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The Effect of Degradation and Stabilization on the Mechanical Properties of Polymers Using Polypropylene Blends as the Main Example

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Summary: Degradation can result from a variety of chemical, physical and mechanical mechanisms, most of them involving a reduction of molecular weight and thus a decrease in the mechanical performance of the degraded polymer. A clear understanding and control of these mechanisms is absolutely essential: without stabilization some polymers (e.g. PVC, polyolefins) would not survive their processing undamaged. In this paper an overview of the different degradation mechanisms, their effect on molecular chains, and the methods used to characterize the extent of degradation will be given. Subsequently we establish some fundamental relationships between the microstructure and the mechanical performance (of thermoplastic polymers) using differently aged and stabilized polypropylene (PP) - EPR compounds.

In particular we investigate the influence of two types of heat stabilizers (*phenolic antioxidants* and *hindered amine stabilizer* HAS) on the degradation behaviour of test specimens thermally aged at 120 and 135°C respectively. From an investigation of the changes with aging time in structure and low-strain properties (yield stress, strain at yield, tensile modulus) and from the differences in the evolution of the fracture properties a molecular model of the chain scission mechanisms and of inter-lamellar connectivity (through tie-chain molecules) has been established, which allowed an explanation of the gradual change of the dominant deformation mechanism from cold drawing to crazing and brittle fracture.

Keywords: chain scission; inter-lamellar connectivity; thermo-oxidative degradation; toughness

Introduction

The term *degradation* designates the irreversible and generally detrimental changes in molecular and macroscopic polymer properties, such as the length and configuration of chains, of sample morphology, stiffness and integrity or optical appearance. Degradation must be distinguished from "aging" which simply indicates that a change in some properties occurs with

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time. Changes through aging need not be irreversible or detrimental (as shown by the de-aging or rejuvenation of a glassy polymer by appropriate thermal treatment or by the quite favourable aging of wine).

There are different origins of degradation, which are generally classified as *chemical* (hydrolysis, depolymerisation or other radical reactions), *thermo-chemical* (with and without oxygen present), *photo- and/or radio-chemical*, *physical* (e.g. through crystallisation or *electrical* effects), *mechanical* (stress-induced chain scission during processing or in-service life), *environmental* (including environmental stress-cracking ESC) or *biological* (reaction with enzymes, damage from animals). Evidently there can be strong synergisms between the different damaging processes (see [1-4] for a discussion of the fundamental aspects of degradation and stabilization of polymer materials).

On a molecular level the most notable degrading effects due to the above mechanisms are the scission of chains (followed by loss of material strength and toughness), the formation of chromophore groups (discolouration), and/or the modification of functional properties. In all studies and applications of polymer materials subject to degradation it is desirable to quantify the damage done to the material. The above effects are widely used for that purpose: the *discolouration* of a specimen can be observed with the naked eye (the optical inspection is a rapid, inexpensive and for some systems surprisingly effective qualitative method); the concentration of particular, mostly *oxygen-containing groups* (such as -C=O, -ROOH, -CHO, -C=C-) can be quantitatively monitored by IR spectroscopy; the intensity of *chemiluminescence* is an extremely sensitive tool to trace the rate of degradation; the *decrease of molar mass*, probably the most detrimental effect, is determined by GPC or viscosimetric techniques; the *loss of mechanical strength* and extensibility, which are a direct consequence of the decrease of molar mass, also provide a measure of the advancement of a degradation process, as does the *loss of stability* in thermo-gravimetric analysis.

The basic molecular, physical and mechanical aspects of thermo-oxidative degradation and stabilization will be discussed using as an example the results of an extended research project on polypropylene and its blends carried out at the Swiss Federal Institute of Technology, Lausanne (EPFL) [5-7].

Principles of Thermo-Oxidative Chain Reactions and Stabilization Approaches

Oxidation and degradation of polyolefins proceeds via a radical chain mechanism with initiation, propagation, branching and termination steps. This process is called "autoxidation" since it proceeds in a self-catalyzed manner when a natural or synthetic organic compound is exposed to oxygen. The degradation path is indicated in Figure 1.

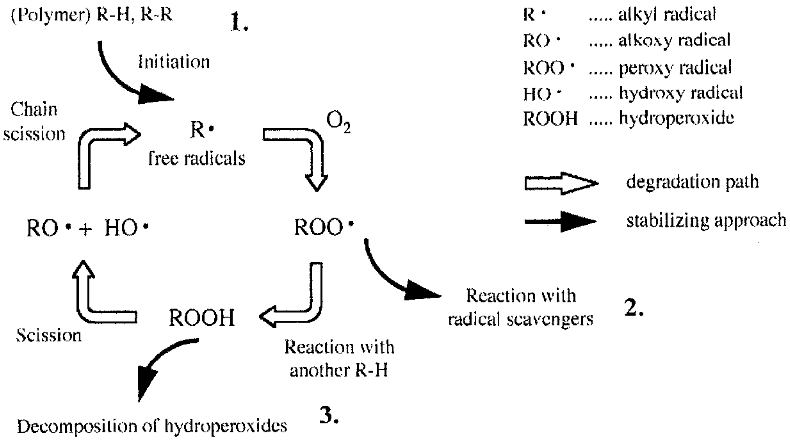

Figure 1. Degradation path for polyolefins. Appropriate stabilizing approaches are the reduction of the rate of radical initiation (**1.**), the inactivation of peroxy radicals (**2.**) and the neutral decomposition of hydroperoxides (**3.**).

Initiation (**1.** in Fig.1) occurs through the formation of some free radicals R• (by one of the causes specified in the introduction: heat, mechanical stress, high energy radiation and/or impurities such as metal ions, catalyst residues or sensitive functional groups as hydroperoxides). If oxygen is present, the free radicals react rapidly with it to form peroxy radicals, which are also highly reactive and *propagate* the reaction chain. Their elimination through radical scavengers (**2.** in Fig.1), therefore, is an important stabilizing approach. Otherwise peroxy radicals will react with other chains by hydrogen abstraction (cleavage of - the weakest - C-H bond), thus transforming into hydroperoxides (ROOH) and *at the same time* creating a mid-chain radical in the attacked chain. Both species take part in subsequent reactions. Hydroperoxides are known to be relatively unstable, and their scission into two active radicals, RO• and •OH, leads to branching of the reaction chain, multiplication of free radicals and formation of main-chain alkoxy and peroxy radicals. The radicalization of a polyolefin chain weakens the C-C bonds in β position to the free electron, reducing the activation energy for chain scission to some 100 kJ/mol [8], which corresponds to that of a RO-OH bond. The so-called β-scission of mid-chain alkoxy and peroxy radicals yields oxygen containing end groups such as aldehydes, ketones, lactones and new alkyl radicals (R•), which propagate the chain reaction. These scission reactions are at the origin of the reduction of molecular weight, which generally constitutes the most important damage. (An unstabilized 120-μm thick PP-film degrades to powder in less than 6 min if exposed to 149 °C under normal atmosphere conditions [1].)

In looking at the reaction chain presented in Figure 1 it becomes apparent that three main factors determine the rate of degradation: (a) all the parameters which lead to the first bond scission event (heat, light, impurities, mechanical stress), (b) the level of concentration and mobility of all the *reactive* species (oxygen, free radicals, highly unstable hydroperoxides), c) the strengths of the bonds involved in a propagation reaction. (For a detailed discussion of the role of chain configuration and bond strengths on the mechanisms and kinetics of oxidative and photo degradation we refer to the literature [1-4] and to the contribution by Rivaton et al. [9]).

Notwithstanding the choice of tacticity and the accidental presence of thermally weak bonds (resulting from e.g. a head-to-head configuration), bond strengths are normally fixed for a given polymer. The inhibition or the retardation of oxidation reactions must therefore proceed via the factors a) and b).

The following stabilizing approaches are commonly used [2].

(1) Elimination of the parameters which cause the first scission of primary bonds. The exposure of a plastic article to heat and light and contact with metals during service cannot be avoided, but the damaging effects of light and of metal ions towards the initiation of autoxidation can be reduced by adding pigments, UV absorbers or *quenchers* and so-called "metal deactivators".

(2) Scavenging of free radicals. The reduction of the number of reactive free radicals is one of the most effective approaches in both heat and light stabilization. A variety of stabilizers with radical scavenging activity are available.

(3) Decomposition of hydroperoxides. Hydroperoxide decomposers are additives, which decompose ROOH in a controlled way without intermediate formation of free radicals. The resulting reaction products are stable and do not lead to further oxidation reactions.

Here the effects of degradation on sample morphology and performance of polypropylene compounds are investigated, using two different stabilizers (a) *hindered phenols* (PHENOL) and (b) *hindered amine stabilizers* (HAS). Sterically hindered phenols are very effective radical scavengers. Their principle mode of action is twofold: a) the transfer of a hydrogen atom to a peroxy radical (ROO•), which results in the formation of a hydroperoxide (ROOH) and a phenoxy radical (Fig. 2a) and b) the coupling of the phenoxy radical with another peroxy radical, leading to its deactivation (Fig. 2b).

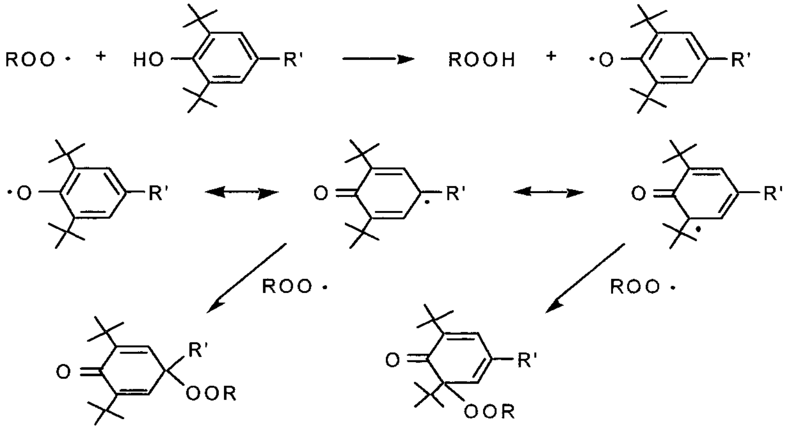

Figure 2. Sterically hindered phenols are effective scavengers of peroxy radicals (see text for details).

HAS stabilizers are compounds based on the 2,2,6,6-tetramethylpiperidine moiety (Fig. 3). The substituent at the nitrogen atom may differ. In the case of Chimassorb 944, which is investigated here, the substituent is hydrogen.

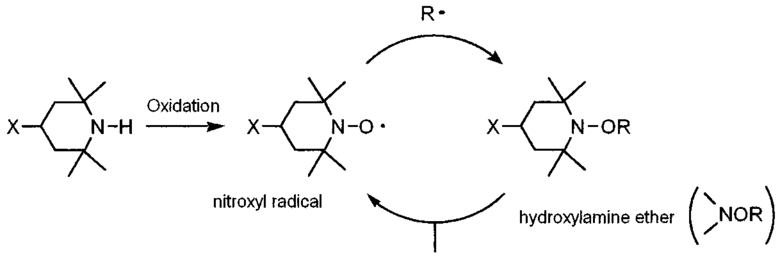

Figure 3. Stabilization mechanisms in hindered amines (HAS). A nitroxyl radical is formed by oxidation of HAS, which is the active species in the stabilizing process. This is able to deactivate an alkyl radical (R•), which leads to the formation of a hydroxylamine ether (NOR). The NOR is subsequently involved in a number of reactions in which nitroxyl radicals are regenerated (and macromolecular peroxides, ROOR, alcohols, ROH, or ketones, R_1COR_2 are formed) and secondary peroxy radicals are deactivated.

In the context of this investigation it is important to indicate that the nitroxyl radical is the active species in the stabilizing process; it is not present in the virgin specimen, but is formed in a first oxidation step. The nitroxyl radical takes part in a reaction cycle involving radical scavenging, regeneration of nitroxyl radicals and deactivation of peroxy radicals. The stabilization mechanisms in hindered amine stabilizers are numerous, they strongly depend on the concentration of stabilizer and reaction products and are not yet fully understood (see [1-4] for a resume on the extensive literature).

Tenacity and Optical Appearance

The stabilizers examined in this study give rise to characteristic differences in degradation kinetics, mechanical behaviour, and optical appearance of the protected polypropylenes. Thermal aging leads to a marked yellowing, especially in phenolic stabilized systems, where the discolouration is due to the formation of quinone compounds (reaction products of phenolic antioxidants). The discoloured zones or *spots* appear after a certain aging period - commonly referred to as the *induction period* t_i. It is the most striking feature of phenolic stabilized compounds that *during* the induction period most mechanical properties and the average molecular weight remain essentially *unchanged*, whereas a sudden and strongly accelerated decomposition of the samples sets in at t_i (Fig. 4). The total loss of strength generally puts an end to any useful service.

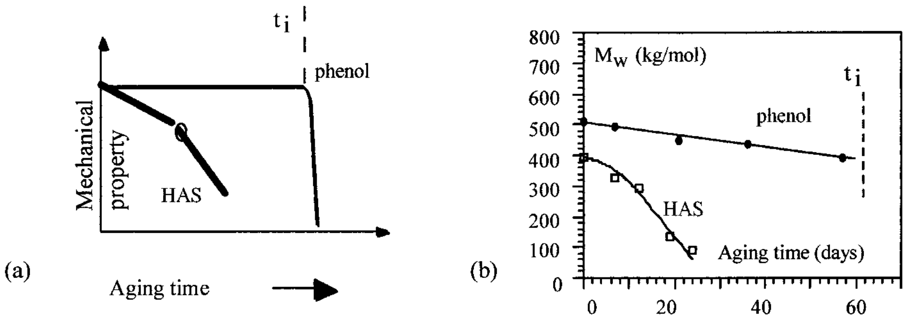

Figure 4. Typical degradation behaviour of phenol- and HAS-stabilized polypropylene; a) change of mechanical performance, b) change of molecular weight (see text for discussion).

The yellowing of HAS stabilized samples is less pronounced than that of phenolic stabilized tensile bars. Whereas HAS samples do not decompose in a catastrophic manner, they show, however, a significant deterioration of their mechanical properties and average molecular weight prior to the first appearance of oxidation zones. From Figure 4 it must be deduced that there are important differences not only in the mechanism of stabilization but also in the point of attack on the macromolecules, which have to be further analyzed. In any event, the reduction in chain length can be considered as the single most important damage effect in thermo-oxidative degradation.

Material Used and Ageing Procedure

Polypropylene from PCD Polymere GmbH., Linz, was investigated. The following table indicates the basic molecular characteristics provided by the manufacturer for the five compounds used. The rubber content of the two in situ polymerized heterophase PP-copolymers (reactor blends) was 10 – 15 wt%

Table 1 . Molecular characteristics of the polypropylene compounds used.

	PP homopolymers (Designation)					PP-reactor blends	
	M	R	K	D	B	KSC	BEC
MFI (230°C / 2.16 kg)	180	25 - 30	8	2 - 3	0.2	8	0.2-0.3
M_w (kg/mol)	140	250	380	540	1 250	360	900
M_n (kg/mol)	30	55	78	110	230	77	180
Polydispersity	4.7	4.6	4.8	5.0	5.4	4.7	5.0
Matrix M_w (kg/mol)						340	850

Dumbbell-shaped tensile specimens with dimensions: width x thickness x gauge length = 4 x 1 x 25 mm^3 (ISO 527-2 5A) were aged at 135°C and 120°C in forced draft air ovens. After defined periods of aging, samples were removed from the ovens for further investigation. Mechanical properties of thermally aged PP compounds were then determined by means of tensile tests (carried out at deformation rates of 10 mm/min).

Effects of Degradation on Mechanical Properties

Gensler [5-7] thoroughly investigated the aging effects on mechanical properties and their molecular origins. The stress-strain curves shown in Figs. 5 and 6 further reflect the characteristic differences between the two stabilizers, namely an only slight reduction of strain at break of phenolic stabilized samples after extended aging at 135°C (Fig. 5), whereas HAS stabilized samples loose some extensibility after 3 days already, and all of it after 32 days (Fig. 6).

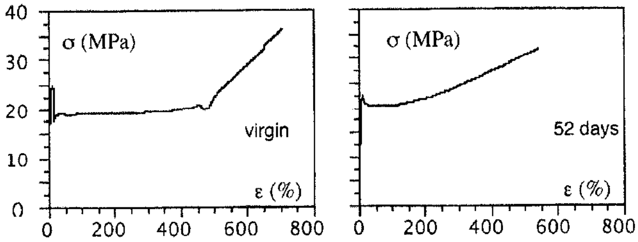

Figure 5. Comparison of stress strain curves of high Mw phenolic stabilized blends (BEC) before and after 52 days of aging at 135°C. Young's modulus, yield stress and plastic flow stress remain practically unchanged, only the strain at break is somewhat reduced.

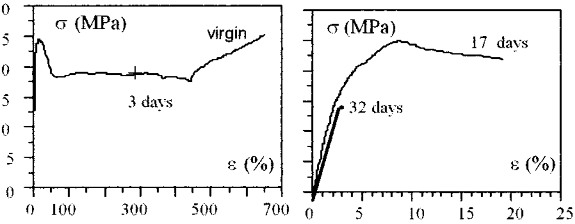

Figure 6. Comparison of stress-strain curves of high Mw HAS stabilized samples (BEC) before and after 3, 17 and 32 days of aging at 135°C. Young's modulus initially increases (due to recrystallisation after chain scission), there is no yield or plastic flow after 30 days of aging, and the strain at break is already reduced to 300% after three days of aging.

The degradation during aging of all samples starts at the surface, where the concentration of oxygen and of secondary reaction products is highest and where some defects from previous handling may have caused mechanical weakening. Thus, in loading an aged sample many cracks are initiated at the surface (Fig. 7a) before final fracture occurs. The fracture surface (Fig. 7b) and the stress-strain curve (Fig. 6) reveal, however, that (after 17 days of aging) the bulk of the sample has retained some plasticity.

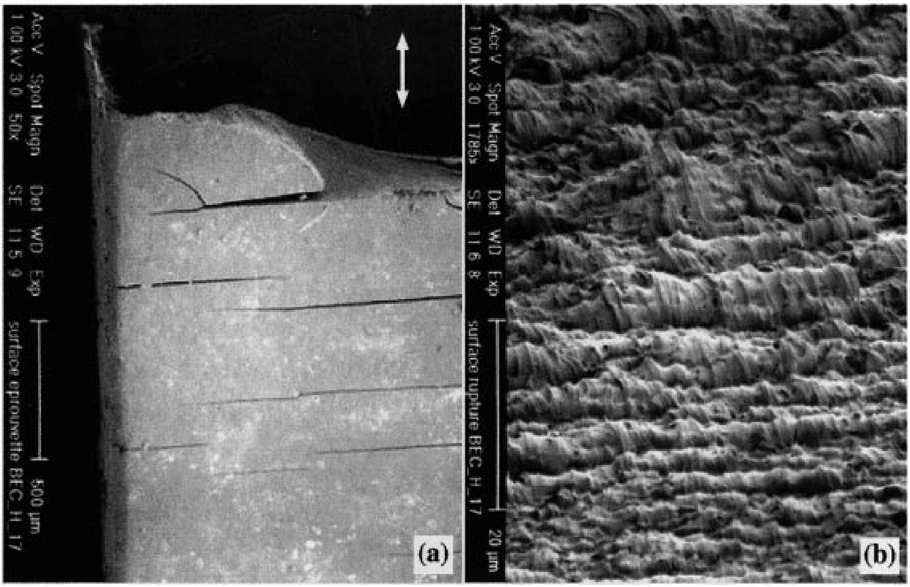

Figure 7. a) Surface cracks in a loaded and broken HAS sample (PP BEC) aged for 17 days at 135°C, b) Fracture surface still showing some localized plastic deformation (after [5]).

As we have seen above, thermal aging leads to an increasing loss of molecular weight and the mode of fracture changes from the ductile cold drawing of the virgin samples to brittle fracture. We distinguish 5 different categories (listed according to decreasing capacity to absorb deformation energy): (1) *Cold drawing*, i.e. pronounced plastic deformation by shear yielding; (2) *Shear yielding and crazing* (mixed behaviour); (3) *Multiple crazing with a yield point*; (4) *Multiple crazing without a yield point*, and (5) Formation of a *single craze or crack*. A deformation mechanism map has been compiled in Figure 8, which shows that the starting Mw also has a certain influence, although the lifetime is much less affected than expected and stays at around 16 days for the Mw-range from 250 k to 1250k.

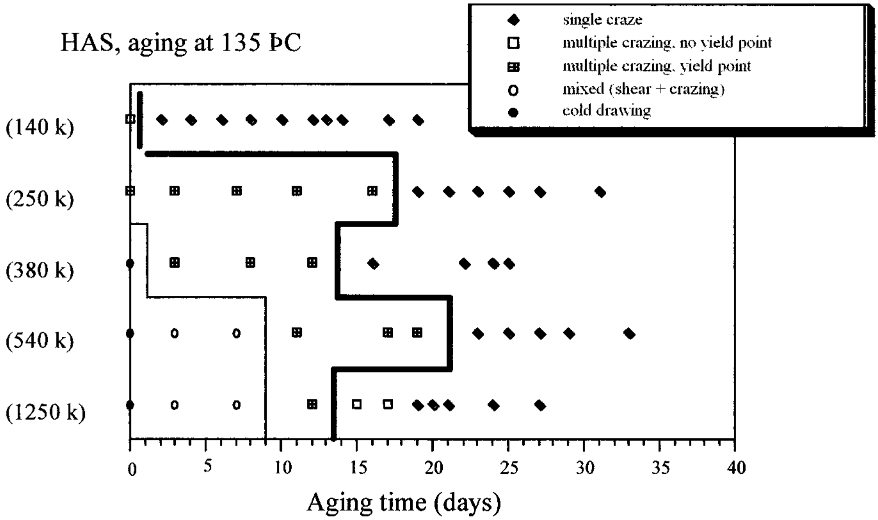

Figure 8. Development of embrittlement of HAS stabilized homopolymers as a function of aging time at 135°C and of starting molecular weight. The transition from ductile to brittle fracture is indicated by a heavy line; in the absence of any other descriptor, the time corresponding to this transition may be used as an indicator of the lifetime.

Molecular Analysis

The main purpose of this study has been a molecular analysis of the damaging processes. We have already seen that the average molecular weight changes during the induction period: slightly with the phenolic stabilized material and more notably with HAS (Fig. 4). A much more pronounced difference was shown by the polydispersity index $P = M_w/M_n$, which increased from 4 to 6.2 with PHENOL and decreased (to 2.6) with HAS. This means that the average degradation event with PHENOL has a propensity for *depolymerisation* (which is the inverse of polymerisation, e.g. the splitting off of monomer units M_o from a chain end), whereas random chain scission seems to dominate in HAS. The Mw-change caused by a single splitting event is maximum if the largest chain is halved (lower limit of the resulting Mw), it is small if the smallest chain looses a monomer unit (upper limit of M_w). The mechanisms of *depolymerisation* (M_i-M_o $\rightarrow$ M_i + M_o) and *random chain scission* (M_i- M_j $\rightarrow$ M_i + M_j) have been computer simulated by Gensler (Fig. 9).

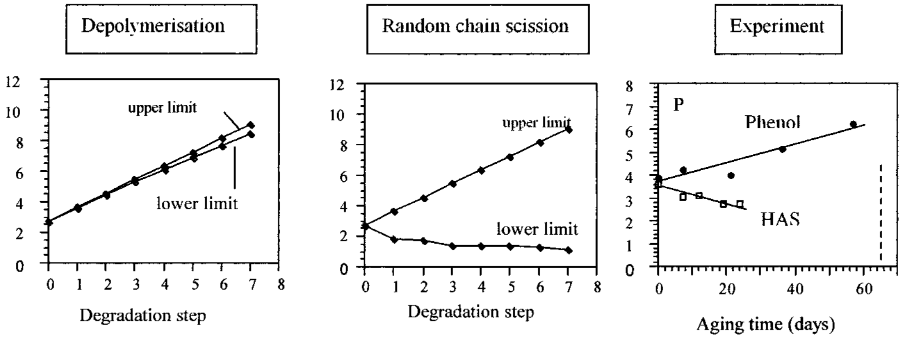

Figure 9. Comparison of the polydispersity changes obtained in experiment (c) with those predicted from computer simulation for depolymerisation (a) and random chain scission (b).

From Fig. 9 it must be concluded that degradation in the PHENOL samples proceeds by scission events located at the chain ends. We can only speculate on the reason for this. Verdu [10] has proposed a depolymerisation mechanism involving hydrogen migration, which apparently is slower than the capture of a chain end radical R• by HAS. Perhaps the higher mobility of the chain ends plays a role as well. Once depolymerisation is slow, loss of molecular weight occurs by cleavage of alkoxy radicals (by β-scission). From our data we have to conclude that scission is not random, but clear preference is given to chain centres, which might be the more readily exposed parts of tie-molecules in the amorphous regions. The observed increase in sample crystallinity and the weakening through loss of connectivity of the crystal lamellae seem to confirm this interpretation.

As we have already seen from the data in Fig. 8, the starting molecular weight has no significant *direct* effect on the time to failure (provided the chains have a certain minimum length). The influence of chain length is felt indirectly through its effect on the degree of crystallinity, which generally increases with decreasing Mw. This leads to slower oxygen diffusion, larger constraints to chain mobility and possible concentration of additives in the amorphous regions, all of which favour a longer lifetime. On the other hand, the concentration of tie-chains increases with Mw. Apparently both tendencies balance each other for both stabilizer agents in the PP-Mw range studied here.

Conclusions

Two different stabilizing approaches have been examined: radical scavenging by sterically hindered phenols (primary antioxidant) and a sterically hindered amine compound (HAS) acting as both radical scavenger and hydroperoxide decomposer. The main difference between the two systems resides in the fact that the phenolic stabilizers are active from the beginning whereas the actually stabilizing HAS-species, the nitroxyl radicals (NO•), have first to be formed by oxidation (Fig. 3). The stabilizing phenol is consumed during aging and will eventually drop below a critical value, which is no longer sufficient to prevent the accumulation of highly unstable hydroperoxides. The sudden decomposition of phenolic stabilized samples after the end of the induction period (Fig. 10a) must therefore be ascribed to the consumption of the stabilizer and to the formation and spreading of highly oxidized zones. As opposed to the concentration of phenol, that of the stabilizing HAS-species, [NO•] increases with time. This means that some oxidation, which is equivalent to some degradation, is necessary to build up [NO•] for further protection (Fig. 10a). The increase in oxygen containing groups reflects these two mechanisms (Fig. 10b).

The different effects on the mechanical properties are well explained by these two mechanisms. The small strain properties in thermoplastics are essentially cohesive in nature, small losses in molecular weight can, therefore, be absorbed; nevertheless, this limit is approached much more readily with HAS than with PHENOL (Fig. 10c). On the other hand, the loss of connectivity through random chain scission of tie-molecules in the HAS stabilized samples is strongly felt with large strain and long term properties, where efficient stress transfer over longer distances is required, such as ultimate stress and strain, impact strength and fatigue resistance [8].

Although not the objective of this study, a remark should be made on the degradation behaviour at $t > t_i$. Towards the end of induction period most of the phenolic stabilizer has been consumed, the concentration has fallen below a critical level, which allows in some sites uninhibited autoxidation, leading to the appearance of dark, almost circular *spots*. George [11] Fayolle, Verdu et al. [12] have studied their growth in detail. They find (for PP-films aged at 130 °C) that the initiation sites result from *random* local variations of stabilizer concentration, morphology, impurities (metal ions, radical initiator) and *edge effects* (cutting) [12]. The growth of these heavily discoloured spots occurs through uninhibited, auto-accelerated *multiplication and diffusion* of free radical sites and oxidation products. Spots grow undisturbed and in a (semi-)circular fashion, if the nucleation rate is low (at lower temperatures). The growth rate (80 μm/h at the indicated conditions) can be predicted from the kinetics of formation and diffusion of radical species and decomposition products.

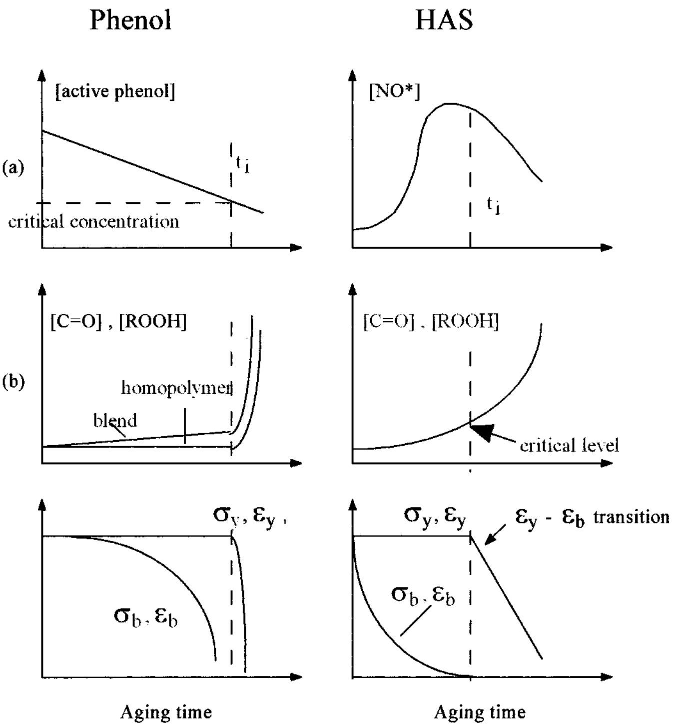

Figure 10. (a) Variation of the concentration of active stabilizer molecules, at the end of the induction period t_i stabilizer concentration has dropped to a critical level (aging temperature T $\geq$ 120°C); (b) variation of the carbonyl and hydroperoxide concentrations in aged samples (note that the rubbery component in the blends contributes slightly more to these groups); (c) schematic representation of the evolution of the mechanical properties of thermally aged samples, large-strain properties (σ_b and ε_b) display a different evolution as low-strain properties (σ_y and ε_y).

As opposed to this, HAS stabilized samples are at $t > t_i$ at a maximum of concentration of the stabilizing moiety [NO•], thus there is no dramatic acceleration of degradation kinetics. However, the damage already incurred at this point is substantial. Since the concentration of active stabilizer molecules (NO• and NO•-transformation products) is low during the early stages of aging, the oxidation of the polymer cannot be prevented in this stage.

Acknowledgements

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