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The Origin and Role of Structural Inhomogeneities and Impurities in Material Recycling of Plastics

Jan Pospíšil*, Zdeněk Horák, Zdeněk Kruliš, and Stanislav Nešpůrek

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague, Czech Republic

Abstract: Characteristics of aged polymers intended for material recycling are emphasized. Specific material properties of aged recyclates, containing new functional groups formed during processing and first-life application (structural polymer inhomogeneities) and metallic compounds, pigments or compounds generated from additives (non-polymeric impurities), are considered from the point of view of their influence on the aging resistance in the second-life applications. Chemical transformations of the polymer matrix together with consumption of stabilizers deteriorate material properties of collected waste plastics in reprocessing and subsequent outdoor applications.

PLASTICS WASTE MANAGEMENT AND RECYCLING POLICY

The commercial boom in plastics in preceding decades has been reflected in development of advanced polymerization (using new catalytic systems) and more aggressive processing technologies. This concerns commodity and engineering homopolymers, copolymers and blends designed for short-term and long-term application in most areas of human activities. However, environmental problems have arisen as a consequence of large quantities of plastics creating industrial scrap (inappropriate parts, offcuts, trimmings) and/or discarding the post-consumer waste (PCW). The latter represents the most painful Janus' head of the plastics development. Individual components of PCW are difficult to analyze (Ref. 1) and sort. PCW attracts public attention due to its visibility and raises political pressures requesting solution to the problem. In the 1990's, this chemical waste became almost a symbol of a throw-away society.

Treatment of the scrap and PCW is, however, an economical and technical problem. The functioning legislation is a helpful tool. The supply of recycled materials has grown much faster than the reprocessing capacities and market. The perceived environmental benefit and the cost/effectiveness ratio of various approaches (including collecting, sorting, cleaning) are strongly dependent on local conditions, the ability to solve problems on an adequate industrial level and an absorbing market for respective new materials arising from recycling (Ref. 2).

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Feasible recycling attempts differing in the environmental benefits involve re-use of the industrial scrap and pure PCW (primary and secondary material recycling, respectively), feedstock regeneration by solvolysis, thermolysis or hydrogenation (tertiary or chemical recycling) and energy recovery by incineration of contaminated and difficult-to-sort polymers (Ref. 3). All the alternatives are valid options from the point of view of preserving natural sources.

Burning without energy reclaim and rotting in landfills, in particular, are the most unfavorable approaches in industrialized countries from ecological and economical viewpoints; most synthetic macromolecules cannot be assimilated by microorganisms, the landfills are overflowing and close to their maximum capacities, prices of landfilling are increasing and a strong opposition is growing against opening new landfills (Ref. 2). Moreover, the ground-waters are potentially polluted.

The PCW reuse, the topic of this paper, is a new branch, called the plastics recycling industry. However, reprocessing cannot be considered as the final disposal mode of PCW, even if a cascade principle aiming at both high-value applications and downcycling (for less critical applications) is applied. (The contaminated materials are intended to be recycled chemically as the ultimate phase of the cascade.) Reprocessing has its specificity. Large producers of plastics have a declining tendency to recyclate reprocessing. Well adjusted processing conditions according to the PCW composition and process control are more necessary for the recyclate than for virgin plastics (Ref. 4). Reprocessing has been, therefore, more and more based on activities of fast growing and consolidating smaller companies (Ref. 5). For those, information dealing with specific material properties of recyclates and ways of their upgrading are of primary interest.

CHARACTERISTICS OF AGED PLASTICS FOR MATERIAL RECYCLING

A successful material recycling depends on purity and uniformity of the plastic waste. History of the polymer synthesis, primary processing and application, and recovery source are factors influencing both properties. Single-polymeric post-industrial scrap is the best raw material. Low-contaminated and sorted PCW from single polymers has still good chances, in spite of admixtures of small amounts of other polymers. Their presence in commercial-scale recycling cannot be avoided (e.g., small amounts of polypropylene, PP, in high-density polyethylene, HDPE). Polymer mixtures arise, for example, also from HDPE produced by either Ziegler- or Phillips-type catalysts (Ref. 6). The commingled PCW is the least attractive raw material. It is a blend containing approximately 80 % of short-life packagings based on various polyolefins and lower amounts of polystyrene (PS), poly(ethylene terephthalate) (PET) and poly(vinyl chloride) (PVC) (Ref. 7). More durable engineering plastics, such as polyamides (PA), polycarbonate (PC) or poly(phenylene oxide) (PPO) will be present in PCW in increasing amounts in the future.

As compared with the relevant virgin polymer, recycled materials differ in mechanical properties and resistance to degradation. This is due to changes on macromolecular level (structural polymer irregularities arising during degradation), admixtures of other polymers, and presence of various inorganic and organic compounds, i.e., non-polymeric impurities (Refs. 3,8). Notched Izod impact, Young's modulus of elasticity, tensile strength-at-yield and elongation-at-yield are physical properties considered important for rating the recyclate (and its blends with virgin polymers) (Ref. 8). Conventional methods are used to check the melt flow index and processing stability by multiple extrusion tests (Ref. 6) and oven-aging tests as well as by weatherometer or Xenotests to check the long-term heat stability and weathering resistance; spectral methods are used for analyses of chromophoric impurities (Ref. 9). Specially adjusted methods are necessary to check the presence of metallic contaminants and residual stabilizers.

Polymeric structural inhomogeneities

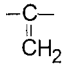
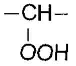
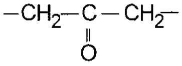
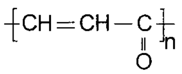
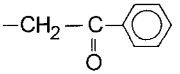
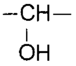
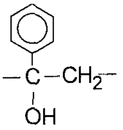
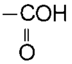
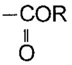
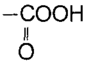
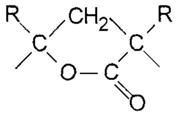
Structural inhomogeneities (or irregularities) are formed during processing and long-term application. Studies with PE, PP, PS and PVC provide sufficient information about the chemical character of new functionalities and mechanisms of their formation. Principal polymer-bound unsaturated moieties and oxygenated structures are listed in Table 1.

Unsaturations characteristic of vinylene (**1**), vinylidene (**2**) and vinyl (**3**) groups arise during processing in PE (Ref. 6). Isolated vinylenes (**1**) and conjugated vinylene sequences (**4**) arise in processing of PVC and were detected also in aged PS (Ref. 10). In addition to increased unsaturation, processing results in oxidation and changes in molecular weight affecting material properties and product performance. All the adverse effects continue during material reprocessing.

Oxygenated structures also arise during processing and, in particular, in the course of thermal and photochemical aging (Ref. 11). Free-radical species, such as peroxyls, alkoxyls, acyls and acylperoxyls are generated as precursors of polymer-bound oxygenated structures and migrating low-molecular-weight compounds.

Principal polymer-bound oxygenated structures include hydroperoxides (**5**), aliphatic carbonyls (**6**), α,β-unsaturated carbonyls (**7**), phenyl-conjugated carbonyls (**8**), aliphatic hydroxyls (**9**), benzylic hydroxyls (**10**), carboxyls (**11**), esters (**12**), percarboxyls (**13**) and lactones (**14**). Fourier-transform infrared spectroscopy combined with chemical derivatization of oxygenated plastics with ammonia, sulfur tetrafluoride, sulfur dioxide or nitrogen oxide is a useful tool for identification of individual functional groups (Refs. 9,11).

Table 1 Principal polymer-bound unsaturated moieties and oxygenated structures

No.	Structure	IR absorption, cm^{-1}
1	$-CH=CH-$	965-968, 1650
2	 $-\underset{CH_2}{\underset{\|}{C}}-$	887
3	$-CH=CH_2$	909-912
4	$-[CH=CH]_n-$	1880
5	 $-\underset{OOH}{\underset{\mid}{CH}}-$	free 3550-3552 associated 3400-3420
6	 $-CH_2-\underset{O}{\underset{\|}{C}}-CH_2-$	1718-1724
7	 $\left[CH=CH-\underset{O}{\underset{\|}{C}}\right]_n$	n=1 1696 n>1 1605
8		1690
9	 $-\underset{OH}{\underset{\mid}{CH}}-$	free 3610 associated 3360-3380
10		3540
11	 $-\underset{O}{\underset{\|}{C}}OH$	1710-1715
12	 $-\underset{O}{\underset{\|}{C}}OR$	1740-1744
13	 $-\underset{O}{\underset{\|}{C}}OOH$	1740-1750
14		R=H, methyl 1740-1744 R=phenyl 1732

Structures **5-8** are considered as harmful light-absorbing impurities (chromophores, Ch) sensitizing photodegradation of recycled plastics. Their concentration depends on the inherent resistance of the plastic and character, intensity and duration of the environmental stress. This means that recyclates from different sources are damaged (oxidized) to very different degrees. Changes on super-molecular level accompany oxidative damages during aging as well.

Most complete mechanistic data on formation of structures **5-14** are available from investigation of saturated carbon-chain and hydrocarbon-based polymers (Ref. 11). The mechanistic data have been adapted for description of oxidative transformations of unsaturated hydrocarbon polymers (isoprene- and butadiene-based elastomers), copolymers of dienes with styrene, polymers containing hydrocarbon segments alternating with amide or ester units, and of PVC. All these polymers are common impurities in PCW. Structure-specific oxygenated moieties are formed in aromatic PA, PC or PPO (Ref. 11), i. e., in polymers expected to contribute to PCW in a near future.

Reactions (1)-(3) schematically describe the free-radical chain oxidation and explain formation of chromophores absorbing actinic solar light (hydroperoxides ROOH and carbonyl species) in originally non-absorbing (light-transparent) polymers. Carbon-centered macroalkyls R• are formed from a polymer RH in the first step of reaction (1). The reaction is initiated by thermal, mechanochemical, radiation or metal-catalyzed processes. Oxidation of R• accounts for alkylperoxyls ROO• and hydroperoxides ROOH. The latter are harmful chromophores. Homolysis of ROOH is the branching step of the chain oxidation and results in alkoxyls RO• and migrating free radicals HO•. Non-oxidative transformations involving R• (Eq. 2) result in products formed by chain scission, branching or crosslinking via recombination and disproportionation.

$$\mathrm{RH} \xrightarrow[\Delta,h\nu]{M^+} \mathrm{R}\bullet \xrightarrow{O_2} \mathrm{ROO}\bullet \xrightarrow{RH} \mathbf{ROOH} \xrightarrow[\Delta,h\nu]{M^+} \mathrm{RO}\bullet + \mathrm{HO}\bullet \qquad (1)$$

$$\mathrm{R}\bullet \longrightarrow \text{products} \qquad (2)$$

$$\mathrm{RO}\bullet \xrightarrow[h\nu]{} \textbf{carbonyl species} \qquad (3)$$

In the subsequent step (3), RO• undergoes β-scission under formation of carbonyl species (e.g. **6**, **8**). Unsaturated carbonyls **7** arise similarly from unsaturated groups **1-3** and **4**, hydroperoxidized in α-position to the double bond. Carbonyl compounds **6-8** are dangerous chromophores. They absorb UV light in the actinic part of the solar radiation and excited states, Ch*, are formed (Eq. 4, Ch = >CO). In their triplet states, they are involved in a sensitized formation of macroalkyls R• (Eq. 5), in formation of singlet oxygen, $^1O_2$, by energy transfer to ground-state oxygen (Eq. 6) ($^1O_2$ oxidizes unsaturated species -CH_2-CH=CH- to hydroperoxides (Ref. 11)) and in sensitized homolysis of ROOH via an exciplex (Eq. 7).

$$\mathrm{Ch} \xrightarrow[h\nu]{} \mathrm{Ch}^* \qquad (4)$$

$$\mathrm{Ch} \xrightarrow{RH} \mathrm{Ch} + \mathrm{R}\bullet \qquad (5)$$

$$\mathrm{Ch}^* + {}^3O_2 \longrightarrow \mathrm{Ch} + {}^1O_2 \qquad (6)$$

$$\mathrm{Ch}^* + \mathrm{ROOH} \longrightarrow [\mathrm{Ch...ROOH}]^* \longrightarrow \mathrm{Ch} + \mathrm{RO}\bullet + \mathrm{HO}\bullet \qquad (7)$$

Reactions (4)-(7) explain the harmful sensitizing effect of >CO and ROOH generated in the polymer first life on aging. Hydrolysis accounting for the reduction in molecular weights and formation of terminal amino groups and carboxyls is a source of inhomogeneities in aliphatic PA and PET (Ref. 12).

Chemical changes in aged polymers are irreversible. The rate of their development is faster in recyclates than in the relevant virgin material. Moreover, heterogeneities in polymer degradation are detected on molecular and supermolecular scales (Ref. 13). A random distribution of highly oxidized sites in the polymer bulk was experimentally evidenced (Ref. 14). Formation of localized oxygenated structures is a common phenomenon in thermal oxidation of polyolefins, PS, polybutadiene (PB) and PVC, in copolymers containing easily oxidizable diene-based segments, such as styrene-butadiene-styrene triblocks (SBS), high-impact PS (HIPS) or acrylonitrile-butadiene-styrene polymers (ABS), and in photooxidized plastics (concentration profiles indicate oxidized surface layers). Localized sites with accumulated oxygenated polymer impurities interacting with light according to Scheme 2 are more prone to deeper oxidation and have thermo-initiating and photosensitizing effects. It may be extrapolated that the degradation rate of hydrocarbon polymers is dependent on the content of chromophoric impurities (Ref. 15). Localized oxidation in polymers is also initiated by heterogeneous distribution of harmful non-polymeric impurities (such as metals; see below). Degradation spreads from the heavily oxidized localized sites or zones by energy transfer and probably also by migration of low-molecular-weight free radicals (Ref. 16). The process proceeds through primary microcracks, participating in the ultimate fracture of the material. Crack growth will occur in the presence of tensile stress and polymer failure occurs when localized defects merge into percolation clusters. The breakdown of stretched macromolecules in the interspherulitic regions is a particularly detrimental effect in the degradation process.

There is another detrimental consequence arising from localized oxidation centers. During reprocessing of recyclates, the heavily oxidized sites together with the virgin polymer are distributed more or less homogeneously within the blend and render the whole blend prone to accelerated oxidation in outdoor exposure (Ref. 17). The introduced chromophores thus "intoxicate" the virgin plastic and accelerate its oxidation. Thus, the oxidative transformations induce physical damages (discoloration, formation of surface cracks), changes in insulation efficiency, increase in polarity and mechanical changes contributing to the product failure (decrease in impact strength, modulus of elasticity, yield, elongation-at-break, and tensile stress (Ref. 13)). The impact of chemical changes (oxygenated structures, chain scission, crosslinking) on physical properties continuously attracts attention. Various studies are available explaining some relations occurring in solid polymers. Thermal oxidation induces changes in spherulitic structure (observed as volume reduction), as reported for HDPE. Oxidative scission preferentially occurs at the chain folds where the molecules are strained. This process increases the level of crystallinity due to the more efficient packing of crystallites (Ref. 18). Contrary to this, crosslinking arising in HDPE degradation can destroy its regular crystalline structure. Some volume changes due to photooxidation result in chemorecrystallization and account for changes in residual stress distribution in PP (Ref. 19). Hence, chemorecrystallization and changes in spherulite size due to aging affect mechanical properties of aged polymers (Ref. 15). However, generalization is difficult for recyclates. Plastics with enhanced crystallinity and molecular orientation mostly show less degradation. This is most probably due to a lower solubility of oxygen and reduced mobility of low-molecular-weight free radicals participating in spreading of the oxidation. For example, low-oriented PP is strongly affected by UV radiation, while high-oriented PP does not change under the same conditions. However, the relations are unpredictable. For example, experimental data were found indicating acceleration of degradation by increased crystallinity or orientation (Ref. 15).

Nonpolymeric impurities

A rather variable mixture of mineral and organic low-molecular-weight compounds, either mingled or formed during the polymer preceding life (external impurities), contaminate the recycled material. The impurities include:

⇒ Molecular fragments formed by photooxidation and photolysis of component polymers (such as acetophenone arising from PS), considered as migrating sensitizers and potential intoxicants.

⇒ Residues of polymerization catalysts.

⇒ Various metallic oxides or ions introduced during processing (extrusion, milling, compounding) from containers or with metal-contaminated fillers or reinforcing agents.

⇒ Printing inks, paint residues, pigments.

⇒ Residues of fatty and oil materials.

⇒ Residues of adhesives, e.g. glue in PET.

⇒ Transformation products of processing and long-term stabilizers.

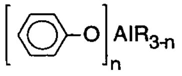
Although present in trace amounts, some of the material-specific or accidental contaminants are detrimental for material properties of PCW due to their catalytic or photosensitizing effects. This further enhances degradation sensitivity of aged plastics containing oxidation-born chromophores and having a reduced stabilization protection due to the stabilizer consumption in the preceding lifetime. Activities of the most common non-polymeric impurities are hereinafter specified in more detail.

Residues of polymerization catalysts

Refinements in existing polymerization catalyst systems affect not only morphology but also aging resistance of ethylene and propylene homopolymers and copolymers, the mostly recycled polymers. Titanium tetrachloride/magnesium chloride/triethylaluminium (for the Ziegler-Natta process), bis(cyclopentadienyl)chromium(II)/silicon dioxide (for Phillips or Union Carbide processes) and bis(triphenylsilyl) chromate/silicon dioxide/triethoxyaluminium are examples of typical polymerization catalysts and co-catalysts for HDPE. In recyclates from various sources, catalyst residues of different categories are present. Their content varies depending on the production technology. The recycled HDPE is an example of a mixture of materials produced by different processes (using diferent catalysts). Individual materials cannot be separated; therefore, the collected HDPE potentially contains catalysts from different technologies, all of them being considered as impurities. Analyses of HDPE revealed (Ref. 20) the presence of the following elements (ppm) silicon (85), chromium (2.5), magnesium (10), aluminium (24), titanium (9), vanadium (10), zirconium (2) and chlorine (10). A correlation was found between the enhanced concentration of Ti residues in PP films and their reduced photostability measured by the embrittlement time (Ref. 21). The concentration effect of killed Ti(III) in thermooxidized PP was dependent on temperature. This is revealed by a combined catalytic and thermal influence on polypropylene hydroperoxide decomposition: at low temperatures (50 °C), the ROOH decomposes only by Ti catalysis (the effect of Ti concentration). At 130 °C, both thermal and catalytic decomposition of the ROOH takes place making the Ti concentration effect much less important. Metal ions (M, such as Ti, V, Cr, Zr) from catalyst residues, similarly to some metallic ions from other contamination sources, oxidize phenolic antioxidants (InH) to phenoxyls (Eq. 8), converted subsequently to various products (Ref. 22).

$$\mathrm{InH} + \mathrm{M}^{n+} \longrightarrow \mathrm{In}\bullet + \mathrm{M}^{(n-1)+} \tag{8}$$

They also deactivate phenolics by complexation accounting for the loss of the chain-breaking activity due to formation of phenol aluminates (**15**), titanates (**16**) and analogous complexes of chromium or zirconium (Refs. 22,23). Both the oxidation and complexation of phenolic antioxidants have been considered as a "depleting" stabilizer consumption (Ref. 24).



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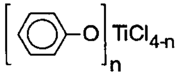

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Complex **16** also contributes to intensive discoloration of aged polymers and is strongly oxygen-sensitive (Ref. 23). Formation of metal complexes from catalyst residues with hindered amine stabilizers (HAS) has been considered as well (Ref. 25). Most probably, the complexation is not detrimental for the HAS activity.

Fortunately, the concentration of residual transition metals from catalysts is mostly very low in modern polyolefin products. The catalyst residues differ in their pro-oxidative activity: Ti and Al from Ziegler-Natta catalysts are poor pro-oxidants compared with chromium residues from silica-supported catalysts (Ref. 26). De-ashing step in application of highly effective chromium-based catalysts was eliminated. This accounts for residual Cr in the product (the residual silica is chemically inactive). Chromium concentration as low as 1 ppm has a profound effect on thermooxidative stability of HDPE. In contact with air, Cr(III) species, powerful pro-oxidants, are formed (Ref. 26). All experience indicates that Cr-based catalyst residues are more effective decomposers of ROOH and, consequently, more dangerous pro-oxidants in polyolefins than Ti-based catalysts. Moreover, Cr-based catalysts enhance concentration of terminal vinyl groups (type **3**) in produced HDPE. Even this makes the material more prone to oxidation and crosslinking (Ref. 20) (in Ti-based HDPE, having a higher saturation, chain scission predominantly takes place (Refs. 6,20)). No simple correlation seems to exist between the Cr content and UV stability of HDPE (Ref. 26). The concentration effects are dependent on the polymer matrix: as high concentration as 20 ppm of

Cr(III) ions provided a stabilizing effect in PP. It is, therefore, evident that metal ions can exert both strong catalysis and/or inhibition, depending on the polymer matrix, environmental effects and the valence state of the metal. This duality in metal ion effects has been observed for copper, cobalt, manganese, titanium, and iron (Ref. 26).

Due to hydrolysis, hydrogen chloride is generated from residues of metal chlorides in Ziegler-type catalysts (Refs. 23,25). Free hydrogen chloride participates in the retro-Friedel-Crafts dealkylation of sterically hindered phenolic antioxidants, catalyzes hydrolysis of phosphite processing stabilizers, deactivates HAS by protonation and corrodes metallic parts of the processing equipment (this, in turn, enhances the content of metallic impurities). Magnesium chloride, the solid support of Ti catalysts, has been suspicious of contributing to dealkylation of phenolic antioxidants (Refs. 22,24).

Alkylaluminiums (polymerization co-catalysts) from catalyst residues should be fully deactivated before the exit of polyolefins from the reactor due to their high reactivity with phenolics (formation of **15**) and oxygen (Ref. 23). They are oxidized to peroxides $ROOAlR_2$ prone to depleting phosphite stabilizers by oxidation to phosphates. This is one of the stabilizer-depleting mechanisms in Ziegler-type polyolefins. Their reaction with HAS accounting for $AlR_3...HN<$ complexes does not seem to be harmful (Ref. 25).

Other metallic impurities

Of common metallic impurities introduced into polymers, ions of copper and iron rank among the most dangerous species. In addition to oxidizing phenolic antioxidants and phenolic parts of UV absorbers (Ref. 22), they catalytically homolyze alkylhydroperoxides (Eqs. 9,10) and accelerate in this way the oxidative degradation of polymers (Ref. 27).

$$ROOH + M^{n+} \longrightarrow RO\bullet + HO^- + M^{(n+1)+} \tag{9}$$

$$ROOH + M^{(n+1)+} \longrightarrow ROO\bullet + H^+ + M^{n+} \tag{10}$$

On light absorption, transition metal compounds can produce free radicals in polymers by an electron-transfer process and triplet sensitization (Ref. 11).

Due to the localization of metallic impurities and residues of polymerization catalysts within the polymer matrix, the impurities participate in heterogeneous initiation of degradation from metal-contaminated centers (Ref. 16). The presence of localized metallic centers as well as of over-oxidized sites renders stabilizers unable to fully inhibit degradation spreading from these preexisting centers.

Fillers

Common fillers (non-contaminated with metals) such as talc or calcium carbonate provide some photoprotection of surface layers of recycled PP (Ref. 28). They may, however, enhance the crack sensitivity due to an inadequate bonding between the filler polymer.

Pigments and dyes

Pigments (insoluble) and dyes (soluble) are generally used to improve aesthetic look and application properties of plastics. They might have a devaluating effect in post-consumer recyclate (PCR). Appearance and transparency of commingled recyclates are deteriorated by low amounts of colored plastic components containing either white (such as TiO_2 or ZnO) or colored pigments, including carbon black. The potential dual role of pigments - either photoprotection or photocatalysis and/or sensitization of degradation (Ref. 11) - was not a problem particularly elucidated with recyclates. We have to extrapolate potential detrimental effects from data dealing with pigmented virgin polymers. White inorganic pigments have been proved to catalyze photooxidation of polyolefins, aliphatic PA and polydienes (Ref. 29). The complex mechanism includes formation of active oxygen species on the pigment surface. Photooxidation chain reaction is triggered in the next phase. Photodegradation and chalking result in the final step (Ref. 30).

Sensitizing effects of organic colored pigments on polymer matrix (phototendering) and correlation with the pigment particular structures are still under elucidation. Involvement of excited pigments in the triplet state has been considered as the mechanism participating in formation of radicals $R\bullet$ or singlet oxygen in the initial steps (Eqs. 4-7, Ch = pigment). Yellow, orange and red pigments were shown to be more harmful sensitizers than other colored pigments (Ref. 31). It is very probable that some products of the dye or pigment photolysis actively participate in activation of polymer degradation. This might be associated with photophading of dyed and pigmented polymers (Ref. 32). Moreover, physical states of colorants and the substrate as well as the complex character of the environment (humidity and temperature in particular) play a role in polymer degradation.

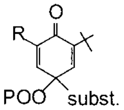
In the presence of metal-free carbon black, we do not expect any detrimental effects concerning degradation characteristics of recycled plastics. It should be noted, however, that the photostabilizing effect of carbon black is not sufficient to provide outdoor protection due to high contents of photosensitizers in recyclates (Ref. 33).

Transformation products of processing and long-term stabilizers

Application of different classes of stabilizers is mandatory to gain safe processing and long-term application of virgin polymers under environmental stress. Hindered phenolic antioxidants, trivalent phosphorus compounds (processing stabilizers), activated organic thio compounds (long-term heat stabilizers), UV absorbers of different classes and HAS (photo-antioxidants and thermal stabilizers) are common stabilizers for polyolefins streaming in PCW. Combinations of these stabilizers ensure safe application of plastics during their first lifetime. Metallic soaps and organotin compounds are heat stabilizers for PVC. However, there is no perpetuum mobile in stabilizer activity. Protection of polymers is gained at the expense of the stabilizer lifetime, due to its high chemical reactivity with harmful free-radical or peroxidic species (ROO•, ROOH) and actinic solar radiation. Hence, the stabilizers are stepwise transformed in a process classified as "sacrificial" consumption (Ref. 24). Preferential consumption occurs in the randomly accumulated oxidizing sites in the polymer bulk and in surface layers Ref. 16). In the oxidation-undamaged zones, the stabilizers remain unconsumed.

The sacrificial consumption of stabilizers is not the only process responsible for their chemical transformations: they are depleted by atmospheric oxidizing pollutants (ozone, nitrogen oxides), residues of polymerization catalysts, oxidizing metallic impurities (see the preceding text), by photolysis or energetic radiation (in γ-ray-sterilized packagings) (Refs. 22,24). The depleting consumption preferentially proceeds in randomly distributed sites. The structures of new compounds formed from stabilizers by sacrificial and depleting consumptions are mostly identical (Ref. 24). The products accumulate stepwise in the aged polymer matrix and, consequently, are present also in recyclates. Some of their typical structures and properties (Refs. 22,34) are mentioned in the following text.

Relatively long-living phenoxyls are formed from phenolic antioxidants (chain-breaking or primary antioxidants) via reaction with alkylperoxyls $POO^{\cdot}$ or oxidizing impurities. Phenoxyls are transformed in the following step into alkylperoxycyclohexadienones **17** (R=methyl, *tert*-butyl; *subst.* means the rest of the molecule), phenolic coupling products and, in the final phase, quinone methides **18**, including their oligomers.



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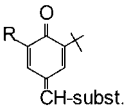
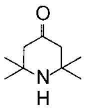
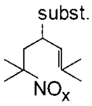


18



19



20

Hydroperoxycyclohexadienones (**17**, P=H) arise during polymer weathering. Compounds of the **17** type are thermo- and photoinitiators. According to the recent analysis (Ref. 35), quinone methides **18** and its oligomers contribute only slightly to polymer stabilization.

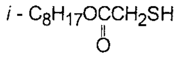
Highly conjugated quinone methides cause some discoloration. Transformations analogous to those mentioned for phenolic antioxidants have been also described for phenolic moieties of light stabilizers having structures of substituted 2-hydroxybenzophenones, 2-(2-hydroxyphenyl)benzotriazoles or analogous derivatives of benzoxazole, pyrazole or 1,3,5-triazine (Ref. 24). This transformation fully destroys the UV protecting mechanism.

Secondary antioxidants include processing stabilizers such as tris(2,4-di-*tert*-butylphenyl) phosphite or tetrakis(2,4-di-*tert*-butylphenyl) biphenyl-4,4′-diyldiphosphonite, and long-term heat stabilizers such as dialkyl 3,3′-thiodipropionates. Secondary antioxidants form synergistic combinations with phenolic antioxidants (Ref. 22). Sacrificial transformation of trivalent phosphorus stabilizers accounts for the presence of structurally related phosphates or phosphonates (Ref. 34), which do not impart harmful effects. By thermal or hydrogen chloride-catalyzed hydrolysis, acid products such as $(HO)_2POR$, H_3PO_3 or H_3PO_4 are stepwise formed from both trivalent and pentavalent phosphorus-containing species. They corrode processing equipment and are suspected of formation of polymer-insoluble salt precipitates or clusters (Ref. 36), such as $Ca[OP(OR)_2]_2$, influencing rheological properties and/or acting as nucleating agents in semicrystalline recyclates.

Sulfoxides and sulfones and their transformation products formed by thermolysis and oxidation (organic S-acids, thiosulfinates, thiosulfonates) and, in the ultimate phase, sulfur dioxide and sulfuric acid are formed from dialkyl 3,3′-thiodipropionates (Ref. 34). Esters of acrylic acid are among the sulfurless transformation products. Some of the products have disagreeable organoleptic properties. All acid products deactivate HAS (Ref. 37).

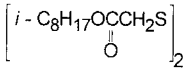
Nitroxides, hydroxylamines and *O*-alkylhydroxylamines (Ref. 37) are transiently formed from 4-substituted 2,2,6,6-tetramethylpiperidines (HAS) but all these compounds remain active stabilizers. Compounds **19** and **20** are among the final products. After opening the piperidine ring, HAS lose their stabilizing effect.

We also have to consider transformation products of PVC heat stabilizers as impurities in the commingled recyclate. Chlorides of barium, calcium, zinc or lead are formed from the respective metallic soaps of higher fatty acids. From organotin stabilizers, such as dibutyltin bis(2-ethylhexyl thioglycolate) and dibutyltin dichloride, mercaptan **21** and disulfide **22** are formed (Ref. 38).



$i\text{-}C_8H_{17}O\underset{\underset{\displaystyle O}{\|}}{C}CH_2SH$

21



$\left[i\text{-}C_8H_{17}O\underset{\underset{\displaystyle O}{\|}}{C}CH_2S\right]_2$

22

The residual concentration of active stabilizers in recyclates has been in many cases reduced below the “minimal-effect” level, no longer capable of protecting the aged polymer with accumulated pro-oxidants (Ref. 39). Hence, recycled plastics, more sensitive to processing degradation and atmospheric aging than the respective virgin materials, are mostly only insufficiently protected by the residual stabilizers (Refs. 3,17).

EXPLOITATION POSSIBILITIES AND LIMITS OF MATERIAL RECYCLATES

The crucial and decisive condition for successful development of the material-recycling industry is an end-use market capable of absorbing products fabricated from recyclates. Moreover, the public must be made aware that consumer products made of recycled plastics often match those made of the virgin material. Processors and producers of plastics additives in particular try to develop techniques and designs providing recyclates with properties satisfying requirements for the high-value use, especially in closed-loop applications. Production of lower-grade recyclates (down-cycling) should occur only at the end of the material recycling line, according to the cascade principle (providing, after repeated recycling, material with progressive contamination). Heavily oxidized and contaminated PCW having low residual mechanical properties, and residues of polymers categorized as “photodegradable” have to be fully excluded from material recycling (Ref. 3).

High-value application of recyclates, for outdoor service in particular, requires upgrading of low-contaminated recyclates and/or their blends with virgin materials by a proper restabilization assuring a safe reprocessing and long-term use, application of anti-acids blocking acid impurities in recyclates, improvement of material properties by properly selected compatibilizers, fillers reducing oxygen diffusion, and reactive additives repairing molecular weight of hydrolytically degraded polymers (Refs. 3,17,40). Discoloration due to polymer degradation usually does not limit the use of recyclates in most technical applications. Repigmentation improving uniform appearance is a common process in color-sorted closed-loop recycling (Ref. 17). Concentrates of pigments, color correctors, masking discoloration due to degradation are commercially available. In spite of the progressive quality improvement of the recyclate properties, there are some limits restricting their general application in packagings used in direct contact with food. The hazard exists of extraction of potential intoxicants arising from uncontrollable plastics application (e.g., traces of pesticides or other agrochemicals, engine oils, solvents) and of toxic or hazardous contaminants from some polymer components (such as flame retardants, lead compounds from PVC). Trace impurities are dispersed in the whole mass of the recyclate. Various oxygenated polymer-bound structures formed during aging are non-extractable and, hence, not considered dangerous (Ref. 41). However, some migrating low-molecular-weight degradation products have been considered as hazardous contaminants (Ref. 42). Moreover, all polymer components participating in the recycled blend must be regulated by law for food-contact applications. The regulations are consistent with legislative responsibilities protecting the public. Stringent safety regulations are under examination on a case-by-case basis. This includes rigorous tests on strictly declared maximum levels of individual potential contaminants in the recyclate. Another condition for the food-contact approval was defined as “plastics that have not been broken down into their building blocks” (Ref. 5). “Non-objective letters” have been granted for different non-fatty food-contact packaging purposes (Ref. 42). Development of a three-layer material, with the recycled PET in the middle, is a solution for food-contact applications (Ref. 4).

Understanding relationship between structure and activity of stabilizers with respect to their toxicity is still an open problem. It is understandable that all additives - either residues from the first-life application or used for recyclate upgrading - must obey regulations for food-contact use if such application is considered (Ref. 42). A detailed examination was performed with some phenolic antioxidants, light stabilizers and HAS. The absence of genotoxicity was confirmed. Quinone methides arising in low amounts from phenolic antioxidants are not considered dangerous (Ref. 43).

In spite of economic (fluctuating prices of virgin plastics and the resulting difficult planning of the recycling economy) and technical problems and specific restrictions in application, the market with recyclates will definitely grow, substituting a part of virgin polymers. Knowledge of material properties of recyclates allows to use an upgrading system matching high-quality applications (Refs. 3,17,40). In this sense, the technical effort parallels ecological expectations of recycling 25 % of the total plastic products by the end of the millenium.

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