxidants like SE4, N30 and T783, also influence crack propagation rate, but in a lesser extent than the application stabilizers.

The analysis of the results showed that the majority of polymer and pipe properties

are independent of storage time. The occurrence of chemical reactions including hydrolysis is unambiguously proved by the strong discoloration of the pipes and the decrease of OIT. Leaching, especially after hydrolysis, contributes also to the decrease of residual stability. The crystalline structure of the polymer changes, crystallinity increases as a result of soaking, but this is not the main factor determining mechanical properties, including the rate of crack propagation of the pipes. The type of the application stabilizer plays a crucial role in the determination of properties, which do not depend on the time of soaking, but on some other factors (see section 3.3).

### **3.2. General correlations, effect of processing**

We analyzed the effect of storage time on properties in the previous section in accordance with the goals of our study. Storage time influences some properties only in a limited extent and definitely did not account for differences in the effect of the various combinations of additives. Obviously, some other factors determine the properties of the pipes and we have not considered the effect of processing, i.e. pelletization and pipe production yet. The effect and efficiency of additive packages are routinely characterized by multiple extrusion runs; all 25 compounds produced underwent the process. The results of such an experiment are presented in Fig. 9 showing the effect of the number of extrusions on the vinyl content of the polymer. According to the figure vinyl content decreases with increasing processing history and the packages can be divided into two groups just as before. Large differences can be observed in the initial vinyl content of the polymer containing the two groups of application stabilizers, and this difference does not change during multiple extrusions, the correlations run parallel to each other. Most of the changes in the structure of the polymer take place during the first extrusion and these changes depend very much on the type of the application stabilizer present. The structure developed in the

first extrusion step does not change much during further processing, and definitely not during soaking. As a consequence, the chemical structure of our polymer is determined by reactions occurring in the first processing step.

One would expect that the rate of crack propagation should depend on the physical structure of the polymer. We expected crystallinity to play an important role in the determination of crack propagation rate, but the comparison of Figs. 7 and 8 shed some doubt on the existence of a close correlation between the two quantities. In order to check the relationship more explicitly, the rate of crack propagation was plotted against crystallinity in Fig. 10. Although some tendency can be observed on the plot, we cannot talk about strong correlation at all. Crystallinity influences crack propagation, but some other factor or factors influences it more strongly. The rate of crack propagation is plotted against the vinyl content of the polymer in Fig. 11. We obtain a much closer correlation between a quantity related to the chemical structure of the polymer and crack propagation than with crystallinity. Since most chemical reactions taking place during processing and storage in water were shown to be closely related to each other [35], we can conclude that the final properties of the pipes including crack propagation are determined by a few chemical reactions taking place during processing, and mainly in the first extrusion step. The direction and extent of these reactions are strongly influenced by the type of the application stabilizer used.

### **3.3. Discussion**

The rather surprising fact that basically the first extrusion of the polymer determines the final properties of polyethylene pipes needs further considerations. Similarly, the lack of change in some properties and considerable variation in others merits additional thoughts. We tried to summarize the factors and processes of granulation, pipe extrusion

and soaking in a scheme presented in Fig. 12. Chemical reactions take place during extrusion among oxygen, the polymer and the stabilizers. These reactions change the structure of the polymer mostly resulting in long chain branches, and in the transformation and loss of the stabilizers. The reactions of the stabilizers are usually accompanied by discoloration, which is, however, much weaker than the color change observed during soaking [35].

Various processes take place also during storage in warm water. Stabilizers may react with each other, with oxygen dissolved in the water, and they also hydrolyze [27]. These reactions and the leaching of the stabilizer or its small molecular mass transformation products formed by hydrolysis result in discoloration, additive loss and the decrease of residual stability (Figs. 5 and 6). The polymer basically does not take part in these reactions; its structure does not change significantly as shown by the constant value of functional groups (Fig. 3) and MFI (Fig. 4). On the other hand, the physical structure of the polymer changes, its crystallinity increases (Fig. 7) and most probably other features of crystalline structure are also modified (e.g. lamella thickness, number of tie molecules). Nevertheless, not these physical changes, but the chemical structure of the polymer developed in the first extrusion step seems to determine the mechanical properties of the pipes. Slow crack propagation rate measured on pipes depends much more strongly on the chemical structure of the polymer (Fig. 11) than on crystallinity (Fig. 10). The reactions of the application stabilizers play a crucial role in the determination of the chemical structure of the polymer, but their type and reactions are important also during soaking, in the loss of additives and the decrease of OIT. The mechanism of crack propagation and the influence of the fine structure of the polymer chain on it need further study.

#### 4. CONCLUSION

Pipes prepared with a wide range of additive packages were stored in warm water

for a year and the study of their properties showed that chemical reactions take place both during processing and soaking. The chain structure of the polymer seems to be modified only during processing, but not during storage, at least in the time scale of the study. The direction and extent of changes is determined mainly by the type of the application stabilizer, but primary antioxidants also influence them to some extent. Soaking modifies the physical, but not the chemical structure of the polymer. On the other hand, the chemical reactions of the additives determine color and stabilizer loss thus the residual stability of the polymer. The chemical structure of the polymer has a larger effect on final properties, on the rate of slow crack propagation and failure than the physical structure of the pipes. As a consequence, the application stabilizer plays an important role in the determination of the performance of the pipes. The exact chemical reactions taking place during processing and soaking, the mechanism of crack propagation and the influence of the chain structure of the polymer on it need further experimentation and study.

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## CAPTIONS

- Fig. 1 Chemical structure of the stabilizers used in the study.
- Fig. 2 Crack propagation in a prenotched pipe. Package: E330/C944.
- Fig. 3 Independence of vinyl content of the time of storage in water. Effect of the application stabilizer. Primary antioxidant Ethanox 330. Symbols: (■) SE4, (●) N30, (▲) T783, (▼) C944, (◆) T622.
- Fig. 4 Effect of soaking on the melt flow index of pipes prepared with various additive packages. Primary antioxidant C1790. Symbols: (⊠) SE4, (⊗) N30, (⊘) T783, (⊙) C944, (⊚) T622.
- Fig. 5 Effect of soaking time on the color of the pipes. a) HO10/N30, b) E330/C944. Soaking time: 0, 3, 5, 7 and 12 months from top to bottom.
- Fig. 6 Decrease of residual stability (OIT) with soaking time for pipes prepared with HO10. Symbols: (□) SE4, (○) N30, (△) T783, (▽) C944, (◇) T622.
- Fig. 7 Changes in the crystallinity of PE pipes as a function of storage time at 80 °C. Primary antioxidant Hostanox O10. Symbols: (□) SE4, (○) N30, (△) T783, (▽) C944, (◇) T622.
- Fig. 8 Effect of storage time and additive package on the rate of slow crack propagation in pipes produced with Hostanox O10. Symbols: (□) SE4, (○) N30, (△) T783, (▽) C944, (◇) T622.
- Fig. 9 Changes in the vinyl content of the polymer stabilized with HO3 in multiple extrusion experiments. Symbols: (■) SE4, (●) N30, (▲) T783, (▼) C944, (◆) T622.
- Fig. 10 Lack of correlation between the crystallinity (first heating) of the pipes after soaking and the rate of crack propagation for the entire set of samples.

Symbols: primary antioxidant = PAO, application stabilizer = AS.

PAO: HO10, AS: (□) SE4, (○) N30, (△) T783, (▽) C944, (◇) T622;

PAO: HO3, AS: (■) SE4, (●) N30, (▲) T783, (▼) C944, (◆) T622;

PAO: HO310, AS: (▣) SE4, (⊙) N30, (▲) T783, (▼) C944, (◆) T622;

PAO: E330, AS: (■) SE4, (●) N30, (▲) T783, (▼) C944, (◆) T622.

PAO: C1790, AS: (⊠) SE4, (⊗) N30, (⊗) T783, (⊗) C944, (⊗) T622.

Fig. 11 Effect of the chemical structure of the polymer chains (vinyl content) on the rate of crack propagation in pipes stabilized with all 25 additive packages. Symbols are the same as in Fig. 10.

Fig. 12 Scheme outlining the main processes occurring during the processing and soaking of PE pipes and the factors determining their properties.

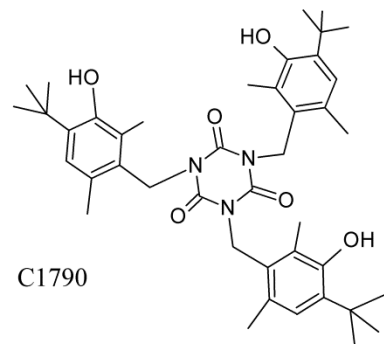
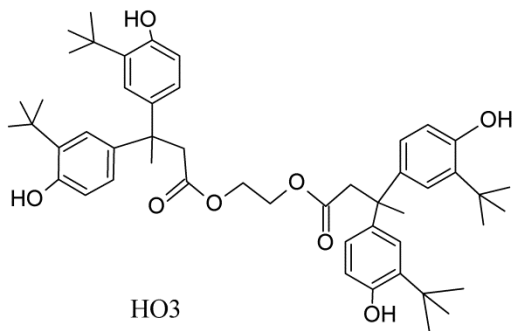
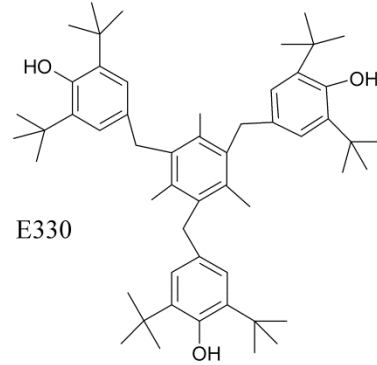
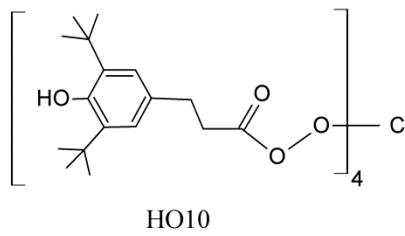
Table 1 The primary antioxidants and application stabilizers used in the study

Trade name	Abbrev.	Chemical name	Supplier	Molar mass (g/mol)
Hostanox O10	HO10	Pentaerythritol tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate]	Clariant	1178
Hostanox O3	HO3	Bis[3,3-bis-(4'-hydroxy-3'-tert-butylphenyl) butanoic acid]-glycol ester	Clariant	794
Hostanox O310	HO310	1:1 mixture of HO10 and HO3	Clariant	–
Ethanox 330	E330	1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene	Albemare	775
Cyanox 1790	C1790	1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethyl benzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione	Cytec Industries	699
Hostanox SE4	SE4	Distearyl-3,3'-thiodipropionate	Clariant	683
Hostavin N30	N30	Polymer of 2,2,4,4-tetramethyl-7-oxa-3,20-diaza-dis-piro[5.1.11.2]-heneicosan-21-on and epichlorohydrin	Clariant	>1500
Chimassorb 944	C944	Poly[[6-[(1,1,3,3-tetramethylbutyl)amino]-1,3,5-triazine-2,4-diyl][(2,2,6,6-tetramethyl-4-piperidiny) imino]-1,6-hexanediyl[(2,2,6,6-tetramethyl-4-piperidiny)imino]]	Ciba SC	~2550
Tinuvin 622	T622	Butanedioic acid, dimethylester, polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidine ethanol	Ciba SC	~3550
Tinuvin 783	T783	1:1 mixture of T622 and C944	Ciba SC	–

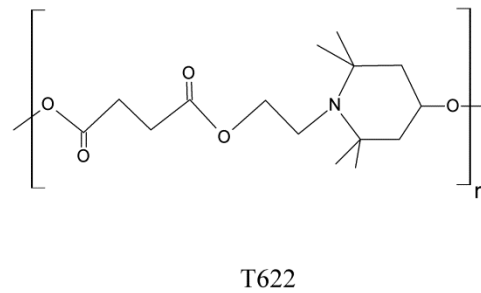
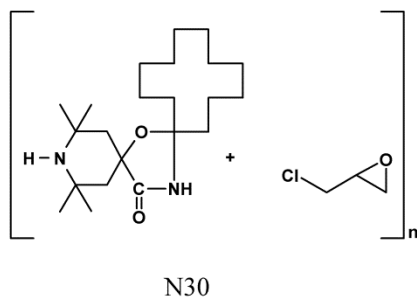
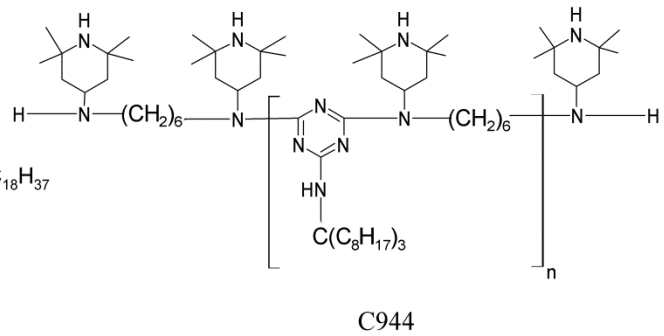
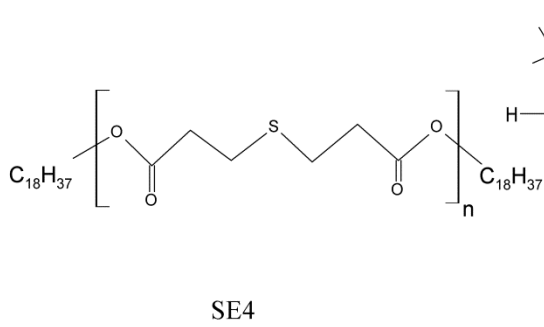
Figures

Tátraaljai, Fig. 1

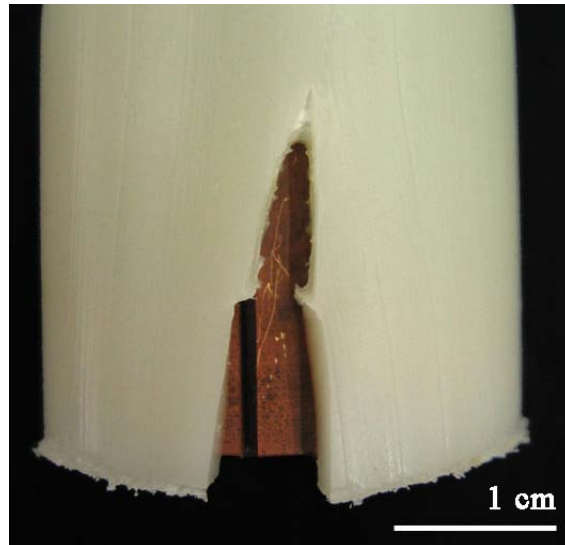
Primary antioxidants



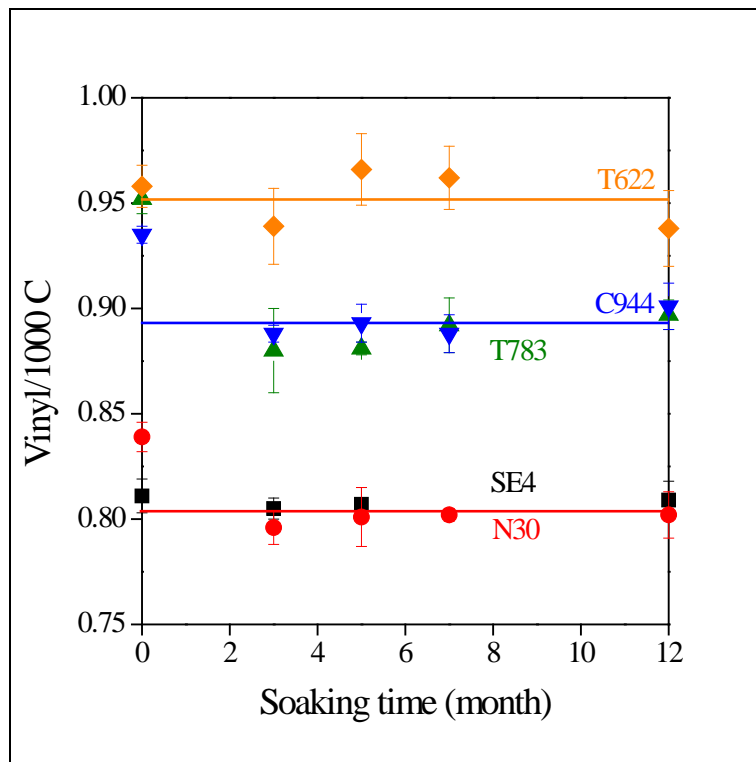
Application stabilizers



Tátraaljai, Fig. 2

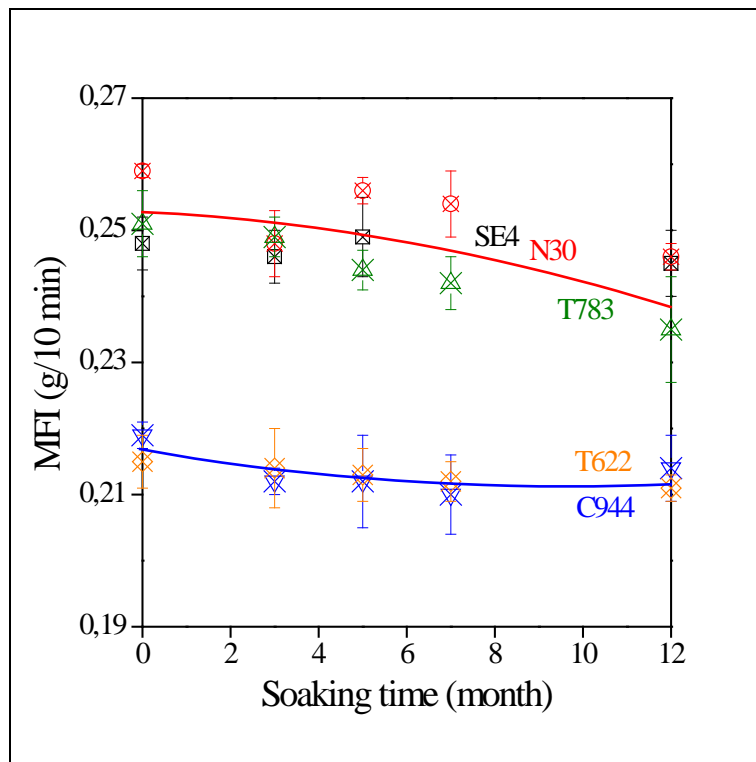


Tátraaljai, Fig. 3





Tátraaljai, Fig. 4



Tátraaljai, Fig. 5

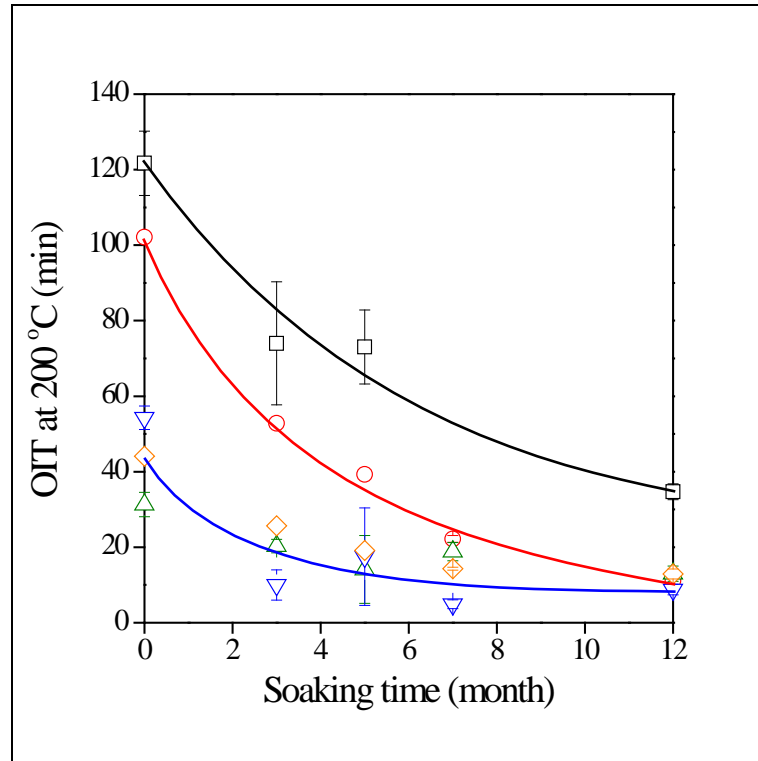


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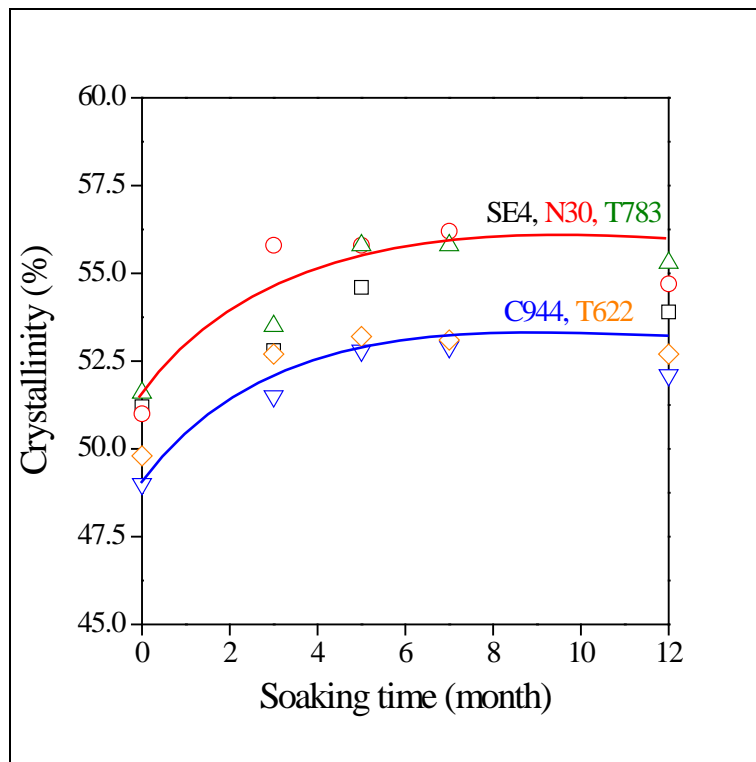


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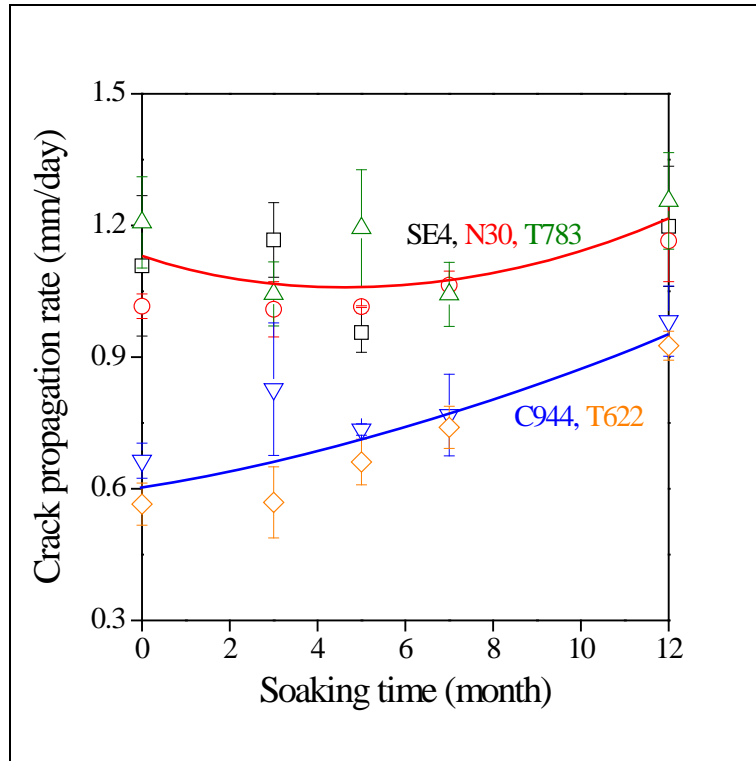
Tátraaljai, Fig. 6



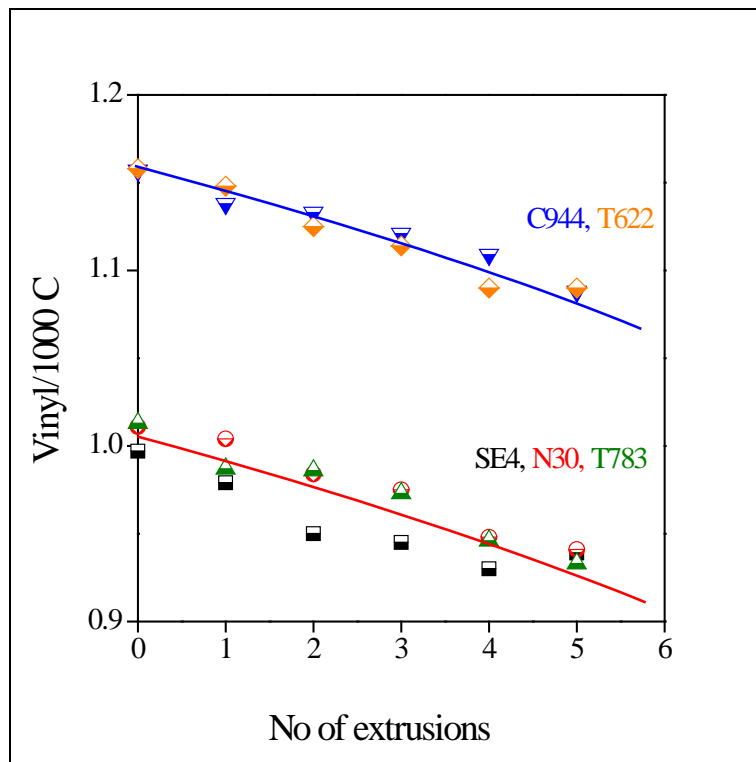
Tátraaljai, Fig. 7



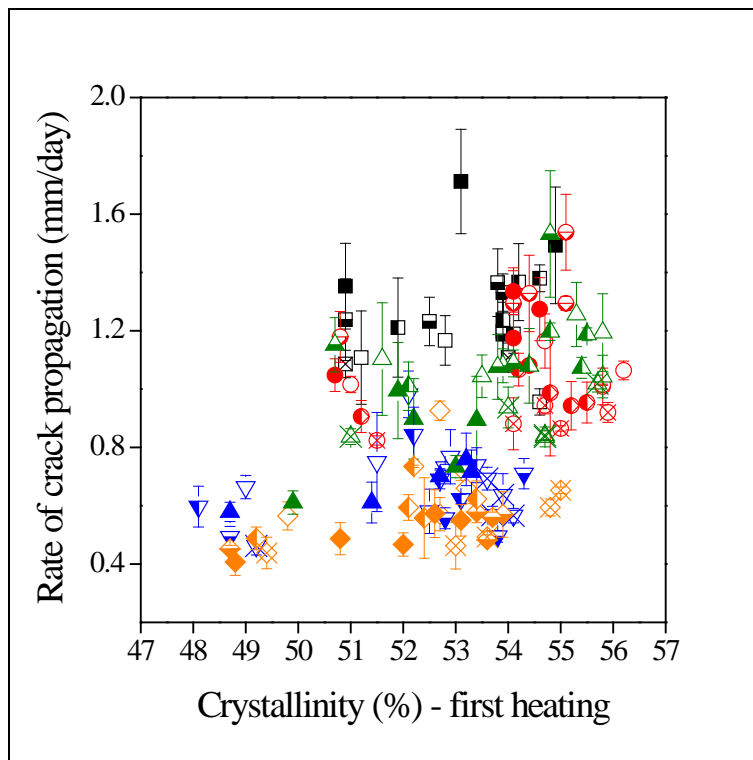
Tátraaljai, Fig. 8



Tátraaljai, Fig. 9



Tátraaljai, Fig. 10







Tátraaljai, Fig. 12

