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Polymer waste: controlled breakdown or recycling?

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This paper discusses two possible strategies used in plastics waste disposal: one is materials recycling the other is controlled breakdown including biological thermal or chemical degradation. The first is accompanied by a possible minimum of degradation, the macromolecular structure remains intact, rather post-stabilization is the main target. Here the key issues are selective waste collection, compatibleness of otherwise incompatible polymers and the exploration of possible upgrading. Special care should be paid to harmful additives. If the polymer is thermoset, mechanical or partial chemical degradation (devulcanization) is necessary for recycling but linear polymers may also be partially degraded into useful oligomers. A special case of partial degradation is biodegradation or controlled photo-oxidation. Pyrolysis and energetic utilization (incineration) correspond to complete degradation. An example is discussed to demonstrate the principles in detail from our own practice related to automotive shredder waste.

Keywords: plastics, recycling, controlled degradation, automotive shredder waste

1 Introduction (Times New Roman size 10 Bold) [Title above the middle line]

Owing to their immense advantages, such as low density, mass processability and free shaping behaviour plastics became an indispensable part of our life in the 20th century. As a part of crude oil processing industry the production of monomers and polymers became the essential part of chemical industry and the processing of plastics created a whole branch of new technologies and resulted in several inventions. Plastics packaging materials meant a quantum leap not only for the food industry but for durable products as well. Heat insulation became easily available for housings, an invaluable asset since the beginning of the oil price crisis. But this is only one side of the coin. We have to face the dark side as well: due to their slow degradation and to the irresponsible customer behaviour our environment is becoming heavily contaminated by bulky waste which may endanger the biological equilibrium. Although not comparable with the hazards caused e.g. by the production and used fuels in various engines, plastics are fiercely attacked by environmentalists, often without offering or even considering alternatives. Plastics, as macromolecular organic compounds, can be utilized in two basic ways: either without breaking down the macromolecular structure (materials recycling) or by splitting them into low molecular compounds (energetic utilization, feedstock recycling etc.). A special case of degradation became especially favoured in the past decades: controlled degradation where our knowledge on biological or thermo-oxidative degradation is utilized to tailor the lifetime of the product and its raw material. Due to size limitations in this article we review only briefly the problem and some basic methods used to solve it. We will have a close look at certain groups of wastes and their disposal/utilization. The listing of options will be followed by a demonstration of the principles on an actual recycling development project.

2 Literature – the state of the art

The main components of plastics are macromolecules, which are mostly linear molecules consisting of divalent monomers [57]. Occasionally either due to polymerization defects or conscious engineering they contain trivalent or even tetravalent units which results is chains with short or long chain branching (short or long being defined by the length of the main chain). Such macromolecular systems become visco-elastic liquids above their glass transition temperature (if they are amorphous) or above their crystalline melting point (if they are semi-crystalline) thus they can be re-shaped into useful products. These macromolecular systems are called thermoplastics. If the number of multivalent units increases or if the branches can join each other the system of linear molecules becomes a single network (thermosets), which does not flow anymore above the glass or melting temperatures, only the rigid resin becomes soft rubber (elastomer).

Commercial plastics are, however, are much more than simple polymers or macromolecules, they are artfully designed compounds. Almost all plastics contain low molecular additives [94], mostly stabilizers (heat stabilizers, antioxidants, light stabilizers, and possibly several others, as antistatics, lubricants, plasticizers, fire retardants etc.). Although they are present in relatively small amounts, they play a decisive role in plastics recycling. Besides additives other components, as fillers and reinforcements [40] are also added to the compounds to modify their mechanical, electrical, thermal etc. properties and their price. Several plastics contain more than one polymeric components, notable examples are blends (or alloys) [83] and impact modified plastics [73]. As polymer pairs compatible in the thermodynamic sense are very rare, these multi-polymer systems usually exhibit hetero-phase structure, where the morphology of the components and their interfacial properties (most notably interfacial adhesion) are very important in determining the final properties of the compound.

The vast majority of plastics produced are thermoplastics: according to recent European statistics [[www.americanchemistry.com/production-and-sales-data-by-resin-2009-vs-2008]] in 2012 about 14% of the plastics produced in Europe belonged to the thermosets, while in another representative market, in the USA [68] the corresponding figure was also close to 14%. Therefore the plastic recycling problem is mostly related to thermoplastics, although the amount thermosets and rubbers (which, by themselves, including natural and synthetic rubber, also account for about 10% of the plastics consumption) is considerable, and they require separate recycling technologies due to their crosslinked structure which precludes melt processing. Within thermoplastics usually commodity plastics, engineering plastics and high performance plastics are distinguished [56]. Within commodity plastics the main groups are polyolefins (polyethylene, polypropylene and their copolymers), vinyls (PVC and vinyl chloride copolymers), styrenics (polystyrene, including expandable and impact modified grades) and PET (polyethylene terephthalate). Engineering plastics are more varied (polyurethanes, polyamides, non-PET polycondensation polyesters, polycarbonate, engineering styrenic copolymers, as ABS, SAN etc., fluorinated plastics and so on). High performance polymers, such as polysulfones, polyether-sulfonates, polyphenylene sulphide, liquid crystal polymers, polyimides etc. exhibit special heat, chemical and other resistance. In this order (commodity – engineering – high performance) the production decreases, the performance (especially the maximum continuous use temperature) and price increases.

According to recent statistics [61] the European market demand in 2012 was 45.9 million tons, of which 17% was low and linear low density polyethylene, 12% was polypropylene (polyolefins, total 48%), 11%

was PVC, 7% was polystyrene (including the expandable grades), 7% was PET, 7% was PUR, while the rest (about 20%) accounted for all other kinds of plastics. In terms of applications 39% went for packaging, 21% for building and construction (B&C), 8% for automotive, 5% for electrical and electronics (E+E) industry, 4% for agriculture, 23% for all other segments.

Table 1 Typical composition of municipal solid waste, data from the United States, 2010 [11]

Waste class	**Amount**
Paper	28%
Glass	5%
Metals	9%
Plastics	13%
Rubber, leather textile	8%
Wood	6%
Yard trimmings	13%
Food scraps	14%
Other	4%

Table 2 Typical composition of plastic waste within MSW [12]

Plastic type	**Amount**
Low density polyethylene	23%
High density polyethylene	19%
Polypropylene	14%
PVC	6%
Polystyrene	9%
PET	10%
Others	19%

Table 3 Twelve principles of green engineering [13]

No	**principle**
1	Designers need to strive to ensure that all material and energy inputs and outputs are as inherently non-hazardous as possible.
2	It is better to prevent waste than to treat or clean up waste after it is formed.
3	Separation and purification operations should be designed to minimize energy consumption and materials use.
4	Products, processes, and systems should be designed to maximize mass, energy, space, and time efficiency
5	Products, processes, and systems should be “output pulled” rather than “input pushed” through the use of energy and materials.
6	Embedded entropy and complexity must be viewed as an investment when making design choices on recycle, reuse, or beneficial disposition.
7	Targeted durability, not immortality, should be a design goal.
8	Design for unnecessary capacity or capability (e.g., “one size fits all”) solutions should be considered a design flaw.
9	Material diversity in multicomponent products should be minimized to promote disassembly and value retention.
10	Design of products, processes, and systems must include integration and interconnectivity with available energy and materials flows.
11	Products, processes, and systems should be designed for performance in a commercial “afterlife”.
12	Material and energy inputs should be renewable rather than depleting.

The most important sources of plastics waste, according to the consumption statistics quoted above are:

- Plastics conversion, processing waste, scrap, (in-house)
- Packaging waste (selectively collected)
- Post-consumer waste (selectively collected)
- Municipal solid waste (MSW)
- Agricultural waste
- Construction and demolition waste (B&C)
- Automotive waste (end-of-life vehicle, tires)
- Electrical and electronic waste (E+E)

Although the composition of municipal waste varies somewhat in various regions of the world and the classifications used to describe the composition are far from being uniform, the relative amounts and classes listed in Table 1 are representative. The distribution of plastic types in MSW roughly corresponds to the consumption statistics (Table 2). From the distribution of plastics by application quoted above it follows that the largest amount of plastic waste comes from the packaging sector, although B&C, automotive and E+E waste should be addressed too, individually.

2.1 Materials recycling

As mentioned in the abstract, there are two, basically different approaches to dealing with plastic wastes. The first philosophy is based on “preserve as much as possible”. The “zeroth order” approximation is the reduced consumption of plastics, also called “green engineering”, which is not limited to plastics, but all structural materials. Some principles of this environmentally benign green engineering are summarized in Table 3. The next level of this philosophy is “remanufacturing” [www.lboro.ac.uk/microsites/mech-man/research/ipm-ktn/pdf/Technology_review/remanufacturing-towards-a-more-sustainable-future.pdf] or “disassembling” [69] where the plastic (and other) parts are not re-processed (melted) actually, but are re-used either as they are or after minor modification. Remanufacturing is well known in relation to toner cartridges and the sustainability issue between recycling and remanufacturing is largely decided by quality and reliability [www.eurovaprint.eu/fileadmin/eurovaprint_files/pdfs/EuroVAprint_Position_Paper_LCAs_toner_ink_cartridges.pdf]. Disassembling could and should be aided by design (self-disassembling constructions, built-in information on disassembling etc.). However interesting and important these approaches are, our main target now is to study and evaluate recycling methods which involve at least the melting and/or partial breakdown of the molecular structure of the polymeric waste components. Let us turn our attention now to the most widespread “materials recycling” method in the field of plastics recycling, based on melt processing. Within this regranulation is most widespread, where first a compound is produced which can be processed alone or in combination with virgin material. In line compounding is also possible, where compounding is immediately followed by processing (e.g. injection). When choosing melt reprocessing the following issues should be considered:

- purity (selective waste collection, mixed polymer waste problem, compatibleness, commingled waste, solid contaminants, removal of dangerous components, separation of waste components)
- degradation during use and regranulation (post-stabilization, synergistic and antagonistic effects of additives, molecular weight changes, chain extension)

Now let us investigate briefly these problems. Purity is very important, as polymers, due to the low mixing entropy are normally not miscible with each other – not even two grades of the same kind of polymer (e.g. two PE-LD types), even less polymers of e.g. different branching level (e.g. PE-LD with PE-HD), or with different, although chemically related structures (e.g. PE with PP) [77]. The plastics industry learned to handle these problems to a certain degree, as e.g. linear low density and low density polyethylenes were “blended” routinely for a while, to improve processability (especially melt strength) [63]. Heterogeneous polymer mixtures usually exhibit much lower elongation at break values than any of their components, unless special additives are used. One way of improving interfacial compatibility is to use copolymers (mainly block copolymers [82], although in some cases random copolymers may also be used for special purposes [51], as impact modification). As block copolymers are relatively expensive and sophisticated products, block copolymers are frequently produced *in situ* using the principles of reactive extrusion or reactive compounding [37,48]. Block copolymer formation may be achieved either by the addition of a small amount of radical precursor (e.g. peroxide) or by using oligomers with reactive end-groups.

Nevertheless, reprocessing is the easiest if the scarp used for it consists of relatively homogeneous macromolecular components, in terms of chemical composition, tacticity, molecular weight distribution and additives. These conditions can be achieved easiest in the case of in-house scrap, or “regrind” which utilizes defect parts, sprue (injection moulding), film edge (film extrusion) etc. after grinding. The acceptable regrind rate is determined empirically (limited by the unavoidable degradation during processing), but it is usually maximum 10 wt%.

Selective plastic waste collection is much more effective than separation of waste components, therefore wherever it is possible, this should be realized. This can be most easily done with packaging waste [23], although good selective waste collection is possible with certain kinds of B&C waste, as e.g. PVC window frames, plastic pipes, cable insulation [[www.plasticseurope.org/documents/document/20120316100543-summary_of_plastic_b&c_waste_management_analysis160312.pdf]]. Of all packaging waste about 19% is plastic [[ec.europa.eu/eurostat/statistics-explained/index.php/Packaging_waste_statistics]], which is higher that the plastic content of average MSW. Plastic bottles, wrapping films is retail stores can be collected with reasonable efficiency and relative purity, although in the case of bottles polyolefins and PVC (which is rarely used for this purpose nowadays) can be relatively easily separated from PET, the most widespread plastic bottle material. PET recycling is a special problem which will be touched later, but polyolefins (polyethylene and polypropylene) can be recycled relatively easily – although usually some degree of downgrading is inevitable, especially in the case a specialty films, such as shrink film, stretch film, cling film etc. Representative analysis of mixed plastic film waste [42] shows that the polyethylene content (LD+HD) is about 45-65%, the polypropylene content is 15-18%, the multilayer content is 8-15%, while there are 5-10% solid contaminants (paper, rigid plastic, metal) and 8-10% moisture (this latter partly comes from wet cleaning). In order to be processable PP and multilayer content should be minimized. Volatiles should also be removed (also during extrusion). When using recyclates in plastic processing (e.g. film, bottle, pipe, sheet etc. production) multi-layer technologies are preferred with the recyclate in the central layer.

A plastics recycling plant technology line usually consists of the following units [18, 19, 30]:

- crushing
- sorting non-plastic components
- sorting plastic components (PVC and other halogen-containing components should be recycled separately from all others)
- regranulation line (usually twin screw extruders or kneaders)

2.2 Mixed plastic waste

Mixed plastic packaging waste, other mixed plastic wastes and plastic/non-plastic mixed wastes can be separated by various techniques, depending on the form and properties of the waste components:

- spectroscopic selection
- density based methods (air classification, sink-and float)
- magnetic separation (for ferrous metals)
- eddy current separation (metals)
- wetting/swelling properties
- triboelectrification

Commingled plastic waste poses special problems not only because of the incompatibility of the polymer pairs being present is them, but also because of the special degradation characteristics of the PVC component (polyvinylidene chloride and chlorinated PVC behave similarly, but they are usually not present in a normal plastic waste). Handling the "PVC" problem in mixed plastics recycling [45] has long been investigated, as PVC begins to degrade and lose HCl at temperatures which are customary processing temperatures for other components of the mixture. This early degradation is accompanied by strong discoloration. If relatively pure PVC waste can be collected (e.g. window and door profiles, pipes, cable insulation, packaging materials), they can be regranulated by themselves. In view of the complicated formulation of PVC-s (both unplasticized and plasticized ones) this is a delicate task. The mechanical recycling of PVC waste in the European countries has been reviewed by many [62], and especially good results are achieved for window profiles collected from demolition waste. If PVC is a minority component in mixed plastic waste, its content can be reduced by triboelectric separation or by forced PVC degradation in a preliminary extrusion step, where the majority of HCl is removed and absorbed by bases.

2.3 Electronic and electrical waste

A special case of mixed plastic waste is electrical and electronic (E+E) waste which is dealt with by two EU directives: the WEEE Directive 2002/96/EC and the RoHS Directive 2002/95/EC. Typical electronic waste contains 49% metals, 33% plastic, 12% of the waste comes from cathode ray tubes (which may diminish with LCD and other displays), the rest contains different materials [39]. According to the same source in 2005 in the US about 56% of the WEEE plastics fraction was HIPS, 20% was ABS, 11% was PPE (poly-phenylene-ether, which, together with HIPS constituted a popular blend, called Noryl®), while the residue (13%) contained other polymers. Nowadays probably the PC content is higher due to the widespread use of PC-ABS alloys, but essentially E-waste plastic fraction is a strongly mixed powder of engineering plastics. The most important fraction of electronic waste is that of metals: some precious metals (Au, Pd, Cu, Ni, Sn, Pb) are present there in significantly higher concentration than in natural ores [28], and can be recovered after mechanical separation followed by classical or hydro-metallurgical and electrochemical processes. It is quite possible that it will be less expensive to recover some metals from the E-waste than from natural resources. The plastic fraction is less valuable (mainly because of the necessity of component separation and contamination), nevertheless the constituents a relatively expensive engineering plastics. The E-waste recycling rate increased from 10% in 2000 to 24.9% in 2011 [www.electronicstakeback.com/wp-content/uploads/Facts_and_Figures_on_EWaste_and_Recycling.pdf]. The E-waste problem is not limited to the USA or the EU countries, Asian countries face the same problem

[13]. Separation and reprocessing of the E-waste plastic fraction are somewhat similar to those technologies used in the processing of the automotive shredder plastics residue. Material recycling is very much limited by the technical difficulties of component separation, controlled decomposition into low molecular organic compounds, incineration or co-firing are better suited to this kind of waste.

2.4 Controlled breakdown of chains and networks

PET recycling became important because of the widespread use of this material for bottle and other packaging applications [7]. This technology faces one major problem: the partial degradation of the PET chains during use and especially in the regranulation process, mainly due to hydrolytic degradation. Various approaches have been used to meet this challenge. One is to turn PET waste flakes into fibres [[www.hknonwoven.com/eng/pr/ECOPET%20New.pdf]], as fibre melt spinning requires lower viscosity melt. In this case the main task is to filter the melt thoroughly, as solid contamination plugs the spinnerets [89]. Another solution is to drive further the breakdown process to polyester oligomers or even to monomers – but this belongs to a further part of this paper and will be mentioned there. The problem of reduced viscosity can be solved by adjusting the processing technology: e.g. using injection compression moulding instead of injection moulding [64], using reinforcing fillers, but the most widespread way of upgrading is chain extension [21] which is aimed at the regeneration of the broken chains and restoring the original viscosity. The hydrolytic process is in principle reversible (condensation), but usually chemical coupling agents, as diisocyanates [78, 92] or diepoxides [65] are used both in "pure" PET and in blends. PET chain extenders are discussed at more length in [73].

Now we come to the next step in our train of thought: instead of preserving the macromolecular properties we may try to break down the plastic waste first by mechanical comminution later by molecular breakdown. Mechanical breakdown is an almost necessary preparative process of all plastics recycling technologies, but in the case of crosslinked plastics this can be an essential part of recycling. Most important crosslinked plastics are rubbers (where the glass transition temperature is below room temperature) and thermoset resins (epoxy, vinylester, unsaturated polyesters, phenolics, urea-formaldehyde resins, aminoplasts and hybrid resins) with glass transition temperature above room temperature.

Rubber recycling is very important because of the huge amounts of automotive tire wastes produced every year. Dumping of waste tire is forbidden in most industrialized countries, burning is severely limited by laws, therefore material recycling is necessary. Tires are, however, much more than rubbers, they are complicated composite structures containing textile, metal and rubber components. Tire waste is not uniform in composition, several different kinds of rubbers are used for this purpose (natural rubber, styrene-butadiene rubber, nitrile rubber, butyl rubber etc.). First the non-rubber components must be separated and the residue is transformed into "crumb rubber" by mechanical or e.g. water-jet milling. Basic principles of rubber recycling have been widely described in simple terms [[Recycling rubber, Practical action, practicalaction.org/media/preview/10541]] but highly sophisticated and extensive reviews are also available [41]. The softness of elastomers limits the size and efficiency of grinding. If using room temperature grinding relatively coarse "crumbs" are obtained, while cryogenic grinding allows the production of sub-millimeter particles. Even the latter are, however, "macroscopic" in comparison to normal fillers with a typical diameter of 1-10 microns. Crumb rubber can be compounded into fresh elastomer, followed by vulcanization, it can also be used in the formulation of thermoplastic elastomers [47], or mixed with various thermoplastics, as e.g. HDPE and nylon 6/10 [50]. Crumb rubber is a useful (but not cheap) additive for asphalt in elastic pavements or in the top layer of highways. Deposition taxes, however, may influence economic considerations. The problem with crumb rubber fillers in thermoplastic or in elastomeric compounds is the same which we have to face in the case of milled thermoset composites: the surface is inactive the matrix-filler adhesion is low. It means that either we limit ourselves to low-end applications (e.g. rubber mats, vibration or sound absorbers etc.), or we have to apply expensive post-treatment to the crumb rubber surface. Compatibilization technologies for crumb rubber to improve the interfacial adhesion between recycled rubber and matrix have also been reviewed [25].

Thermoset resins are much lower in production volume than thermoplastics, but (mainly due to their thermal stability) they are indispensable in some key areas (e.g. transport, E+E sector, aerospace, military). Most thermoset composites contain a significant amount of reinforcement (glass, carbon or other fibres). According to recent data within the world consumption 47% of the matrix materials is polyurethane, 19% is unsaturated polyester, 10% is phenolic resin, 18% is amino resin, 5% epoxy, 1% is the rest [12]. Polyester based composites include SMC (sheet moulding compounds), BMC (bulk moulding compounds) are widely used by the transport industry. Pultruded profiles and fibre reinforced laminates are also important. Composite and thermoset recycling methods [35, 79, 90], including recycling of plastic composites (including thermoplastics and thermosets) [6] have been widely reviewed. One possible way of utilizing thermoset composite waste is grinding into fine powder and using the product as inactive filler in other thermoset composites, in thermoplastic composites or in rubbers. This means, however, inevitable downgrading of the reinforcing properties of the fibrous component, as continuous filaments are transformed into chopped or even milled fibre with much less reinforcing activity. Additionally the surface of ground composite powder is inactive therefore surface treatment may become necessary if better properties are to be achieved. Recovery of the reinforcing fibres may be considered if the matrix is thermally or chemically decomposed. It is feasible only for carbon reinforcement which is expensive enough to warrant such a complicated procedure. Anyway milled, chopped or pelletized carbon fibres can be recovered form thermoset composite waste with about 90% of the original properties retained.

The next step in recycling crosslinked systems (rubbers and thermoset resins and their composites) is partial devulcanization, resulting in reactive end- or side-groups. Depending on the degree of the breakdown of the network it is possible to produce thermoplastic elastomers from rubber waste or polyols or other reactive thermoset additives from thermoset resin waste. In the case of rubbers the de-vulcanization agent or peptizing agent can be specific to the curing agent used or can act randomly at any bond of the network. As sulphur vulcanization is by far the most used, many of the peptizing agents (such as diallyl disulphide [33]) are designed to break down the sulphur crosslink. It has been shown [26], that although the bond strengths of C-C and C-S and S-S bonds are fairly similar, but their elasticity is different. Therefore simple thermal devulcanization would lead to an almost random scission of bonds, while if the rubber scrap is exposed to high shear the sulphur bonds would selectively break down. In addition to simple thermal reclaiming also thermo-mechanical, mechano-chemical, radiation-induced or even biological reclaiming technologies are available [[www.centerplastics.com/img/rd/present_status_of_devulcanization_technology.pdf]]. Instead of heat sometimes steam is also used for devulcanization, which can be even successfully applied to silicone rubber. In this case of course the devulcanized rubber should be thoroughly dried afterwards. In the mechano-chemical method more complicated de-vulcanization masterbatches (dimethyl dithiocarbamate, mercapto benzthiazole, thiols, stearic acid, zinc oxide, sulphur) or other chemicals (aryl and diaryl sulphides, disulphides, thiophenols and their zinc salts) are used. Partly devulcanized rubber can be added to new rubber compounds, although in a limited amount. It can also be used as an additive in thermoplastic compounds or as toughening agent in thermoset composites.

Thermoset resins can also be partially degraded to yield useful intermediate chemicals which can be used either as additives in new thermoset synthesis or as low molecular chemicals. Tertiary recycling of unsaturated polyester based composites (SMC) into fuel [1, 20] is possible, as well as solvolysis by supercritical carbon dioxide, water or methanol [55] into useful chemical raw materials. The use of supercritical fluids for matrix degradation is especially interesting, as e.g. in supercritical water several reactions are extremely fast even in the absence of catalysts. Traditional chemical decomposition methods have also been described (e.g. nitric acid for epoxy resins, aminolysis for unsaturated polyesters, glycolysis for thermoset polyurethanes, see [79] above) which may be useful in some applications, e.g. glycolyzed PUR wastes can be re-used as polyols in new PUR formulations. Crosslinked polyethylene, which is neither a rubber, nor a thermoset in the strict sense of the world, should also be recycled with a partial breakdown of the network, e.g. by solvolysis in supercritical methanol [17], although milling and re-compounding is also possible [34, 80]. A combination of the two methods, i.e. continuous extrusion assisted by supercritical solvolysis is also possible.

The partial (controlled) breakdown of two classes of polymers is of special importance, that of polyurethanes (PUR), and polyethylene terephthalate (PET). In the case of polyurethanes hydrolytic or even more solvolytic breakdown (alcoholysis, within that, glycolysis) of the polymeric structure [10, 93] is far more advantageous than pyrolysis or burning. If the glycol exhibits high boiling point, even pressure is not needed and the obtained product can be directly used as a polyol in later PUR synthesis. In some cases typical urethane synthetic catalysts are also added to the glycol/PUR waste system to accelerate and control the reaction. As aromatic amines may appear as side products, they are frequently reacted with e.g. epoxides to obtain less dangerous products. In addition to glycolysis acidolysis, alkaline treatment and aminolysis is also possible. Certain variants of these technologies can also be realized in extruders in the “molten” phase. Chemical recycling of PET (polyethylene terephthalate) also became important [59], although the chemicals obtained in these methods are available from petrochemical plants at relatively cheap price. Nevertheless, the increasing use of PET by the bottle industry makes such utilization viable and necessary. The PET chain, which is formed in a polycondensation reaction can be broken down e.g. by hydrolysis, methanolysis of hydrolysis. If the chain breakdown process is performed under milder conditions, the polyols produced can be utilized for polyurethane synthesis. An effective transformation of PET waste to polyols useful in polyurethanes is possible also via aminolysis using alkanolamines [29].

2.5 Controlled environmental degradation

A special way of plastic waste disposal is controlled degradation “built in” into the plastic product, which becomes effective after the end of life. The advantages of such a concept are obvious:

- if the degradation rate is known and controllable, the lifetime can be designed
- the environmental fate of the product is known

- the manufacturer will have a competitive edge, a marketing advantage related to the "green product"
- new markets or at least niche markets may become available.

There are, however, not less obvious disadvantages and risks:

- such solutions usually involve expensive additives or new raw materials
- development costs can be enormous, their return is questionable
- the new markets may be risky, slowly developing and narrow
- production should be tightly controlled
- decomposition in the planned way requires precisely observed conditions – the consumers should be educated is disappointment is to be avoided
- the most serious problem is cross-contamination with traditional plastics, which would render the recycling of traditional plastics problematic
- therefore degradable plastics should be collected separately (visible identification, labelling)
- the planned application should be carefully designed and engineered to avoid mismatch of planned an real lifetime

There are basically two philosophies used for controlled degradation: one is based on the controlled acceleration of thermo-photo-oxidative degradation, the other is based on bio-degradation. Thermal and photo-oxidation of most polymers (at least that of their aliphatic part) is mainly based on a combined cycle of two cyclic reactions which can be controlled by the use of antioxidants [27]. Under thermal or light impacts alkyl radicals are formed which react with the ambient oxygen, forming peroxy radicals. Peroxy radicals react with other alkyl chains and hydroperoxides and new alkyl radicals are formed. Hydroperoxides may undergo homolysis giving rise to alkoxy and hydroxyl radicals. Alkoxy radicals may also react with alkanes and new alkyl radicals are formed. So-called primary antioxidants (usually sterically hindered phenols or amines) scavenge the reactive radical species by forming stable radicals instead, while secondary antioxidants (usually organic phosphites or sulphides) deactivate hydroxyl radicals. Certain transition metal ions may accelerate the first cycle thus leading to earlier degradation. Such ions are masked by complexing agents in high voltage polyethylene insulations where degradation is to be avoided, or may be added intentionally to agricultural films or other products, where shortened lifetime is required. Pro-oxidants are activated by light or heat under outdoor conditions. Such (environmentally benign) transition metal salts are called pro-oxidants and are available in masterbatch form. Lower molecular species produced by accelerated oxidation are finally available for attack by microbes. In some other cases the degradation does not reach the molecular level, but very fine polymer powder is formed, which is neutral and does not endanger the environment. This process is called oxo-biodegradation [11], its primary use is in agriculture (mulch films, greenhouse films, bags for compost collection). In other applications biological "pro-oxidants", as starch, are used which are more prone to the environmental effects [38]. Companies developing more expensive polymers that are biologically degradable to the molecular level, fiercely debate the claim that identification of oxo-biodegradable films with their products is really justified [58].

In popular "green" parlance plastics from renewable resources are frequently mixed up with biodegradable polymers, but this is a mistake. There are plastics made of non-renewable resources, which are not biodegradable – these are most synthetic polymers. There are polymers made of renewable resources, but non-degradable: an example is polyethylene made in Brazil from ethanol obtained from sugar cane. There are polymers, which are made of synthetic (non-renewable) raw materials, but are degradable – e.g. polylactide can be made from synthetic lactic acid. And finally there are polymers made of renewable resources which are degradable – e.g. bacterial polyesters. When we talk of degradability, it should be clearly stated under which conditions is the material degradable (light? heat? humidity? soil? composting? aerobic? anaerobic?) – otherwise the term is meaningless or misleading. This should be specified in the test used for proving biodegradability [54]. Most frequently used biodegradable plastics belong to polyesters: e.g. PBS = polybutylene succinate, PBSA = polybutylene succinate adipate, PCL = polycaprolactone, PLA = polylactide or polyesteramides [46, 74], [[www.biodeg.net/bioplastic.html]] PLA is in the most advanced stage as far as applications are concerned, here the major problems are related to the price and to the relative rigidity of films, injection moulded or blow moulded articles made of this material. These problems can be alleviated by copolymerization, plasticization or blending. The main area of application is food packaging. Proper composting conditions should always be provided for the collected biodegradable waste if complete decomposition is required. At present polymers of biological origin cannot replace traditional ones in most applications but a gradual market gain is expected in the near future.

The highest degree of decomposition is complete breakdown – in the form of depolymerization, pyrolysis (thermal breakdown), or energetic utilization, incineration (burning). Burning seems to be an obvious solution especially for hardly separable, mixed plastic wastes (such as E+E waste, automotive shredder or commingled plastic waste) but it has its own problems: high humidity content (2-25%), relatively high inert content (5-40% - resulting in slag formation), widely varying and relatively low heating value (13-25 MJ/kg – comparable with that of wood but much less than that of pure polymers, coal or oil). Co-incineration with municipal solid waste or sewage sludge is also possible, but the presence of acidic gaseous products and heavy metal contamination in the dust requires attention. Pyrolysis in reductive atmosphere (CO, CO2, H2 mixture formation) is also possible. Commingled plastic waste can also be reprocessed by pyrolytic technologies. This broad term involves various technologies, as [36]

- hydrous pyrolysis (steam cracking) at 300-350 °C and at relatively low pressure (<12 MPa), resulting in light hydrocarbons
- hydrothermal liquefaction at 300-350 °C and 12-20 MPa, resulting in an aqueous slurry of liquid hydrocarbons
- anhydrous pyrolysis above 350 ° and above 12 MPa pressure, resulting in a whole series of cracking products (gas, oil, char).

This is the best with polyolefin waste. In case of incineration or co-firing the amount of halogenated, nitrogen and sulphur containing residues in the waste should be reduced to avoid environmental pollution or basic slag formers should be used.

Depolymerization as a term is mostly used in relation to polycondenstaion polymers as polyamides (nylons) [60], polyesters [43], polylactides [[www.carbios.fr]], sometimes to biopolymers, as cellulose [67] although thermally induced and catalysed depolymerization can be applied to silicones [24], vinyl polymers [76].

2.6 Selection of best technology – Life Cycle Assessment

As shown by the long list of methods mentioned, almost always there is a range of possibilities to recycle plastic waste. There is no general answer regarding the environmental friendliness of any of the listed approaches based on materials recycling, programmed breakdown or energetic recycling, as the optimum solution depends on a series of factors, as the amount of waste, raw materials involved, cleanliness of waste, easiness of collecting the waste etc. By now a general methodology discussed below has been developed that allows the preliminary assessment of various production or recycling technologies, called Life Cycle Assessment (LCA) [32], which takes a “cradle to grave” approach and calculates not only energy consumption but also CO_2 emission, ozone layer depletion effects, resource consumption, ecotoxicity and much more. It requires a fairly broad database regarding raw materials and technologies and, although the method can be debated, especially the relative weight factors ascribed to the various effects, this method is presently the most effective one for assessing the consequences of replacing one material or technology by another one. Eco-efficiency assessment of plastics recycling methods has been performed [31], LCA of a concrete intractable plastic waste to artificial crude oil technology [3] is available, a comparative study of practices in various European countries [72] based on the LCA philosophy has been issued, and we can also cite a Scandinavian analysis on the economic background and feasibility of plastics recycling [2]. Mitsubishi Electric devoted a whole issue of their journal "ADVANCE" to environmental issues covering not only plastic recycling, but also household appliances waste collection, separation and design-for-disassemble methods already in 2001 [22]. Conscious waste management always starts with proper design taking into account the results of "end of life analysis" [87]. Relatively few publications deal with the direct comparison of materials recycling methods with energetic or feedstock-recycling. A comprehensive LCA analysis [91] of PVC insulated cable waste compared two materials recycling technologies (one termed "internal" involving hot milling of the waste directly reused in cable production, the other called "external" is the customary removal of the insulation followed by regranulation), energetic utilization and landfill from the viewpoint of CO_2 emission saving with the following results: internal recycling: 1.2-1.5 kg CO_2eq/kg saving, external recycling 0.1-1.5 kg CO_2eq/kg saving, exergy recycling 0-0.57 kg saving CO_2eq/kg, landfill causes 0.07-0.09 kg CO_2eq/kg. The authors also draw our attention to the fact that restricted materials (as e.g. certain phthalates, lead stabilizers etc.) hinder or even prevent recycling. The methodology is interesting because it also takes into account avoided processes as beneficial factors. With respect to eco-design it is emphasized that long life is frequently more important (even form the environmental point of view!) than recyclability, thus this latter aspect cannot always be taken into account if the two viewpoints are in conflict. In addition to materials effects on the environment price estimates should also be compared although here only the orders of magnitude can be reliably estimated. A Master's thesis [66] has been devoted to the materials flow and exergetic analysis of two alternative processing technologies of municipal solid waste: in one of them the whole MSW is incinerated, in the second one the plastic component is separated and used for materials recycling. The answer is not black and white, the advantages depend on the percentage of virgin plastic that can be replaced by the recyclate. If it is >16%, the separate treatment of plastic waste is advantageous with respect to natural source depletion, but if is <16% direct incineration is exergetically favoured. Even these examples show that in deciding between technologies of waste management scenarios a quantitative rather than qualitative view should be taken with possibly the best input data.

A British organization "WRAP" published a series of high quality LCA analyses on various raw materials, among others plastics [52]. They studied 28 cases, of these 8 in more detail and 59 scenarios. The cases included commodity thermoplastics and some thermosets. Incineration was accompanied by electricity recovery only in some cases and combine heat and electricity production in other cases. Pyrolysis as an option was investigated with mixed plastics only. Their conclusions are fairly equivocal with respect to plastics recycling. Mechanical recycling is more favourable than incineration or landfill although pyrolysis is an emerging technology which may become competitive with mechanical recycling. When mechanical recycling, incineration with energy recovery and pyrolysis are all compared, mechanical recycling was the most favourable, while pyrolysis was either more favourable than incineration or they were comparable. The pre-eminence of mechanical recycling is due to the avoidance of energetic and environmental problem accompanied with virgin plastics production. All this has to be put in perspective, however, as this very attractive result is obtained with assuming 1:1 replacement rate of virgin by recycled plastics and nearly 100% purity of waste. None of these assumptions are realistic, however, especially for mixed plastics.

It should be mentioned that while most of the methods reviewed so far are related to centralized waste collection and recycling technologies, nowadays alternative ways, as “distributed recycling” [44] should be considered. The idea is based on the availability of relatively cheap “open source” equipment called “RecycleBots” which convert thermoplastic waste into locally used 3D printing filament, thus making recycling an attractive option even in not too densely inhabited rural areas.

In the following paragraph we try to demonstrate the principles mentioned before on an actual waste recycling project performed

3 A case study – plastics recycling in the automotive industry

This case study is based on the novel research outcomes and experiences of the corresponding author’s research group at Budapest University of Technology and Economics (BME).

Two projects of BME, “Magnetic Sorting and Ultrasound Sensor Technologies for Production of High Purity Secondary Polyolefins from Waste” W2Plastics [[Magnetic Sorting and Ultrasound Sensor Technologies for Production of High Purity Secondary Polyolefins from Waste – W2Plastics Project www.w2plastics.eu]] project and “Elaboration of Recycling Technologies for Non-metallic Automotive and Electronic Wastes Avoiding Further Deposition of Organic Materials” Recytech [[Elaboration of Recycling Technologies for Non-metallic Automotive and Electronic Wastes Avoiding Further Deposition of Organic Materials - Recytech project, www.recytech.hu/index.php?lang=e]] project targeted to solve the problems related to the organic content of waste fractions derived from the treatment of end of life vehicles (ELVs) in order to fulfil the European legislation (COM/2001/0031, 99/31/EC, 2000/53/EC, 2002/96/EC, 2003/108/EC). These directives aim at fostering the development environmental friendly technologies to reduce the environmental impact of human activities, to protect the environment, to minimize depletion of resources. According to these laws 95% utilization rate should be achieved for end-of-life vehicles (ELVs) by 2015, within this at least 85% should be material utilization.

Recytech (2009-2011) was subsidized by the Hungarian Technology Programme for research and development that may serve solutions for material recycling and energetic recovery of organic output fractions from shredding end-of-life vehicles (ELVs). The aim was to reduce the amount of the deposited useful materials, typically plastics. The W2Plastics (2008-2013) international project supported by FP7 programme of European Union aimed to develop a cost-effective and clean technology based on Magnetic Density Separation (MDS) and Ultrasound process control to recover high-purity polyolefins from complex wastes.

The tasks of Budapest University of Technology and Economics were the followings in the abovementioned projects:

- Definition of the requirements by market analysis using questionnaires in the automotive industry in more countries.

- Elaboration of a methodology for the characterisation of mixed polymer wastes which can be adapted to other waste sources as well. Qualification of incoming materials, evaluate and document their characteristic properties, in order to determine the separation limits: which are the cutting density borders for MDS in order to recover relatively pure fractions for materials recycling, separating from the remaining fraction feasible for feedstock recycling or energy recovery via pyrolysis.
- Upgrading without breaking down the chemical structure of polymers – materials recycling.
- Upgrading with influencing the chemical structure of polymers - pyrolysis.

3.1 Definition on the output requirements (market analysis based on questionnaire)

The mass of usage of secondary plastics is mostly determined by their quality and price, therefore it is necessary to collect and evaluate the related aspects and expectations from the potential secondary-plastics consumers. To appropriately handle both important aspects an adequate questionnaire has been worked out and sent to automotive plastics end-product manufacturers asking them to fill it in. With the evaluation of these returned the papers basic parameters for the technology development were determined.

To sum up the results, it can be stated that the plastics processors usually reuse only their own waste, and only a few companies accept waste from external sources. Generally there is no specification system for the external plastic waste; it should only meet certain agreed parameters, which are controlled by the accepting company or sometimes by the waste supplier.

Currently the percentage of the applied secondary plastics in the production of the primary products usually varies between 5 and 25%, depending on the technology, but in certain cases it can reach up to 50%. Recycled plastic materials can be used as secondary raw materials mainly in non-visible, non-coloured, non-load-bearing parts, when no further processing is done, in non-prestige brands. Constant composition, hardness, elasticity, UV-stability, (long)-term heat resistance, recyclability were the most important parameters, which should be considered in order to increase the ratio of the secondary plastics.

As for the legal and economic factors facilitating the increased use of the secondary plastics, several companies declared that even though the most important driving force remains the price reduction, it would be considerable incentive if the OEMs would be obligated to take back their products for reuse by themselves or subcontractors. We also realized that several automotive companies set unjustified requirements (i.e. they over-insure themselves by using primary raw materials only, not even allowing the reuse of internal processing waste), which may be altered by introducing the necessary legal measures.
Further details on the market analysis and questionnaire are available in the cited article [81].

3.2 Elaboration of complex waste characterisation protocol for polymer wastes, determination of separation boundaries

Automotive waste originated from the car shredder plant of Alcufer Kft. (Hungary) [[Alcufer Ltd. www.alcufer.hu/en/]] was used in the abovementioned projects. First of all oil, fuel, battery, catalytic converter, rims and all the liquids were removed from abandoned car in the depollution and dismantling process. After this step the car is shredded with a hammer mill, grinding the cars into primary lumps. This shredding process results in a mixture of ferrous metal, non-ferrous metal and shredder waste which are separated by magnetic classification. Ferrous and non-ferrous metals, the so-called shredder heavy fraction, can be sold. Shredder waste consists of glass, fibre, rubber, plastics and dirt, which is separated into shredder light fraction and dust. The shredder light fraction contains a large amount of plastics, but an adequate separating technology has to be found to recover it [49].

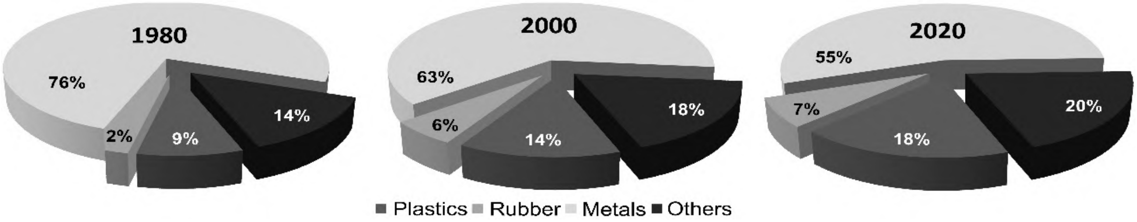

Figure 1 Changes in the composition of the cars over decades

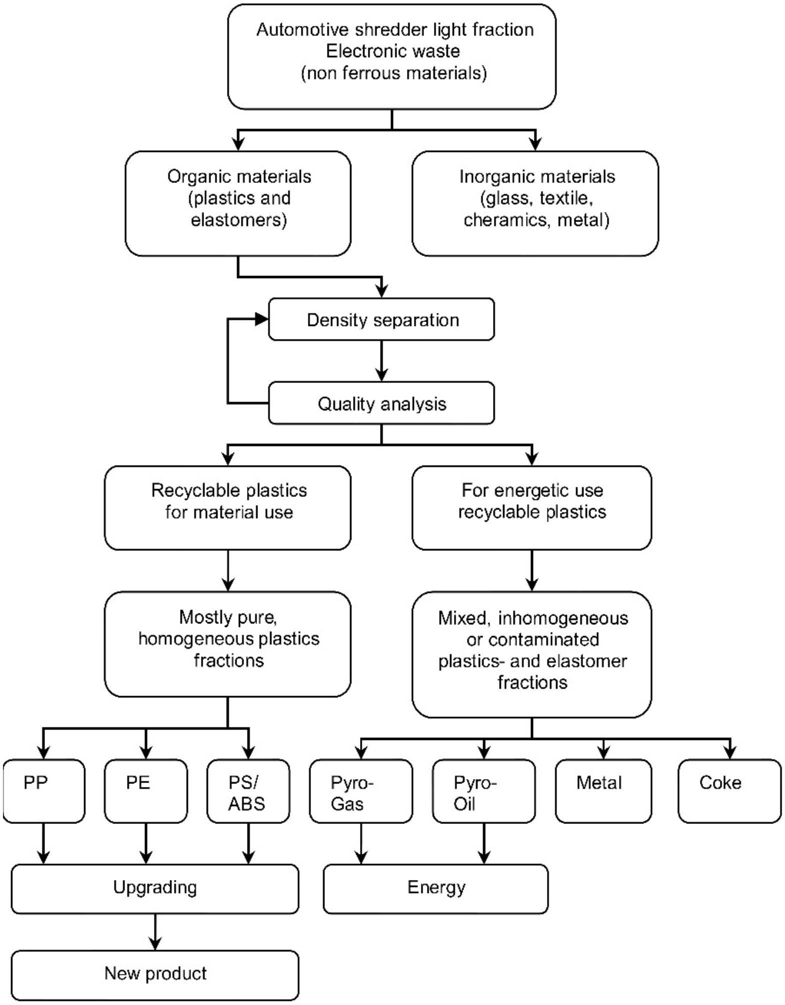

Figure 2 Plastic recovery from car shredder light fraction

According to the European Directives 95% utilization rate should be achieved for end-of-life vehicles (ELV) by 2015, within this at least 85% should be material utilization. As the ratio of plastics is increasing [88] (more than 10%) (Figure 1) the recycling of this material is indispensable in order to comply with the rules.

In order to ensure the required properties inferred from the evaluation of the questionnaire, such as constant composition, favourable mechanical and thermal properties, a comprehensive waste characterisation and an effective separation method is indispensable. In our projects Magnetic Density Separator (MDS) was used to increase the recovery of pure plastics from shredder light fraction, and a complex waste characterisation protocol (Table 4) was elaborated to determine the separation density boundaries and the properties of each polymer fraction in order to recover sufficiently pure fractions for materials recycling [8,75], separating from the remaining fraction feasible for energy recovery via pyrolysis (Figure 2).

Table 4 Waste characterisation protocol used for automotive shredder waste light fraction

Aim	Method	Aim	Information
Separation	**FTIR**	general identification of polymers	major components
	Raman	identification of minor components	degree of degradation
	TG	determination of the filler content	composition-density correction
	LP-FTIR	identification of black polymers	polymer composition, pyrolysis
	DSC	quantity, quality of crystalline phase	purity of fractions, expected thermal behaviour and reprocessing temperature
Characterization	**MFI**	characterization of the melt	expected flow properties for reprocessing
	SEM	characterization of the morphology	expected mechanical properties
	Mechanical tests	mechanical properties	value of the developed product

For representative analytical characterisation in the stage of “preparation for separation” the received mixed plastic wastes flakes with average size of 5-8 mm were cryogenically ground to powder-like (2 mm) particle by an analytical mill using liquid nitrogen. The ground samples were analysed with Fourier Transform Infrared Spectroscopy (FTIR) in order to characterize the main polymer components.

All fractions were analysed by FTIR in order to characterize the main polymer and filler components [84], while Raman mapping gave information on the nature of major and minor components and on their ratio in the mixture [85]. Laser pyrolysis-FTIR (LP-FTIR) ensured the identification of dark particles, which could not be readily identified by other methods.

This new hyphenated analytical method, Laser pyrolysis-FTIR (LP-FTIR) was developed at lab scale at the Budapest University of Technology and Economics by combining the method of micro scale modelling of fire circumstances, applying a laser and FTIR analytical monitoring technique in order to analyse the chemical changes in the gas phase [16]. The technique is based on FTIR analysis of gaseous products originating from laser induced decomposition of polymers in a specific combustion cell (in air or inert atmosphere) at different laser power levels, which allows the identification and quantification without the loss of any component. This method is used for modelling of the pyrolysis (dark flame zone, between the polymer and the flame); therefore it contributes to the understanding of polymer degradation mechanism, toxicity, as well as the effect of different additives using gas phase analysis.

As the evolved gases are specific and depend on the type of the polymer, they can be used as fingerprints; therefore the new method was successfully used in the characterization of polymer waste including black particles (based on the polymer-specific fingerprint-like decomposition products).

Thermal analytical methods as, Differential Scanning Calorimetry (DSC) and Thermogravimetric (TG) were used to determine the purity, expected thermal behaviour and reprocessing temperature of each fraction. According to previous experiences of the authors, the degradation temperature of the sample presents the main component; e.g. if the temperature is below 470ºC, the main component is PP.

In filler content measurement approximately 15 g of each fraction was heated up to 900°C until all the organic components were eliminated. The quantity of the fillers was determined by means of residual mass measurement, while the composition was analysed by an FTIR spectrometer. It has to be noted here that the filler fraction does not contain carbon clack, because it was eliminated together with the organic components.

Table 5 Analysis of separated automotive shredded waste plastic fractions

Density of waste fractions [g/cm^3]	**Main component**	**Polymer content [%]**	**Polymer ratio [%]**	**Filler content [%]**	**Fillers**
-0.88	PP	18	20%	0.9%	Talc, $CaCO_3$
0.88-0.89		57			Talc, $CaCO_3$
0.89-0.90		88			Talc, $CaCO_3$, TiO_2
0.90-0.91		96			Talc, $CaCO_3$, TiO_2. Glass fiber
0.91-0.92		87			Talc, $CaCO_3$, TiO_2. Glass fiber
0.92-0.93	PP+PE	91	7%	1.6%	Talc, CaC_3. TiO_2, Glass fiber
0.93-0.94		91			Talc, $CaCO_3$
0.94-0.95	PE	~100	10%	1.4%	Talc, $CaCO_3$
0.95-0.96		92			Talc, $CaCO_3$
0.96-0.97		51			Talc, $CaCO_3$
0.97-0.98	Filled PP	34	3%	6.1%	Talc, $CaCO_3$
0.98-0.99		32			Talc, $CaCO_3$
0.99-1.00		55			Talc, $CaCO_3$
1.00-1.05	PS+ABS	83	12%	5.3%	Talc, $CaCO_3$, Glass fiber
1.05-1.10		97			Talc, $CaCO_3$, Glass fiber
1.1-1.15	Filled resin, rubber	98	48%	12.9%	Talc, SiO_2 (amorf) (($CaCO_3$)), Glass fiber
1.15-1.2		96			SiO_2 (amorf), Talc, (($CaCO_3$)), Glass fiber
1.2-1.25		94			SiO_2 (amorf), Talc, Glass fiber
1.25-1.3		81			SiO_2 (amorf), Talc, Glass fiber
1.3-1.35		93			SiO_2 (amorf), Talc, Glass fiber
1.35-1.4		87			SiO_2 (amorf), Talc, Glass fiber

Table 5 represents the result of the "preparation of separation" analysis that allows determining borderlines between different types of polymers. With adequate density limits, the following polymer types can be well recovered: polypropylene (PP), polyethylene (PE), polystyrene and acrylonitrile-butadiene-styrene (PS+ABS), although the presence of mineral fillers may lead to fractions of varying purity. From Table 5 it is obvious that under 0.92 g/cm^3 quite pure PP can be recovered, because PE appears in the range of 0.92-0.97 g/cm^3, resulting in a mixed fraction with a density of 0.92-0.94 g/cm^3. The fractions of 0.97-1 g/cm^3 density contain mainly PP, but in filled form. Styrene containing polymers like PS and ABS can be recovered in the range of 1-1.1 g/cm^3. Above 1.1 g/cm^3 the composition is so heterogeneous and highly filled that its material recycling is challenging, and should rather be used for energy recovery. The main fillers found in the wastes were talc, calcium-carbonate, silica, titanium-dioxide as white pigment, and glass fibre as reinforcement.

On the basis of the spectroscopic analysis, the products containing the same main components were mixed, compounded, and test sheets were formed by hot pressing before the stage of characterisation of separated fractions. During characterisation Melt Flow Index (MFI) is used to determine the flow properties of polymer melts in order to determine their optimal processing conditions, which also influences their field of application. High melt flow rate corresponds to low molecular weight, therefore these polymers are processed mainly with injection moulding; low melt flow rate corresponds to high molecular weight, therefore these polymers are processed mainly with blow moulding or extrusion. Mechanical properties; tensile tests, three-point bending tests and impact tests were carried out to investigate the performance of the polymer wastes fostering to find the optimal product form. Mechanical properties indicate that with adequate separation better properties can be achieved even without using additives or upgrading (Figure 3).

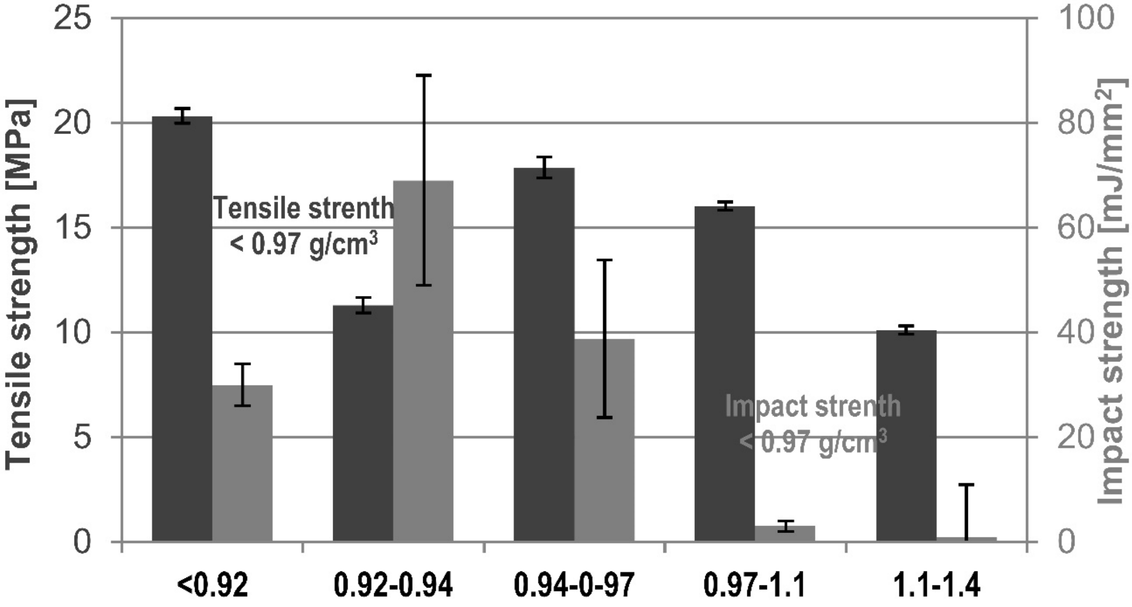

Figure 3 Mechanical properties of the density-separated waste plastics

Taking Scanning Electron Microscopy (SEM) images from density fractions of automotive waste, the morphology and homogeneity of the density fractions could be determined and used for predicting the expected mechanical properties. Better homogeneity predicts better mechanical properties.

As a general conclusion it can be stated, that the handling of polymer wastes largely determines the success of the analysis and recycling; with cautiously determined separation limits not only the polyolefinic, but also higher density polymers can be recovered successfully. Fraction with the highest purity is usually the lowest density one, which can be well applied as a base material for further developments.

3.3 Upgrading opportunities - Materials recycling

In the case of materials recycling without the degradation of the chemical structure of polymeric components, secondary plastics can made attractive for the industry only if they can fulfil their requirements at a reasonable price. Using upgrading with special additives (for example stabilizers, reinforcing fibres, flame retardants) and technologies, recycled plastics can be endowed by new valuable properties. Suggestions were elaborated for each density fractions.

Recycling of the PP fraction

The reprocessing of the purest polypropylene fraction <0.92 g/cm^3 (REC) is obvious and its properties more or less approach those of the virgin material depending on its degree of ageing, therefore in the industry they may be admixed to virgin material. If outstanding mechanical properties are necessary, glass fibre (GF) and polypropylene mat reinforcing additives can be successfully used although poor flammability properties are achieved. If the composite matrix and the reinforcing fibre were made of the same type of polymer (in this case polypropylene), they are so-called self-reinforced (SR) composites. The processing window for creating these self-reinforced composites is usually 15–20°C which means that the melting point of the matrix is lower than the melting point of the fibre; therefore the matrix material can melt and impregnate the non-melted fibres. By self-reinforcement (SR-REC) 5 times higher tensile strength, 2 times higher flexural strength and 4-times higher perforation energy were achieved [85]. Although the tensile and flexural strength of the recycled matrix could be more effectively increased using glass fabric reinforcement (GF-REC), the prepared self-reinforced composites are given preferences from environmental aspects considering that their density is much lower and, in contrast to glass fibre reinforced composites, they are easily recycled by simple reprocessing methods at the end of their life-cycle (Figure 4).

Improved properties can be ensured by changing the composite processing technology as well. Flammability and mechanical properties of composites produced by simple melt mixing and lamination were compared [15]. The composition of the samples was the same in both composites. Chopped glass fibre was used as reinforcing agent in recycled polypropylene waste separated from automotive shredder residue, and intumescent flame retardant system served for the reduction of flammability with the application of recycled polyurethane as a charring agent. In mixed composite the recycled polypropylene matrix with <0.92 g/cm^3 density, flame retardant additives, compatibilizer and reinforcing glass fibre was homogenised in the melt phase, but in layered structure the shell contains the flame retardant additive, and the core is reinforced by chopped glass fibre with compatibilizer (Figure 5).

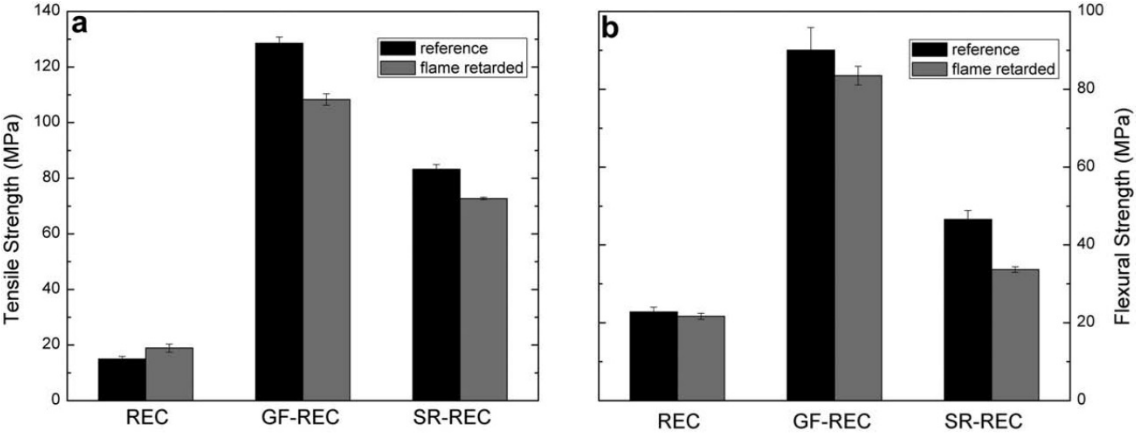

Figure 4 Mechanical properties of recycled PP composites without reinforcement (RC) and with glass (GF-REC) or self-reinforcement (SR-REC) [14]

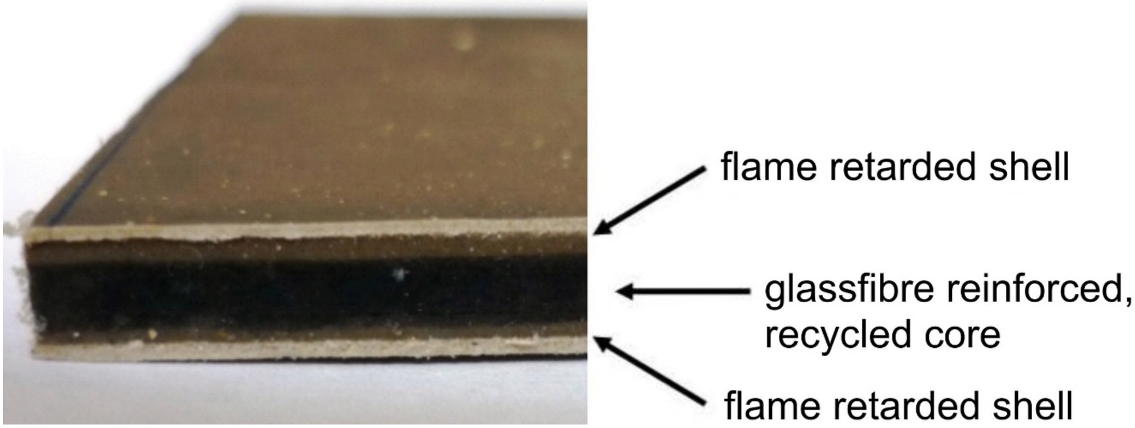

Figure 5 Structure of laminated composite containing recycled PP waste [15]

By changing the structure of the composite the deterioration of mechanical properties caused by flame retardant additives could be compensated by lamination (Figure 6). The mechanical properties of the flame retarded recycled layered composite reached the properties of the reference polypropylene, therefore the composites containing recycled materials are still acceptable for certain engineering applications.

Concerning the fire properties the heat release rate (HRR) results shown in Figure 7, it can be concluded that the flame retardant system significantly reduced the peak heat release rate (pHRR) of both mixed and layered composites compared to the matrix materials, which means that its igniter effect is decreased. However, comparing the different technologies applied for producing the composites, it was found that the application of layered structure delayed the time to pHRR and also the burning by approx. 200 s. Delay in time-to-ignition and pHRR ensures higher chance for escape from a burning building containing this material. Specimens containing recycled materials usually burnt longer, but with lower intensity (pHRR).

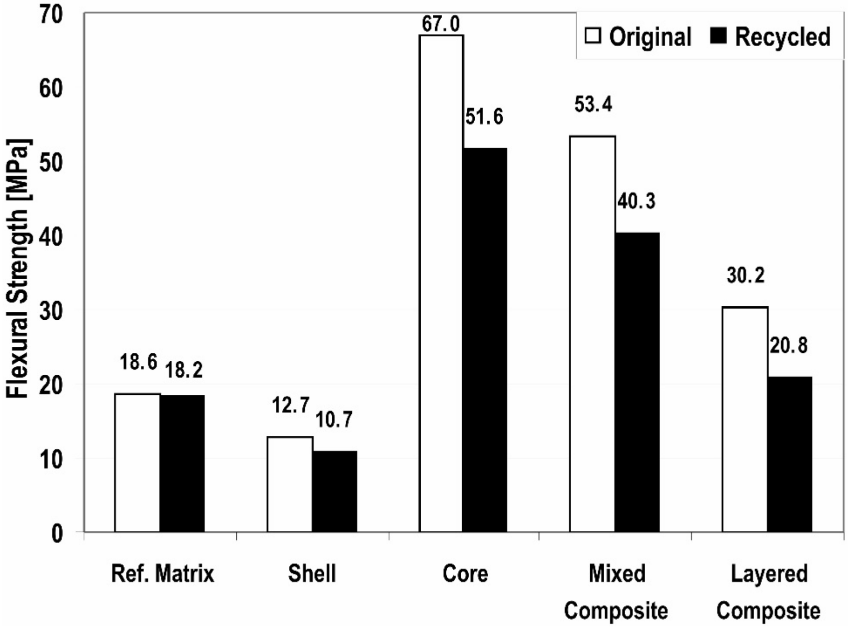

Figure 6 Flexural strength of original and recycled composites: In the letter case the properties of the melt mixed composite are compared with those of the layered composites, showing also the properties of the shell and of the core separately.

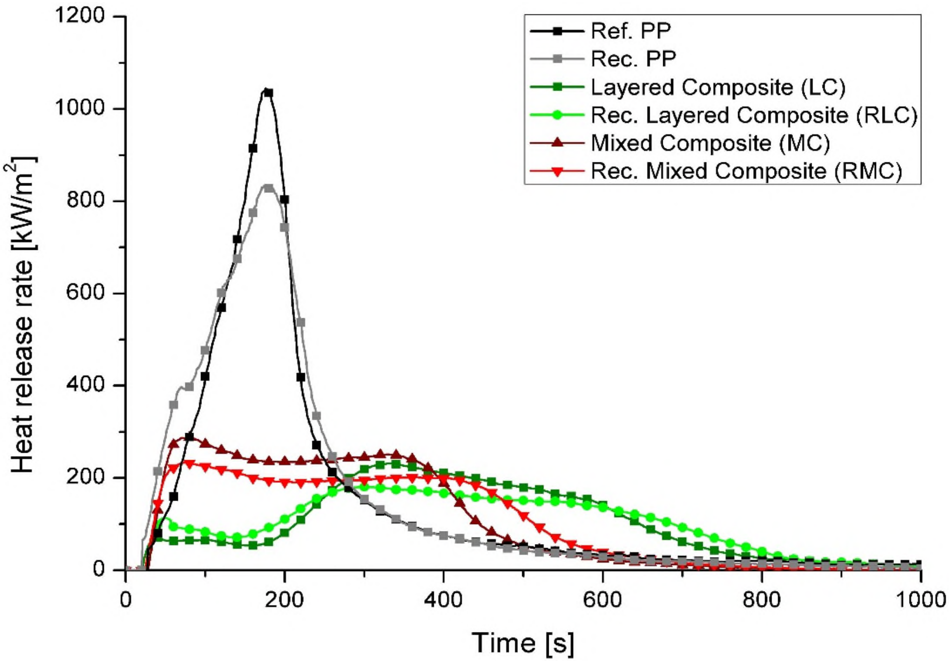

Figure 7 Heat release rate of virgin PP, recycled PP, layered composite (shown in Figure 5) with virgin and with recycled materials, and of a melt-mixed composite of identical overall composition made of virgin and of recycled PP material.

Recycling of the mixed polyolefin fraction

A car door opener (Figure 8) was made of the 0.92 – 0.94 g/cm^3 density fraction of the separated automotive shredder waste (containing approximately 80% PE and 20% PP) by injection moulding using the mould designed for the purposes of the W2Plastic project. The aim of this product development was to present a solution for the re-use of automotive waste in the automotive industry by meeting its high quality requirements even by secondary raw. To reach this goal 30% glass fibre was used to ameliorate the mechanical properties, in addition to 0.8% stabilizer used for re-stabilizing the waste polymer [70]. As reference materials ABS and PE were used. The mechanical properties of car door openers produced from reference materials and waste polymer were compared. Taking into account the application as car door opener, especially the bending modulus, the maximal bearable stress and deflection as a function of working temperature were interesting. Furthermore, fatigue tests were also made.

Figure 8 Picture of the car door opener made of recycled PP polymer [70]

Based on the results, it was concluded, that the addition of 20% PP taken from the 0.92 – 0.94 g/cm^3 density fraction of automotive waste was favourable in terms of the tested mechanical properties, which were in all cases definitely better than in case of pure PE and accepted as a raw materials for the same car door opener. Most properties of car door openers made from recycled polymer upgraded with glass fibres were quite close to those of ABS based products (this primary material is generally used for these purposes), in case of fatigue test the recycled polymer had even much better properties than ABS.

Two component injection moulded prototypes using all fractions

Dog-bone tensile specimens were prepared by an Engel ES 200H type two component injection moulding machine from all automotive polymer waste fractions applying the composition shown on Figure 9.

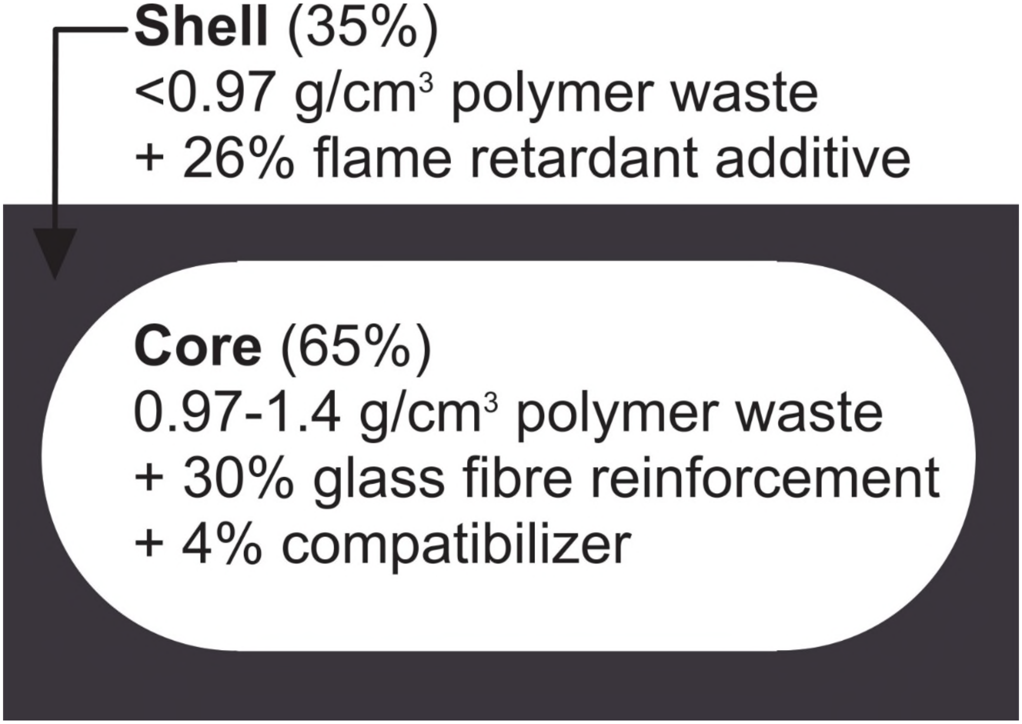

Figure 9 Structure and composition of two component injection moulded specimen made of all fractions of automotive shredder residue

During production, in the first step flame retarded PE + PP waste was injected, followed by the core material in the second step, therefore the core of higher density and viscosity pressed the previous shell material to the wall of the mould, thus ensuring the desired final shape.

The shell structure is made of recycled polyolefin material which has high resistance against potential dynamic load, and the added flame retardant is responsible for keeping the product non-flammable under atmospheric conditions (Figure 9). The core material contains glass fibre reinforcement. The orientation of the fibres corresponds to the visible flow lines formed during moulding. The presence of the compatibilizer is not significant due to the small amount compared to the behaviour of a homogeneous core, which is confirmed by the following mechanical testing.

The mechanical characteristics of the manufactured products were compared with those of the waste fractions used (mixed polyolefin <0.97 g/cm^3 containing PP, PP+PE and filled PP, 0.97-1.1 g/cm^3 PS+ABS, 1.1-1.4 g/cm^3 mixed fraction) before upgrading. Based on these the improvement in mechanical properties, when certain additives were applied, could be assessed.

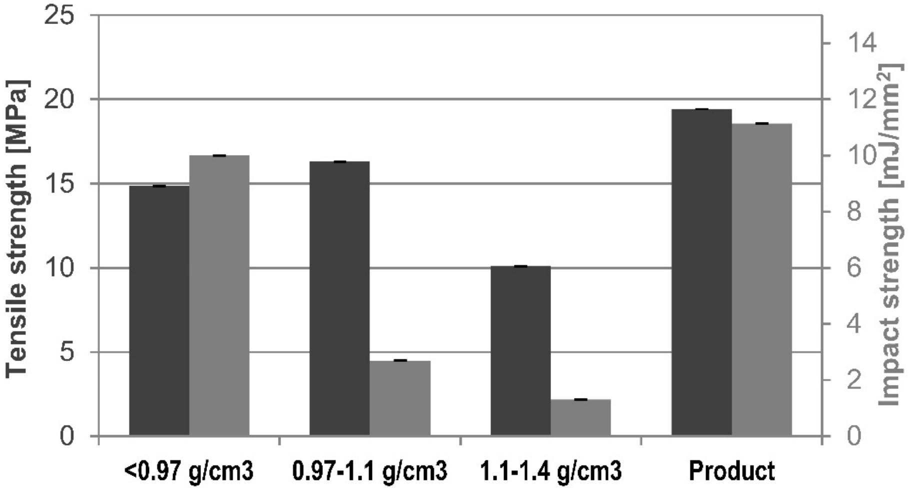

Figure 10 Tensile and impact strength of the automotive shedder fractions alone and of the core-shell structure made of them after upgrading by reinforcement and compatibilization, as shown in Figure 9

In Figure 10 the measured tensile strength and impact strength values are presented. In the case of waste fractions with higher density a significant decrease in tensile strength occurred. The best strength results (19.43 MPa) correspond to the manufactured two-component injection moulded specimens. The compatibilizer applied in the core material successfully improved the compatibility between the different polymer phases, the core became more homogeneous, and as a consequence, the different polymer types were able to better work together. The 30% glass fibre added could contribute to a further improvement in strength. Based on the evaluation of the tensile test results it can be concluded that the addition of the chosen additives to the secondary raw materials resulted in quality improvement.

The impact strength results (Figure 10) are not surprising. It is well known that PE and PP are tough materials with prominent energy absorption capacity, which has been also confirmed by our experimental results. It can be observed that the fractions with higher density showed quite rigid behaviour. In the case of the two-component injection moulded products the measured 11.14 mJ/ mm^2 impact strength is prominent. The measured value can be ascribed to the shell structure, which is composed of polyolefins and adds up to 35% of the product. Although the core material consists also of polymers with higher density, which are more rigid and which constitute the more significant part of the product, the developed core-shell structure resists remarkably well also the dynamic impacts. Although the specimens also contain 30% glass fibre in the core material, which was expected to further decrease the energy absorption capacity of the material, the applied compatibilizer, which noticeably promoted the cooperation between the components of the core material, could counterbalance the expected decrease in the energy absorption capacity.

It can be stated that by skin-core injection moulding a product could be successfully manufactured, which is resistant even to dynamic stresses. It can be established that upgrading was successfully accomplished also in terms of this indicator, as a 4-fold improvement in impact strength could be achieved when compared to that of the polymer types from the density fraction between 0.97-1.4 g/cm^3 used in high amount in the recycled product.

It is important to highlight that our aim was the reprocessing of the entire amount of the recovered plastic waste. Based on the mechanical test results, the objective is feasible. In the case of vehicles the resistance against flame is adequate when the product to be manufactured cannot be ignited at atmospheric conditions or it's burning or glow is not long-term.

3.4 Upgrading opportunities - pyrolysis

During the LP-FTIR investigation of highly filled mixed plastic waste (density range $1.1 < \rho < 1.4$ g/cm^3), with a filler content of 12.9%, gases as methane, ethane and ethylene evolved and charring of the surface was observed (irradiation time: 1 min, laser power: 7.5W, 1 min). During the Scanning Electron Microscopic (SEM) analysis of the charred solid phase residue fibre-like nanoscopic and microscopic objects were observed (Figure 11). After a literature overview, it became obvious, that under these conditions carbon nanotube formation is probable; polypropylene as carbon source, mineral clay as integrated catalyst, and the CO_2 laser ensures fast heating [5, 53].

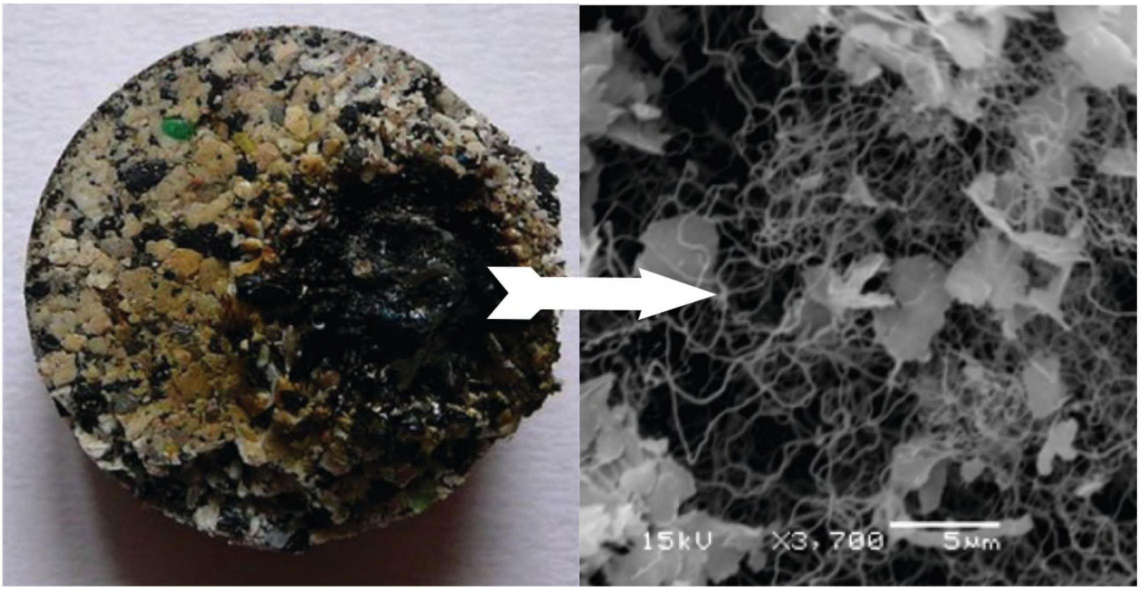

Figure 11 Optical and scanning electronic micrographs of the heaviest fraction of automotive shredder wastes after laser pyrolysis

The identification of these objects was performed by Scanning Electron Microscopy (SEM) and Raman spectrometry, their atomic composition was investigated by Energy Dispersive Spectrometry (EDS) and their wall structure and thickness was determined by Transmission Electron Microscopy (TEM).

Based on SEM investigation of the pyrolysed waste fraction of 1.1-1.4 g/cm^3 density it became obvious that these objects are present in a wide diameter range (100 nm - 3 μm). Also thin (100 nm) and straight and thick (3 μm) but disordered structures were observed depending on their position on the sample, which presumes different circumstances. With EDS it was verified, that the main element present in the residue is carbon with a negligible amount of Si.

Raman spectrometry was used to identify the synthesized carbon objects. Based on the comparison of the spectrum of the sample to the commercially available Nanocyl (Nanocyl™ NC 7000) it was found that the sample contains relatively strong and wide D-band compared to the G-band reflecting structural defects and the presence of amorphous structure in the walls of the synthesized CNF/CNTs.

The SEM image demonstrates the dense structure of the fibre-like objects formed by the pyrolysis of waste polypropylene sample. In order to get information about the wall structures, TEM analysis was performed. The sample shown a highly disordered thick walls can be identified as carbon nanofibre (CNF) with turbostratic wall structure [86].

After pyrolysing highly filled polymer wastes under specific circumstances, not only gases but also carbon nanofibres (CNFs) can be produced, that makes the plastic wastes much more valuable.

4 Conclusion

In this paper we tried to outline very briefly the two basic philosophies used in recycling plastic waste: materials recycling and feedstock recycling with partial (controlled) degradation in-between the two extremes. Materials recycling is the best method in terms of environmental effects, it brings the most saving in greenhouse gas emission, but it is limited to relatively pure wastes, which assumes careful selective waste collection. This is feasible with some types of packaging waste. Reprocessing of mixed plastic waste taken e.g. from municipal solid waste or from the thermoplastic fraction of B&C (demolition) waste, E+E waste or car shredder residue requires much more ingenuity in terms of compatbilization, modified processing technologies, composite structures etc. Partial breakdown of linear polymers by chemical means (PET) or by controlled themo-oxidative or biological degradation is limited to certain types of polymers, but is very useful in these cases. Thermoset (crosslinked) polymers can be reprocessed by mechanical breakdown, by chemical breakdown (peptization, de-vulcanization or solvolysis) or by pyrolysis (feedstock recycling). Complete breakdown to chemical subunits (pyrolytic breakdown under various conditions using catalysts to gases, liquids and charred residue) is in principle available to almost all kinds of polymer wastes – the chemicals obtained can be used for new synthesis or as fuels. Solid polymer waste can be directly incinerated, although the slag formation may be high and the calorific value may be limited. Burning the gaseous and liquid pyrolytic products is less problematic. All these options should be taken into account when designing a new product. The number of components should be reduced and the design should alleviate dismantling and separation of components of different chemical composition. Hazardous components should be avoided form the beginning.

These principles and some recycling opportunities are demonstrated in the second part of the paper based on original research results. As a consequence on automotive shredder waste residues, it is clear that with the separation of polymer types, with adequate selection of additives and composite processing technologies allow not only recycling, but in several cases the upgrading of waste plastics. Glass fibre and self-reinforcement, stabilizer, and flame retardant additives were used successfully to produce composites and products containing recycled materials that are still acceptable for certain engineering applications. After pyrolysing highly filled polymer wastes under specific circumstances, not only gases as methane, ethane and ethylene were evolved, but investigating the charred surface carbon nanofibres (CNFs) with turbostratic wall structure were observed, that makes the plastic waste much more valuable.

These principles are demonstrated in the second part of the paper on automotive shredder waste residues. Fractionation, separate and combined processing, the use of additive and composite processing technologies allow not only recycling but in several cases upgrading of the waste material. Even in the case of feedstock recycling interesting new by-products may be obtained: in this case the formation of carbon nanofibers was observed.

All these technologies should be rigorously analysed and compared using LCA (life cycle assessment) to avoid subjective decisions and to see not only the qualitative, but also the quantitative aspects. We hope that this paper may be of use for design engineers to take into account the recycling options already in the planning phase.

Acknowledgments

This paper is partly based on the following tutorial [9].

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International Journal of *Design Sciences and Technology*

Design Sciences, Advanced Technologies and Design Innovations

Towards a better, stronger and sustainable built environment

Aims and scope

Today’s design strongly seeks ways to change itself into a more competitive and innovative discipline taking advantage of the emerging advanced technologies as well as evolution of design research disciplines with their profound effects on emerging design theories, methods and techniques. A number of reform programmes have been initiated by national governments, research institutes, universities and design practices. Although the objectives of different reform programmes show many more differences than commonalities, they all agree that the adoption of advanced information, communication and knowledge technologies is a key enabler for achieving the long-term objectives of these programmes and thus providing the basis for a better, stronger and sustainable future for all design disciplines. The term sustainability - in its environmental usage - refers to the conservation of the natural environment and resources for future generations. The application of sustainability refers to approaches such as Green Design, Sustainable Architecture etc. The concept of sustainability in design has evolved over many years. In the early years, the focus was mainly on how to deal with the issue of increasingly scarce resources and on how to reduce the design impact on the natural environment. It is now recognized that “sustainable” or “green” approaches should take into account the so-called triple bottom line of economic viability, social responsibility and environmental impact. In other words: the sustainable solutions need to be socially equitable, economically viable and environmentally sound.

IJDST promotes the advancement of information and communication technology and effective application of advanced technologies for all design disciplines related to the built environment including but not limited to architecture, building design, civil engineering, urban planning and industrial design. Based on these objectives the journal challenges design researchers and design professionals from all over the world to submit papers on how the application of advanced technologies (theories, methods, experiments and techniques) can address the long-term ambitions of the design disciplines in order to enhance its competitive qualities and to provide solutions for the increasing demand from society for more sustainable design products. In addition, IJDST challenges authors to submit research papers on the subject of green design. In this context “green design” is regarded as the application of sustainability in design by means of the advanced technologies (theories, methods, experiments and techniques), which focuses on the research, education and practice of design which is capable of using resources efficiently and effectively. The main objective of this approach is to develop new products and services for corporations and their clients in order to reduce their energy consumption.

The main goal of the *International Journal of Design Sciences and Technology* (IJDST) is to disseminate design knowledge. The design of new products drives to solve problems that their solutions are still partial and their tools and methods are rudimentary. Design is applied in extremely various fields and implies numerous agents during the entire process of elaboration and realisation. The International Journal of Design Sciences and Technology is a multidisciplinary forum dealing with all facets and fields of design. It endeavours to provide a framework with which to support debates on different social, economic, political, historical, pedagogical, philosophical, scientific and technological issues surrounding design and their implications for both professional and educational design environments. The focus is on both general as well as specific design issues, at the level of design ideas, experiments and applications. Besides examining the concepts and the questions raised by academic and professional communities, IJDST also addresses the concerns and approaches of different academic, industrial and professional design disciplines. IJDST seeks to follow the growth of the universe of design theories, methods and techniques in order to observe, to interpret and to contribute to design's dynamic and expanding sciences and technology. IJDST will examine design in its broadest context. Papers are expected to clearly address design research, applications and methods. Conclusions need to be sufficiently supported by both evidence from existing research (reference to existing design research knowledge) as well as strong case-studies from any design discipline. A paper must contain at least one chapter on research questions, methodology of research and methods of analysis (the minimum length is 1500 words). The concluding chapter (the minimum length is 1000 words) will summarise the paper and its results. The concluding chapter also examines and discuss applications, advantage, shortcomings and implications of the investigation for both professional and educational design communities as well as for the people and the society. Also authors are also encouraged to include in this chapter a discussion of the possible future research that is required or is possible in order to enhance the research findings.

The papers considered for IJDST cover a wide range of research areas including but not limited to the following topics: Design research, design science, design thinking, design knowledge, design history, design taxonomy, design technology, design praxeology, design modelling, design metrology, design axiology, design philosophy, design epistemology, design pedagogy, design management, design policy, design politics, design sociology, design economics, design aesthetics, design semantics, design decision-making, design decisions, design evaluation, design sustainability, design logic, design ontology, design logistics, design syntaxis, design ethics, design objective, design responsibility, design environment, design awareness, design informatics, design organization, design communication, design intelligence, design evaluation, design education, design theories, design techniques, design methods, design operations, design processes, design products, design users, design participation, design innovation, design inspired by nature, design case studies, design experiments, etc.

The *International Journal of Design Sciences and Technology* is devoted to further exploration of all themes and issues that are directly or indirectly relevant to the exploration, introduction, discussion of design sciences and technology, cross referencing domains and any other themes emerging in the future.

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[3] **Buxton, W** (1997) Living in Augmented Reality: Ubiquitous Media and Reflective Environments. In: Finne K, Sellen A and Wilber S eds, Video Mediated Communication, Erlbaum, Hillsdale NJ, 363-384

[4] **Dixon, NM** (2000) Common Knowledge: How companies thrive by sharing what they know, Harvard Business School Press, Boston, MA

[5] **Djenidi H**, **Ramdane-Cherif A**, **Tadj C** and **Levy N** (2004). Generic Pipelined Multi-Agents Architecture for Multimedia Multimodal Software Environment, Journal of Object Technology, 3:8, 147-169

[6] **Gorard, S** and **Selwynn, N** (1999) Switching on to the learning society? Questioning the role of technology in widening participation in lifelong learning, Journal of Education Policy, 14:5, 523-534

[7] **World Bank** (2002) Social assessment as a method for social analysis, World Bank Group [www.worldbank.org/gender/resources/assessment/samethod.htm]

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