Pyrolysis for recycling waste composites

M. BLAZSÓ, Hungarian Academy of Sciences, Hungary

Abstract: Pyrolysis is a suitable process for recycling polymer composites because the thermal decomposition products of the polymer matrix evaporate, and thus the reinforcement materials can be recovered and reused. The products of pyrolysis carried out at an appropriate temperature are monomers and other valuable chemicals. This chapter describes the pyrolysis reactions and products of frequently used thermoplastics and thermosets in polymer composites. Published results on pyrolysis of various polymer composites are discussed in order to understand the requirements of successful plastic composite recycling by pyrolysis. The environmental concern related to pyrolysis of flame retardants containing polymer composites is also touched upon and some methods are referred to for decreasing or eliminating toxic and harmful compounds from the pyrolysis products of halogenated flame retardants.

Key words: plastics composites, recycling of composite reinforcement, pyrolysis of polymer matrix.

5.1 Introduction

Thermal methods are successfully applied for waste elimination in general. Among them, combustion has been the most commonly used traditional method to reduce the quantity of discarded objects and garbage. However, in the twenty-first century, uncontrolled combustion is strictly banned worldwide because of environmental pollution from the harmful combustion products and carbon dioxide emissions. In up-to-date incineration plants solid wastes are effectively converted to energy and potential harmful products are trapped in various cleaning units and filters. Nevertheless, most of the value of recyclable materials is lost under combustion in incinerators, and an important part of the polymers used in composites is built not only from hydrocarbons but also from amides and nitriles emitting huge amounts of nitrogen oxides (NOx) in addition to carbon dioxide. Therefore pyrolysis is a more adequate thermal treatment technology for waste polymer matrix composites in which the material is heated in a low oxygen environment.

Pyrolysis is a thermally initiated chemical process that generally decomposes the organic molecules to smaller ones in an inert atmosphere. The
term ‘pyrolysis’ is often misunderstood as meaning a high temperature reaction resulting only in gases and char, but it also means thermolysis of organic macromolecules in the temperature range from 250 to 800°C resulting in gaseous, liquid and solid products. Above 800°C carbonization of the organic material occurs, which is applied as a utilization technology mostly for biomass waste.

Composites with polymer matrix material are produced for various applications and thus a range of different resins can be found in waste composites. The reinforcement part is typically inorganic material, fibres or ground substance. In special cases, polymer is used as the strengthener as well such as Kevlar. The pyrolysis process is a particularly good thermal recycling method for waste polymer composites because the matrix resin is decomposed to valuable feedstock or fine chemicals which evaporate, while the reinforcement is obtained as the solid residue. The preservation of the original quality of the latter is a crucial point of the pyrolytic recycling technology of polymer matrix composites, the main purpose of which is often the recycling of the valuable fibre or powder strengthener.

The thermal decomposition of the polymer matrix of the composite should not differ from that of the polymer alone because matrix and reinforcement materials are separate and distinct on a macroscopic level within the composite. Obviously heat transport may be altered by an inorganic material of quite different heat conductivity from that of the polymer, resulting in differences in the heating rate and temperature gradient in the pyrolyser.

Pyrolysis of the organic macromolecules is initiated by a primary intramolecular endothermic chemical reaction of the following types:

1. rearrangement of chemical bonds followed by elimination of small molecules, and/or separation of the macromolecule in two parts;
2. scission of chemical bonds followed by the stabilization of the unstable fragments.

The temperature necessary for the initiation reaction depends on the activation energy of the chemical change (reactions of type 1 occur at around 300°C, and of type 2 at above 500°C).

Initiation of the thermal decomposition may occur due to defect points of the polymer (structural error, oxidized moieties, etc.) that can reduce thermal stability of the polymer. In polymers of flexible macromolecular chain (thermoplastics) the unstable species formed by initiation are generally macroradicals which are either depolymerized in a free radical chain reaction, producing monomers and oligomers, or transferred to another macromolecule or to another part of the same macromolecule. In the case of radical transfer the polymeric radical is divided into two parts: a smaller
molecule and a smaller radical, and at the end of the radical chain reaction a series of product of broad volatility range is obtained.

In network or cross-linked polymers (thermosets) both types of pyrolysis reaction require higher temperatures because of limited flexibility of the macromolecular segments. Catalysts may facilitate thermal decomposition of polymers by conducting the pyrolysis process through reactions requiring less energy. Thus catalytic pyrolysis generally lowers the optimal temperature of polymer decomposition, and at the same time the products could be different from those obtained without catalyst. Technically catalytic pyrolysis is carried out either in one step or in a coupled arrangement of a pyrolyser and a catalytic converter. Although thermal catalysis proved to be a successful option for utilizing waste polyethylene, this method is not often used for more complicated wastes such as composites.

5.2 Pyrolysis reactions and products of thermoplastics

Polypropylene (PP) and polyamides (PA66, PA6, PA12, PA46) are the most used matrices for thermoplastic composites. Polyesters (polyethylene terephthalate (PET), polybutylene terephthalate (PBT), polyphenylene oxide (PPO)), polycarbonate (PC) and thermoplastic polyurethane (TPU) are also used as matrix material. These polymers liquefy on heating and freeze to a solid state when cooled; they can be remelted. The reinforcement is introduced under melting of the matrix material. Heat-resistant thermoplastics, such as polyetheretherketone (PEEK), polyether sulphone (PES), polyimide (PI), polyetherimide (PEI) and polyphenylene sulphide (PPS) furnish advanced properties to their composites.

The basic thermal decomposition records of thermoplastic polymers applied frequently in polymer composites are shown in Table 5.1. The data have been collected from published works in which thermogravimetric measurements were performed in an inert atmosphere and at a heating rate of 10°C/min.

5.2.1 Polypropylene

PP starts to decompose at around 400°C, when heated slowly (at a rate of 10°C/min) in a thermogravimeter. The volatile formation is fastest at 470°C and the total mass of the polymer is volatilized by 500°C. This means that no solid residue is left after pyrolysis of PP, hence pyrolysis is a promising method for recycling either fibreglass or mineral reinforced PP composites. The surface of glass fibres or other strengtheners is cleaned by the pyrolysis process, which occurs at moderate temperature and does not seriously
influence the original quality of the fibre. In this way pyrolysis may compete with other fibreglass recycling methods (Cunliffe et al., 2003). We may expect that the chemical process of PP thermal decomposition is not altered in the presence of the strengthener if it is sufficiently inert in the pyrolysis processes. Glass is a generally used vessel material in moderate temperature thermal studies of organic substances. Carbon has been observed to have a significant influence on PP decomposition only when the studied carbon black contained non-negligible amounts of functional groups and organic compounds (Jakab and Omastová, 2005). The volatilized pyrolysis products of PP are propylene oligomers produced through a series of free radical chain reactions. The pyrolysis conditions (heating rate, pyrolysis temperature, residence time of the evolved products) influence the product distribution, which is generally composed of some light hydrocarbon gases, a major part of gasoline volatility liquids (including propylene trimer, 2,4-dimethylheptene; tetramer, 2,4,6-trimethyldecene; and pentamer, 2,4,6,8-tetramethyltridecene) and an important amount of higher oligomers of lower volatility. From the point of view of recycling of the whole composite the formula with PP matrix and strong PP fibre strengthener is exceptionally beneficial, resulting in the same pyrolysis products from matrix and strengtheners.

Catalytic thermal decomposition of PP may lead to more valuable products of narrower volatility range and of higher storage stability (Ali et al., 2002); however, the separation of the catalyst from the recycled

<table>
<thead>
<tr>
<th>Thermoplast</th>
<th>Decomposition range (°C)</th>
<th>Mass loss rate (DTG) max. (°C)</th>
<th>Residual mass (wt %)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>400–500</td>
<td>470</td>
<td>0</td>
<td>Czégény et al. (2002)</td>
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<tr>
<td>PA6</td>
<td>370–490</td>
<td>461</td>
<td>0</td>
<td>Czégény et al. (2002)</td>
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<tr>
<td>PA66</td>
<td>390–490</td>
<td>454</td>
<td>0</td>
<td>Bozi et al. (2008)</td>
</tr>
<tr>
<td>PA12</td>
<td>390–500</td>
<td>465</td>
<td>1</td>
<td>Czégény et al. (2002)</td>
</tr>
<tr>
<td>PET</td>
<td>360–490</td>
<td>429</td>
<td>11</td>
<td>Jakab et al. (2005)</td>
</tr>
<tr>
<td>TPU</td>
<td>250–400</td>
<td>330</td>
<td>5</td>
<td>Font et al. (2001)</td>
</tr>
<tr>
<td>PPO</td>
<td>550</td>
<td>54</td>
<td>Montaudo et al. (1994a)</td>
<td></td>
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<tr>
<td>PES</td>
<td>570</td>
<td>48</td>
<td>Montaudo et al. (1994a)</td>
<td></td>
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<tr>
<td>PEEK</td>
<td>550–640</td>
<td>590</td>
<td>55</td>
<td>Day et al. (1990)</td>
</tr>
<tr>
<td>PPS</td>
<td>450–700</td>
<td>600</td>
<td>40</td>
<td>Montaudo et al. (1994b)</td>
</tr>
<tr>
<td>PC</td>
<td>420–600</td>
<td>520</td>
<td>22</td>
<td>Bozi et al. (2007)</td>
</tr>
<tr>
<td>Kevlar</td>
<td>520–800</td>
<td>600</td>
<td>34</td>
<td>Czégény et al. (2002)</td>
</tr>
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</table>
strengthened or a tar-like deposit on the surfaces often observed in catalytic processes of hydrocarbons should be taken into account. The use of AlCl$_3$ as catalyst mixed with the polymer in a batch reactor or in a fluidized bed reduces the process temperature dramatically (Kaminsky and Nuñez Zorriqueta, 2007). The use of a small amount of AlCl$_3$ (0.1%) produces products at 400°C similar to those obtained at 500°C in a non-catalytic process from PP, but it is possible to pyrolyse PP at 300°C when the amount of catalyst is higher. The increase of the amounts of catalyst then leads to an increase of light oil fraction (<C13) and gas fraction amounts.

5.2.2 Polyamides

The generally observed thermal decomposition reaction of aliphatic polyamide (PA) is the scission of amide groups through cis elimination (Blazsó, 2006), resulting in smaller molecules composed of the aliphatic segment of the polyamide (of 4, 6 and 12 carbon atoms in PA46, PA66 and PA12, respectively) terminated by vinyl, amino or nitrile groups. Exceptionally, from PA6 nearly exclusively its cyclic monomer, ε-caprolactame, is formed by pyrolysis through rearrangement of two neighbouring amide groups along the macromolecular chain. From other aliphatic polyamides, cyclic diamides and lower volatility compounds involving amide groups are also formed; thus the various nitrogen-containing pyrolysis products are distributed over a rather wide volatility range. In this way it is not easy to find utilization of PA pyrolysis products. A promising perspective is that of the catalytic modification of pyrolysis products: for instance Bozi et al. (2008) demonstrated that protonic Y zeolite denitrogenates the pyrolysis oil components of PA66 and transforms the hydrocarbon part of their molecules into aromatic compounds.

In aromatic polyamide macromolecular chain (aramide) the amide linkages are attached directly to two aromatic rings, either at 1,4 (Kevlar) or 1,3 positions (Nomex). Decomposition of aramide occurs simultaneously with melting at above 500°C, thus it could not be used as a polymer matrix in composites. But as it is a fibre-forming polymer of excellent high tensile strength, it is often used as reinforcement. Aramide’s value is closely related also to high thermal stability and fire resistance: it can easily survive high temperatures without damage for short periods of time. However, aramide fibre may lose its original exceptional quality under extended heat treatment.

5.2.3 Terephthalic polyesters

Polyester thermal decomposition is assisted by a six atom rearrangement of the carboxylic ester linkage and the carbon atoms of the alcohol that
leads to pyrolysis products with carboxyl and vinyl group. The vapour of terephthalic acid is condensed as a solid material that should be taken into consideration in pyrolysis technology of plastic wastes containing terephthalic polyesters. At above 300°C carboxylic acids are generally decarboxylated evolving carbon dioxide. Consequently the main component of the gaseous pyrolysis products of polyethylene terephthalate (PET) between 380 and 450°C is carbon dioxide, and the compounds of the pyrolysis liquid are terephthalic and benzoic acid vinyl esters. A non-negligible amount of char (about 10 wt%) is also formed.

The thermal decomposition reactions in polybutylene terephthalate (PBT) are similar to those in PET, but PBT pyrolysis takes place at a lower temperature (Kelsey et al., 2005). Moreover, less benzoic acid ester and more acidic compounds are obtained because of the easy cleavage of ester groups producing butadiene. The consequence of butadiene evolution should be that the pyrolysis residue of PBT is negligible, because phenylene fragments of phthalic acid decarboxylation can be stabilized by the hydrogen atoms from the butylene moieties, resulting in volatile compounds (benzene and biphenyl), instead of forming a solid char. In this way from the point of view of strengthener recycling by pyrolysis, PBT is a more suitable matrix in polymer composites than PET.

5.2.4 Polycarbonate

In polycarbonate the carbonate groups are attacked first by pyrolysis. Generally bisphenol A moieties are joined by carbonate in the polymer chain and the oxygen atoms are firmly bonded to the phenol ring. The thermal scission occurs at the carbonyl group, and accordingly, the main volatile products of polycarbonate are carbon oxides and bisphenol A at around 500°C. At higher temperatures phenol and isopropenylphenol are also formed as the dimethylmethylidene segment is cut off the aromatic ring by the scission of the bond between an aromatic and an aliphatic carbon atom. Polycarbonate pyrolysis residue is roughly 20 wt%; the char formation is the result of a lack of enough hydrogen atoms in this aromatic polymer, preventing the coupling of the aromatic radicals during pyrolysis.

5.2.5 Polyphenylether, polyethersulphone, polyetheretherketone and polyphenylenesulphide

Experimental observations proved that the main thermal decomposition product of aromatic polyethers is phenol, while ketone and sulphone chain segments eliminate carbon monoxide and sulphur dioxide, respectively (Montaudo et al., 1994a; Perng et al., 1999; Samperi et al., 2007). Some benzophenone and bis(phenoxy)benzophenone also evolves from PEEK,
indicating that the carbonyl group is eliminated only partially (Day et al., 1990). PPS undergoes cyclization, branching and cross-linking through the formation of aromatic thiols when heated to temperatures exceeding 300°C (Halasa, 1999). Above 600°C sulphur is extruded from the carbonaceous residue of PPS (Montaudo et al., 1994b). The solid residue of pyrolysis is a rather important part of these aromatic polymers because hydrogen abstraction by the small thermal fragment radicals results in a carbonized network structure of low H/C atomic ratio.

5.2.6 Thermoplastic polyurethane

Lattimer et al. (1998) observed that the thermal decomposition of polyurethane composed of aliphatic polyester soft segments starts first with dissociation of the urethane linkage to form products with isocyanato and hydroxyl end groups. The ester chain segments produce cyclic oligomers. In polyether-based urethane similar decomposition of urethane linkages to isocyanate and alcohol was a primary degradation pathway, taking place about 250°C (Lattimer and Williams, 2002). For both polymers, intramolecular exchange to produce cyclic, low molecular weight urethane-containing oligomers was observed. The recovery of the diisocyanate from polyurethane by pyrolysis is strongly influenced by the pyrolysis conditions. In analytical pyrolysers of fast heating rate and short residence time, diisocyanate has been found to be a major pyrolysis product of various polyurethanes by Ohtani et al. (1987), while this reactive product may disappear from the pyrollysate because of the secondary reactions in a larger-scale reactor heated at a lower rate. Polyurethane studied by Font et al. (2001) decomposed in a thermogravimeter in the range 250–400°C, with maximal weight loss rate at 330°C leaving no more than 5 wt% residues. A varnish based on the same TPU decomposed similarly up to 450°C at which temperature a second step of decomposition was observed. The complex pyrolysis process of polyurethane foam was also reported by Dick et al. (2001). The thermogravimetric mass loss curve of the foam studied shows more than one step of fast volatilization in the temperature range from 250 to 550°C and no residue is left above 550°C.

5.2.7 Polyimide and polyetherimide

These polymers are synthesized in the presence of strengtheners in composites because they do not melt as thermoplasts but should not be cured as thermosets. The cleavage of imide ring in PI occurs at 500°C and the rate of pyrolysis is the fastest around 580°C (Hatori et al., 1996). Carbonization is a slow process losing hydrogen atoms first then nitrogen as well, continuing over 1200°C with 52 wt% residue left. Aromatic
hydroxyl, amino and nitrile compounds are the most important volatile products of PI pyrolysis.

Owing to the lower stability of the polyether segment in PEI this polymer starts to decompose at a lower temperature than polyimide and the fastest rate is also lower (Guo et al., 2007). At 800 °C 50 wt% residue was observed but the carbonization had not terminated.

5.3 Pyrolysis reactions and products of thermosets

Polyesters, vinyl esters, phenolic, epoxy, melamine and silicon resins are the standard matrix materials of thermoset composites. These composites are produced by curing the prepolymer mixed with the reinforcement because the thermosetting polymers do not melt after the network structure has been developed. The thermal decomposition of a macromolecular network generally occurs at a higher temperature than that of a chain polymer of similar composition for at least two major reasons. The movement of the segments within a three-dimensional network is restricted, so decomposition reactions going through bonding rearrangement of neighbouring parts of the macromolecule cannot take place as easily as in a chain polymer. In other cases when the thermal decomposition takes place by radical scission, a much faster initiation reaction is required in a network for the effective formation of fragment molecules by radical chain reaction than in a linear polymer chain because of the high probability of termination of the radical decomposition process by recombination of the radicals that are not able to escape from the cage of the network structure from which they originated.

5.3.1 Unsaturated polyester and vinyl ester resins

Thermoset polyesters applied in composites are made of the unsaturated-type polyester macromolecules that are capable of being cured. Curing occurs through coupling pairs of reactive carbon–carbon double bonds with the help of a hardener (i.e. a reactive monomer, such as styrene). Catalyst and accelerator are usually added to accelerate the curing process. The cross-link density of the three-dimensional network formed by curing is determined by the frequency of the unsaturated groups in the polyester macromolecular chain. Ortho- and isophthalic acids are predominantly the dicarboxylic acid constituent of thermoset polyesters, with butane- and butenediol alcoholic components. In vinyl esters the reactive groups are at the ends of the polyester macromolecular chain, thus fewer cross-links are formed by curing.

Typical polyester thermosets of composites have been subjected to pyrolysis at 600 °C by Evans et al. (2000) and the volatile products were identified
by pyrolysis-GC/MS (gas chromatography/mass spectroscopy). Most chemical compounds could be related directly to the diacid and diol building units of the polyester and to the styrene cross-links.

5.3.2 Epoxy resin

In the macromolecule of epoxy resins the ether bonding between aromatic and aliphatic carbons is cleaved at the earliest stage of thermal decomposition, producing volatile compounds between 300 and 400°C and releasing bisphenol A, irrespective of the nature of the hardener. At above 600°C the bisphenol segment is also detached at the isopropylidene group, resulting in phenol and methyl-, ethyl- and isopropenylphenol pyrolysis products. Epoxy resins do not leave noteworthy solid residues following pyrolysis. In composites constructed for application in electric and electronic devices epoxy resins are flame retarded partly replacing bisphenol A by tetrabromobisphenol A. Among the pyrolysis products of such composites are small amounts of bromo-, dibromo-, tribromo- and tetrabromobisphenol A; moreover bromo- and dibromophenols are present (Blazsó, 2006).

5.3.3 Phenolic resin

Methylene groups join phenolic rings similarly along the polymer chain and at the cross-links in the cured network of phenolic resins. During thermal decomposition radical scission occurs at the methylene bridges and the stabilization of the radicals proceeds through hydrogen abstraction. Relatively small amounts of volatile compounds can be formed from this resin of low H/C atomic ratio; accordingly the solid residue of pyrolysis is as large as 30–50 wt% (Horikawa et al., 2003). Phenol and cresol isomers are the main products of pyrolysis evolved between 450 and 620°C (Blazsó, 2006). From a linear phenol–formaldehyde chain polymer (Novolak) dimeric products of thermal decomposition are also formed, namely isomers of methylenebis(methylphenol) and their methyl and dimethyl derivatives (Blazsó and Tóth, 1991; Sobera and Hetper, 2003).

5.4 Pyrolyser reactors for polymer recycling

Thermal decomposition reactions may be carried out in different types of reactor in an inert atmosphere. The reactor chosen should conform to the special requirements of polymer composite recycling, as pyrolysis conditions are limited by the type of pyrolyser. Pyrolyser reactor types utilized worldwide in waste plastics recycling systems are comprehensively described in an overview by Scheirs (2006).
5.4.1 Fixed bed reactor

Plastic waste is first converted to the molten phase in the reaction vessel purged continuously with an inert gas, then heated slowly to the pyrolysis temperature. Soaking is prolonged after the final temperature is reached until no more pyrolysis vapours are evolved. The molten plastic may be stirred to prevent hot-spots. It is essential to remove the carbonaceous char and other solid residue from the pyrolysis chamber to prevent the formation of a thermal insulator layer on the walls that would lower the heat transfer to the plastic in the next batch.

5.4.2 Rotary kiln

The waste plastics introduced in the rotary kiln furnace are conveyed through the reactor by the rotation and incline of the reaction chamber. The rotary motion also homogenizes the mixture, which is necessary for obtaining a uniform temperature. In this continuous feed furnace plastics are heated relatively slowly to the temperature of the kiln depending on the heat conductivity of the waste. Rotary kilns have a long retention time (of one hour or longer). The residue of pyrolysis is burned in a combustion chamber, which is installed at the end of the rotary kiln. Flue gas can be suitably used as fuel for heating the furnace.

5.4.3 Screw pyrolyser

In the horizontal furnace a screw conveyer works at an adjustable speed to obtain the required retention time of the waste plastics to reach completed pyrolysis. Coke is removed during operation; nevertheless, the heat transfer is slow in this pyrolyser. In the Haloclean pyrolyser (Hornung et al., 2003), specially designed for recycling plastics from electronic scrap, different heating zones are independently controlled.

5.4.4 Fluidized bed reactor

An excellent heat and mass transfer is the main advantage of this reactor that is utilized mostly for incineration. A constant temperature throughout the reactor is an additional reason for applying fluidized bed for pyrolysis of polymers. For pyrolysis of plastic waste an inert fluidizing gas and sand or quartz sand bed is applied and continuous polymer waste feed and continuous coke removal is possible. Catalytic pyrolysis can be performed as well using a solid catalyst as bed material (Ali et al., 2002); moreover, steam can be also used as fluidizing gas (Kaminsky and Hartmann, 2000).
5.5  Pyrolysis of polymer composites

The most important factor in pyrolysis technologies is the ability to recycle both polymer matrix and reinforcement of composites; however, the optimal pyrolysis conditions for obtaining a high quality of both kinds of recycled materials may be contradictory. This setback can be critical for a polymer matrix that generates solid pyrolysis residue on one hand, and for a thermally vulnerable strengthener on the other hand. Pyrolysis as a recycling option of polymer composites is still at the stage of rapid development, and industrial scale applications will be available only in the future. Pyrolysis reactors are mostly modelled in laboratory equipment or in pilot plant for the time being in order to aid understanding of the principal factors controlling the processes and for finding the optimal parameters to obtain recycled products of required quality and quantity at the same time.

5.5.1  Fibreglass reinforced thermoset composites

Fibreglass and orthophthalic polyester composite cured with styrene has been pyrolysed in a laboratory stainless steel autoclave at five temperatures between 300 and 700 °C for 30 min by Torres et al. (2000). The composite contained 50 wt% calcium carbonate filler as well. The weight of the pyrolysis liquid and gas obtained was nearly equal to the weight of the pyrolysed thermoset polyester material. The recovered glass fibre was covered by a black layer, the total amount of which was about 3 wt%. The aromatic character of the organic pyrolysis liquid corresponded to the polymer constituents of the composite. Over 90 wt% of the gas products – as expected from aromatic polyester – were carbon oxides.

Cunliffe and Williams (2003) carried out similar laboratory experiments in a fixed bed reactor pyrolysing automotive waste polyester composite at 450 °C. In addition to the pyrolysis oil and gas, a considerable amount of organic solid material was obtained, which proved to be phthalic acid anhydride, the main pyrolysis product of orthophthalic acid ester. In the pyrolysis oil the styrene content was relatively high. In the solid residue the contribution of char was as much as 26 wt%. The glass fibre was cleaned after pyrolysis via oxidation of the carbon deposit and separated from the filler sieving the recovered solid residue. The glass fibres have successfully been reused in polyester composites.

A series of fibre-reinforced polymeric waste have been investigated by Cunliffe et al. (2003) performing thermogravimetric analysis (TGA) and bench-scale pyrolysis experiments. The pyrolysis of the various polymer matrices was generally a single stage process between 250 and 500 °C. The maximal rate of thermal decomposition of unsaturated
polyester, vinylester, phenolic and epoxy resin thermoset matrices was found at around 400°C. However, composites with phenolic and epoxy resin matrices continued to lose mass steadily after polymer decomposition had ended. This decomposition between 600 and 800°C was related to carbonization of the remaining solids. The mass loss rate (DTG) maximum obtained for glass fibre reinforced polypropylene in this work was at 470°C, matching the temperature obtained for polypropylene alone by Czégény et al. (2002) seen in Table 5.1, demonstrating that glass fibre does not influence polymer decomposition. The results of TGA measurements were compared with those from a static-bed reactor and it was concluded that the findings derived from the TGA were applicable to the larger reactor system.

5.5.2 Epoxy resin/carbon fibre composites

Jiang et al. (2007) compared the thermal and thermo oxidative decomposition of an epoxy resin/carbon fibre composite using thermogravimetry. The weight loss due to volatilization of thermal decomposition products from the epoxy resin occurred from 300 to 460°C with a maximum at 420°C both in argon and in air. A further two additional weight loss steps were observed in air only: the first started at 460°C and ended at 580°C, corresponding to a mass loss of 15%, and the last one between 600 and 750°C agreed with the mass ratio of the carbon fibre (58%). Both related reactions were oxidation as proved by the simultaneous plot of the molecular ion curve of carbon dioxide evolution recorded by mass spectrometry. The first reaction was attributed to the oxidation of the char left on the fibre surface after epoxy pyrolysis.

Carbon fibre with epoxy resin matrix has been heated in a microwave cavity in nitrogen atmosphere by Lester et al. (2004). The polymer content was volatilized nearly totally; however, the products condensed in the immediate environment around the heated composite material. The carbon fibres recovered were better cleaned and retained better strength than those recovered after fluidized bed combustion.

5.5.3 Nanocomposites

The increased interest in research and development of polymer nanocomposites will undoubtedly soon raise the problem of recycling both polymer matrix and nanoparticulates of high value of these composites. Carbon nanotubes appear to offer potential for new application of polymer composites that could be not only a mechanically reinforced material but also a conductive and flame retardant one. The thermal characterization data
on polymer composites with carbon nanotube indicate that – in contrast to conventional composite strengtheners – particles of a dimension of less than 100 nm are not always inert in pyrolysis reactions.

Nanoparticles were found to cause a shift of the starting decomposition temperature of isotactic polypropylene (iPP) to 50°C higher at carbon nanotube content of 5 wt%. The stabilization effect of carbon nanoparticles were explained by a barrier effect, which hindered the diffusion of the degradation products from the bulk of the polymer to the gas phase (Vassiliou et al., 2008).

Flame retardant activity of polyamide 6 nanocomposite with multiwall carbon nanotube has been observed but nanoparticles merely acted as inert filler with respect to thermal decomposition in this case (Schartel et al., 2005). The same research group investigated the thermal decomposition of polycarbonate nanocomposite with similar carbon particles and observed a decrease of thermal stability by 100°C with 15 wt% nanoparticles (Schartel et al., 2008).

5.5.4 Catalytic pyrolysis of composites

A catalytic conversion process proved to be effective for recycling plastics and composites used in automotive and aerospace parts (Allred and Busselle, 2000). A variety of polymers and composites are converted into low molecular weight hydrocarbons at temperatures near 300°C that can then be reused as chemicals, fuels or monomers. Metal, glass, fillers and fibres are separated from the hydrocarbons during the process and can be reclaimed for reuse. After catalytic pyrolysis of carbon/epoxy composites only 0.2% residual resin was left on the recovered carbon fibre showing a reduction of tensile strength of 9% (Allred et al., 2001).

Research studies of catalytic modification of PP and polyamide pyrolysate are mentioned above (Bozi et al., 2008). Catalytic pyrolysis can be performed in a fluidized bed pyrolysis reactor as well using a solid catalyst as bed material (Ali et al., 2002). Catalysts are applicable also for eliminating polluting components of electronic and electric equipment waste pyrolysis product: for instance a diminished formation of bromoaromatic compounds takes place in pyrolysis with sodium-zeolites (Blazsó, 2005).

5.6 Pyrolysis conditions for polymer composites recycling

In order to decompose completely the polymer matrix and obtain a cleaned strengthener material at the same time, the pyrolysis temperature is essential, as are also the time of heating up and the residence time of the volatile
pyrolysis products in the hot reactor. Intramolecular reactions within the solid plastic are favoured by a slow heating rate. In some cases this can result in network formation that is carbonized at higher temperatures and char is formed. Fast evaporation of volatile pyrolysis products at a high heating rate and simultaneous sweeping of gaseous phase inhibit the recondensation of reactive compounds that would also lead to char formation. Consequently a high heating rate to the temperature necessary for the fast decomposition of the polymer matrix and short residence time of the evolved pyrolysis product in the reaction zone are recommended.

Although pyrolysis reactions occur first in thermal treatments of solids performed in any atmosphere, further reactions take place in a reactive atmosphere. In air the valuable pyrolysis products of polymer composites are burned and only the heating energy can be recuperated while the reinforcement becomes free of char (Pickering et al., 2000). It was found that low combustion temperatures are necessary in order to maximize residual strength of fibres. A successful elimination of the polymer char from the surface of composite strengtheners can be performed by introducing air in the pyrolyser after the volatile pyrolysis products of the polymer matrix have been already flushed out of the furnace (Pickering, 2006).

An atmosphere of reduced pressure also helps a cleaner recovery of filler or strengtheners from polymer composite waste. Under vacuum the diffusion of the product molecules from the decomposing solid phase is enhanced, and moreover the products are fast eliminated from the reaction zone. Roy et al. (1999) successfully cleaned the carbon black of waste tyre and obtained a pyrolysis oil rich in isoprene and limonene in a vacuum pyrolysis reactor. Introduction of steam in the reaction zone of the pyrolyser unit involves a reaction of water with the primary pyrolysis products and also contributes to the fast decomposition of the polymer matrix. In several cases steam-assisted pyrolysis has led to more valuable products than pyrolysis in an inert atmosphere (Simon et al., 1996).

### 5.7 Environmental concern about pyrolysis products of composites

Polymer composites used in electronic and electric equipment generally contain flame retarding additive that may influence their recycling possibilities. In addition to the modification of pyrolysis temperature a more serious probable change, namely char formation, should be taken into consideration in the case of intumescent flame retardants. From environmental aspects halogenated flame retardant additives should be
examined as possible source of harmful pyrolysis or combustion products when thermal recycling of the polymer matrix is considered. Several studies have been carried out in order to understand the evolution of toxic compounds from flame retarded polymers and to develop methods reducing that risk.

Waste plastics collected from a waste electrical and electronic equipment (WEEE) processing plant has been pyrolysed in a fixed bed pyrolyser heated gradually to 600°C by Hall and Williams (2007). Chlorinated and brominated organic compounds have been detected in the pyrolysis oil while some hydrogen halogenide was present in the gas. The solid residue was high in both metal and halogen content.

An epoxy matrix of a printed circuit board emitted polybrominated dibenzodioxins and dibenzofurans under pyrolysis and combustion as well (Moltó et al., 2008). The source of these toxic compounds was the bromo- and dibromophenols present in significant amounts among the pyrolysis products of the waste board flame retarded with tetrabromobisphenol A (TBBA) segment of epoxy resin. TBBA flame retardant component of polycarbonate decomposed differently from the TBBA units of epoxy, leading to products of higher bromination level at 550°C (Bozi et al., 2007).

A considerable amount of bromo-, dibromo- and tribromobisphenol A was formed at 450°C pyrolysis from an epoxy resin with woven glass fibre strengthener flame retarded with brominated epoxy units (Blazsó et al., 2002). When this printed circuit board material was pyrolysed with sodium hydroxide, an enhanced bromomethane evolved, and a depressed brominated phenol and bisphenol formation was observed. A diminished production of bromophenols took place in pyrolysis with sodium-zeolites as well. Hornung et al. (2003) reported debromination of pyrolysis oil of electronic waste plastics with the polypropylene as a reductive agent. The level of bromophenol contamination was suppressed to an acceptable level and hydrogen bromide evolved.

Braun and Schartel (2008) observed char formation in a glass-fibre reinforced PBT, although the phosphorous flame retardants influenced the decomposition of PBT only slightly.

5.8 Summarizing comments on recycling polymer composites by pyrolysis

From the viewpoint of pyrolysis the differences of thermoplastic and thermoset composites are not as distinctive as from that of material reutilization. The thermoset composites which cannot be reused directly can be
Pyrolysis for recycling waste composites

Table 5.2 Typical practical characteristics of polymer matrices and of their pyrolysis products

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Atomic ratio H/C</th>
<th>Pyrolysis (°C)</th>
<th>Char (%)</th>
<th>Character of liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPU</td>
<td>1.6</td>
<td>300–370</td>
<td>5</td>
<td>Aliphatic ester/aromatic</td>
</tr>
<tr>
<td>Polyester</td>
<td>0.9</td>
<td>370–460</td>
<td>26</td>
<td>Aromatic</td>
</tr>
<tr>
<td>Epoxy</td>
<td>1.1</td>
<td>370–460</td>
<td>15</td>
<td>Alkylphenol</td>
</tr>
<tr>
<td>PBT</td>
<td>1.0</td>
<td>370–430</td>
<td>3</td>
<td>Aromatic acid/aliphatic</td>
</tr>
<tr>
<td>PET</td>
<td>0.8</td>
<td>400–460</td>
<td>11</td>
<td>Aromatic ester</td>
</tr>
<tr>
<td>PA6</td>
<td>1.8</td>
<td>430–490</td>
<td>0</td>
<td>Aliphatic</td>
</tr>
<tr>
<td>PA12</td>
<td>1.9</td>
<td>440–490</td>
<td>0</td>
<td>Aliphatic</td>
</tr>
<tr>
<td>PP</td>
<td>2.0</td>
<td>450–500</td>
<td>0</td>
<td>Aliphatic</td>
</tr>
<tr>
<td>PC</td>
<td>0.9</td>
<td>480–570</td>
<td>22</td>
<td>Alkylphenol</td>
</tr>
<tr>
<td>Phenolics</td>
<td>1.0</td>
<td>450–580</td>
<td>30–50</td>
<td>Methylphenol</td>
</tr>
<tr>
<td>PPO</td>
<td>0.7</td>
<td>520–580</td>
<td>54</td>
<td>Phenol</td>
</tr>
<tr>
<td>PEEK</td>
<td>0.6</td>
<td>560–620</td>
<td>55</td>
<td>Phenol</td>
</tr>
</tbody>
</table>

easily recycled in to feedstock compounds by pyrolysis in several cases. Since the thermal decomposition reactions and the nature of their products is strictly related to the polymer chemical composition and structure (as it was demonstrated in sections 5.2 and 5.3), the physical characteristics such as melting ability is of marginal importance from the aspect of pyrolytic recyclability.

Pyrolysis temperature should be chosen to be high enough for fast decomposition of the given polymer but not too high for avoiding aromatization and carbonization. Char formation is related to the amount of available hydrogen atoms for stabilizing radicals formed by bond scissions in the pyrolysis reactions. Thus the molar ratio of H and C atoms in the macromolecule of polymer matrix is indicative of char-forming ability, namely considerable char formation takes place below H/C value of unity, meaning that the polymer is dominated by aromatic structures. In Table 5.2 the optimal temperature range of pyrolysis for obtaining valuable pyrolysis products from frequent polymer matrix of composites is indicated. The H/C atomic ratio of a given polymer together with the dominating nature of the pyrolysis products could be a basis of predicting the formation of char, as demonstrated by the char deposition ratios in Table 5.2.

5.9 Acknowledgements

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References


LESTER E, KINGMAN S, WONG K H, RUDD C, PICKERING S, HILAL N (2004), ‘Microwave heating as a means for carbon fibre recovery from polymer composites: a


Abstract: The increase in plastic waste represents a serious environmental issue. Plastics consumption continues to grow and while plastic recycle has seen a significant increase since the early 1990s, consumption still far exceeds recycle. Waste plastic can, however, serve as a potential resource and, with the correct treatment, can be reused or serve as hydrocarbon raw material or as a fuel. An overview of the existing waste plastic treatment technologies is provided with an analysis of the available literature on thermal degradation. Thermal pyrolysis results in a random scissioning of the polymer chains generating products with varying molecular weights. Catalytic degradation provides control over the product composition/distribution and serves to lower significantly the degradation temperature. Fundamental aspects of catalysis are presented with a discussion of the correlation of catalyst structure with performance, placing a particular emphasis on the role of zeolites as catalytic materials that have been widely used to promote polymer degradation. Polyvinyl chloride (PVC), highly versatile with manifold applications, is non-biodegradable and bears a high Cl content (56% of the total weight). Waste PVC incineration is very energy demanding and can result in the formation of toxic chloro-emissions with adverse ecological, environmental and public health impacts. The Cl component must be removed from any waste PVC-derived gas or oil before it can be used. The potential of a catalytic dechlorination unit operation to facilitate PVC recycle is discussed with reference to the pertinent, albeit limited, available literature.

Key words: waste polymers, heterogeneous catalysis, zeolites, thermal pyrolysis, catalytic recycling, PVC recycle.

6.1 Introduction

In any progressive approach to waste minimisation, disposal is only an option where the ‘four Rs’, i.e. reduction, reuse, recycling and (energy) recovery options, have been exhausted (McEldowney and McEldowney, 1996). The accepted waste minimisation ‘hierarchy’ is illustrated in Fig. 6.1, which identifies the route to responsible waste management. Catalysis is an integral component in any green processing technology, serving as an important tool to support sustainable development. The deployment of catalysts ensures lower operating temperatures and/or pressures and a
higher selectivity to the target product with a resultant reduction in fuel usage and waste production. Sustainable development is essential to deal with the challenges of a fast-changing world, where the demands on natural resources, the needs of a growing population and the accumulation of waste will inevitably impose restrictions upon how businesses operate. Where a manufacturing process is energy intensive, a controlled recycle/reuse is an effective means of decreasing overall negative environmental impacts (Anastas and Lankey, 2000). The emergence of ‘environmental catalysis’ as a discipline has focused on the development of catalysts to either decompose environmentally unacceptable compounds or provide alternative catalytic syntheses of important compounds without the formation of environmentally unacceptable by-products. This chapter focuses on the former option and considers the role of heterogeneous catalysis in a chemical processing of waste polymers, setting out the advantages of the catalytic approach.

6.2 Waste polymer recycle: motivation

Plastics are synthesised from non-renewable resources and are generally non-biodegradable or the biodegradation process is very slow. As a consequence, waste plastic represents a serious environmental threat that is not addressed by recourse to landfill. However, waste plastic can be viewed as an enormous potential resource which, with the correct treatment, can be reused or serve as hydrocarbon raw material or as a fuel (Williams, 1988).
The scale and range of plastic goods production have led to a diversity of waste streams with the potential for an impending ‘waste plastic mountain’. An average increase in global plastic production of c.10% has been recorded since 1950 with current production close to 250 million tonnes (Plastics Europe, 2007). The versatility and low prices associated with plastic products are the reasons for commercial success. Despite the unstable price of crude oil and petroleum feedstock, the plastics market remains robust. It has been estimated that annual consumption of plastic products in Western Europe approaches 100 kg per person to give a total of over 39 million tonnes, which translates into an estimated c.22 million tonne waste stream (Plastics Europe, 2004). Virgin plastics consumption is illustrated in Fig. 6.2 where a consistent increase is evident from 1995 to 2002. Up to 60% of all waste plastic generated in Europe is still sent to landfill; incineration with energy recovery represents the principal alternative, accounting for c.23% of the plastic waste (Aguado et al., 2006). The extent of polymer recycle falls somewhere between 5 and 25% of total plastic waste (Karagoz et al., 2003a). In the UK, while plastic consumption continues to increase, the ratio of recycle to consumption has also shown an increase (British Plastics Federation, 2004) as illustrated in Fig. 6.3. Nevertheless, consumption still far exceeds recycle.

The management of plastic waste is a pressing environmental issue. Plastic waste is resistant to degradation, contains hazardous additives and is characterised by a low density (i.e. high associated volume), while the separation of different plastic types is problematic (Aguado and Serrano, 1999). Waste plastic recycle can draw on mechanical or chemical treatment. In the former case, physical processes are employed to convert the plastic

\[ 6.2 \text{ Virgin plastics consumption in Western Europe over the period 1991–2002 (Plastics Europe, 2004).} \]
waste into secondary plastic materials while the latter involves a chemical transformation to hydrocarbon chemicals, i.e. in essence a ‘desynthesis’. Mechanical recycling is multisteped with collection, sorting, heat treatment with reforming, recompounding with additives and extruding operations to produce a recyclate that can substitute for the virgin polymer. The percentage of plastic waste that is subjected to mechanical recycling in Western Europe has been estimated to equal c.22% (Plastics Europe, 2004). There is a significant variation in the extent of mechanical recycle in different countries, as is revealed in the entries to Table 6.1. Mechanically recycled plastics typically find use in low grade applications, e.g. in the production of plastic bags, pipes and as composites in construction (La Mantia, 2002). Chemical or feedstock recycling is based on the

Table 6.1 Percentage of waste plastic that is mechanically recycled in Western European countries

<table>
<thead>
<tr>
<th>Country</th>
<th>% recycled</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austria, Belgium, Germany, Italy, Netherlands, Norway, Spain</td>
<td>&gt;20</td>
</tr>
<tr>
<td>France, Switzerland, UK</td>
<td>15–20</td>
</tr>
<tr>
<td>Denmark, Finland, Portugal, Sweden</td>
<td>10–15</td>
</tr>
<tr>
<td>Ireland</td>
<td>5–10</td>
</tr>
<tr>
<td>Greece</td>
<td>0–5</td>
</tr>
</tbody>
</table>

6.3 Plastics consumption relative to post consumer recycling in the UK from 1990 to 2001.
decomposition of polymers by means of heat, chemical agents and catalysts to yield a variety of products ranging from starting monomers to constituent hydrocarbons. Incineration of plastic waste can be coupled with energy recovery but this approach continues to meet with strong societal opposition. Moreover, the Kyoto Protocol has set, as a target, a 20% reduction in carbon dioxide emissions by 2010 (Defra, 2000). Investment and operating costs associated with incineration are significant but economies of scale apply with modern municipal solid waste incinerators having a capacity typically in the range 200–1000 ktonnes/year (Brown et al., 2000). The high costs of incineration can be offset by sales of energy, recovered as heat and/or electricity and the sale of ash and ferrous metal recovered from the combustion process.

Chlorine containing waste is typically xenobiotic and having no analogous compounds in nature, there is no natural means of ameliorating the negative environmental impact. A major problem in the recycling of non-biodegradable polyvinyl chloride (PVC) is the high Cl content, i.e. 56% of the total weight. Incineration of PVC is problematic as it falls into the category of Principal Organic Hazardous Constituents, compounds that are inherently difficult to combust. Complete combustion of such compounds occurs at such high temperatures (>1700 K) to be economically prohibitive while the formation of hazardous by-products (polychlorodibenzodioxins and polychlorodibenzofurans), known carcinogens included on the US Environmental Protection Agency (EPA) Persistent Bioaccumulative Toxics List, can result from incomplete incineration (Hagenmaier et al., 1991; Costner, 1998). Chlorinated dioxins and furans are regarded as the most severe environmental contaminants with toxicities that are orders of magnitude greater than strychnine and sodium cyanide. Immune system damage, reproductive effects/birth defects, cancer and neurological effects have been established for short-term exposure to low concentrations (Thornton, 2000; Pollock, 1989). A comprehensive legislation has been developed to address issues associated with the management of waste plastics. There are a number of European Directives in place (notably the Waste Packaging, End-of-Life Vehicle and Electrical/Electronic Equipment Directives) that set increasingly stringent standards to minimise environmental impact due to waste plastics (Aguado et al., 2006). These directives particularly target a decrease in plastic waste sent to landfill and encourage an integrated approach to encompass prevention of waste at the production stage, reuse to extend productive lifetime, recycling and energy recovery. A chemical processing leading to feedstock recycling as applied to polymer waste represents a positive alternative to landfill with the potential to recover energy and/or raw materials. This approach can serve as a progressive response to existing and impending legislation but viability remains an issue.
6.3 Thermal decomposition of waste plastics

Thermal degradation (pyrolysis and/or cracking) is accepted as a feasible means of waste plastic reuse (McCaffrey et al., 1998; Lingaiah et al., 2001b). Indeed, the viability of thermal cracking has been established (Sakata et al., 2003) and has found application in a number of processing plants (Brophy and Hardman, 1996; Kaminsky and Sinn, 1996). Plastics can be divided into two groups: (i) condensation polymers; and (ii) addition polymers (polyolefins). Condensation polymers, which include such materials as polyamides, polyesters and nylon, can be ‘depolymerised’ via reversible synthesis to the starting diacids and diols or diamines. The latter involves alcoholysis, glycolysis and hydrolysis and is known to deliver high yields of the starting monomers (Cornell, 1995). In contrast, addition polymerisation is not readily reversed as it is an activated process. The thermal cracking of common plastics such as polyethylene and polypropylene has been reported in the literature (Songip et al., 1994; Sharratt et al., 1997; Costner, 1998). Ucar et al. (2002) have evaluated a co-processing of waste plastic with a heavy petroleum fraction blend but a narrow product distribution has yet to be realised. A co-processing of waste plastics with coal has also been considered as a route to fuel production (Ding et al., 1999). The main drawback to thermal degradation is the requisite high temperatures (process is highly endothermic) that results in a very broad range of products (Babu and Chaurasia, 2003; Demirbas, 2004; Kaminsky et al., 2004).

6.4 Catalytic approach to polymer recycling

Catalytic degradation provides control over the product (composition/distribution) and serves to lower significantly the degradation temperature (Garforth et al., 1998). While thermal degradation of polyolefins results in a random scissioning of long polymer chains, the use of a solid catalyst is known to break the chain into smaller units resulting, for instance, in a higher yield of a saturated liquid product (Sakata, 1998). Songip et al. (1994) have proposed an effective process whereby the waste plastic is first cracked thermally in pyrolysis plants and the oil that is produced is then transferred to a catalytic cracking plant and converted to gasoline. Sufficient progress has now been made in the catalytic processing of polyethylene/polypropylene over solid acids (notably silica–aluminas and zeolites) to enable some optimisation of liquid, solid or gaseous hydrocarbon product fractions through the judicious choice of operating conditions, i.e. reaction temperature and reactor configuration (Kaminsky, 1985; Uemechi et al., 1989; Mordi et al., 1994; McCaffrey et al., 1995). There is also evidence that the product composition resulting from polyethylene and polypropylene
degradation can be manipulated through modifications to the catalyst properties (Sharratt et al., 1997; Negelein et al., 1998; Hesse et al., 2001; Serrano et al., 2005; Aguado et al., 2007).

If the polymeric waste contains a halogenated component, as in the case of PVC, thermal degradation generates products with widely varying molecular weights and uncontrolled Cl content (Mordi et al., 1994; Blazó et al., 1995; Williams and Williams, 1999). The tightening legislation makes it essential that the Cl component must be removed from any waste plastic derived gas or oil before it can be used (Lingaiah et al., 2001a). One possible means of imposing control over product distribution is through catalytic degradation, i.e. a catalytic dechlorination can be employed to efficiently remove the Cl component where the starting Cl is converted to HCl, which is easily separated from the target product(s). It was observed in a stepwise pyrolysis of a mixed plastic/PVC feed that the majority of the Cl content was released from PVC (at c.573 K) prior to the degradation of the remaining polymers in a second step (>673 K) (Yanik et al., 2001b). Bockhorn et al. (1998) achieved a 99.6% elimination of Cl in a mixed PVC/plastics feed in a cascade of well-stirred reactors at 603 K. In the pyrolysis of municipal waste plastics, thermal degradation leads to the formation of conjugated double bonds, while the HCl released from PVC attacks these double bonds resulting in the formation of toxic chloroorganic compounds (Martinson et al., 1988). Chlorine separation from household waste plastics by PVC decomposition has been attempted using extruders in oil reclamation plants in Japan (Kaminsky and Kim, 1999). The waste plastics are pressurised and HCl gas is generated but, at high pressure, the HCl can readily react with other organic/inorganic components in the feed and complete dechlorination is problematic. The use of metal oxides as HX adsorbents (Horikawa et al., 1999; Yanik et al., 2001a) and lime and KOH for HX fixation (Kaminsky and Kim, 1999; Brebu et al., 2006) has met with limited success. Separation of halogenated polymers from a non-halogenated polymeric matrix is possible by supercritical fluid extraction but this approach is very energy intensive, which minimises the overall benefit in any recycle operation (Gamse et al., 2000). A PVC recycle strategy involving a one step catalytic processing with concomitant dechlorination certainly represents a progressive option.

A catalytic approach to waste polymer reprocessing has the following positive features: (a) lower operating temperatures (relative to pyrolysis), non-oxidative process with lower energy requirements and no directly associated NOx/SOx emissions; (b) absence of thermally induced free radical reactions that can lead to toxic intermediates; (c) possibility of selective Cl removal (in the case of PVC) with concomitant polymer degradation to a target recyclable product; and (d) operability in a closed system with no toxic emissions.
6.4.1 Fundamentals of catalysis

Various definitions of catalysis have been proposed, but an early classification provided by Wilhelm Ostwald in 1895 is still widely in use: ‘Catalysts are substances which change the velocity of a reaction without modification of the energy factors of the reaction’. This definition excludes substances that accelerate the rate of reaction by entering into reaction with a resultant disruption of the reaction equilibrium. A catalyst works by forming chemical bonds to one or more reactants which facilitates their conversion (Butt, 2000). A more rigorous definition of a catalyst is ‘a substance that increases the rate of reaction without modifying the overall standard Gibbs energy change in the reaction’. This is illustrated schematically in Fig. 6.4. In an uncatalysed transformation collisions between participating molecules must possess sufficient (activation) energy to pass over the energy barrier that is characteristic for that reaction. The reactants form a short-lived transition state or activated complex which reacts to give product(s) (Gates, 1992). Catalyst/reactant interactions serve to lower the energy barrier (transition state is at a lower energy) and enable reaction under more moderate reaction conditions. The catalyst reduces the enthalpy of activation for the forward reaction by exactly the same amount as it reduces the enthalpy for the reverse reaction, there is no entropy change and the free energy change/position of equilibrium remains the same for the catalysed and uncatalysed processes.

![Energy diagram for a catalysed and uncatalysed chemical reaction.](image-url)
6.4.2 Heterogeneous catalysis

Catalysts can be divided into two broad categories: heterogeneous and homogeneous (Steinfeld et al., 1999). Homogeneous catalysis occurs when the catalyst is uniformly dispersed in the reaction mixture, either a gaseous or liquid solution. In a heterogeneous reaction, the catalyst is in a different phase from the reactants, where the reaction occurs at the surface of a solid (catalyst) particle in contact with the gaseous or liquid solution. The main disadvantage associated with heterogeneous when compared with homogeneous catalyst operation is the lower effective concentration of catalyst as the reaction occurs only on the exposed active surface. Moreover, physical transport constraints can result in lower effective reactant concentrations at the catalyst surface relative to the bulk fluid. This is illustrated in Fig. 6.5 for a reaction involving liquid and gaseous (H\textsubscript{2}) reactants promoted by a solid catalyst where the effective H\textsubscript{2} concentration shows a decrease in moving from the gas phase (C\textsubscript{g}) to the liquid phase (C\textsubscript{l}) to the catalyst surface (C\textsubscript{s}), where the reaction occurs.

Catalyst recovery and reuse are, however, far more facile in the case of heterogeneous operation. Any reaction that is promoted by heterogeneous catalysis involves a number of steps: transport of reactant(s) to the catalyst surface; formation of reactant/catalyst complex; surface reaction leading to product/catalyst complex formation; transport of product from the catalyst surface. The surface reaction is facilitated by reactant/catalyst interaction(s) that generates a reactive reactant/catalyst complex. These interactions may be weak, of the ‘non-bonding’ type with the reactant staying intact while sticking to (or adsorbing on) the surface. Alternatively, the interactions may involve the formation of new chemical bonds between the surface atoms and the adsorbed molecule, which necessarily involves extensive

![Diagram](image-url)
reorganisation of the bonding within the reactant. This reactive type of interaction is generally known as 'chemisorption' in contrast to 'physisorption', the term used to describe the weaker unreactive binding of molecules to surfaces (Twigg, 1989; King and Woodruff, 1990).

Physisorption involves weak van der Waals interactions and the adsorption energy is typically in the range 5–15 kJ mol\(^{-1}\), which is much lower than that associated with chemical bonding. Moreover, the van der Waals interaction(s) between adsorbed molecules does not differ significantly from the van der Waals interaction(s) with the surface, with the result that many layers of adsorbed molecules may be formed, as shown in Fig. 6.6. In the case of chemisorption, the reactant may chemisorb intact or it may dissociate (Fig. 6.6); the chemisorption energy is 30–70 kJ mol\(^{-1}\) for molecules and 100–400 kJ mol\(^{-1}\) for atoms (King and Woodruff, 1990; White, 1990; Bowker, 1998). The magnitude of the adsorption coefficient depends on the nature of the surface and the chemical identity of the reacting species. Once the reactant is bound to the surface, it can readily undergo reactions which take place only with difficulty in the gas or liquid phases. This may result from the close proximity of reactant molecules on the surface and/or the changes in bonding consequent upon chemisorption; both are essential

6.6 Schematic showing (a) physisorption and (b) chemisorption involving (i) associative and (ii) dissociative interactions.
Management, recycling and reuse of waste composites

features of the catalytic properties of the solid. The choice of a suitable catalyst for a particular reaction depends on the stability of the complexes formed between reactant and catalyst and/or product and catalyst. These must be stable enough to form and provide an alternative pathway to the uncatalysed reaction but they must not be too stable as this would lead to an increase in the associated activation energy with a consequent lowering of reaction rate.

A heterogeneous catalyst is present as separate particles or agglomerates of particles immersed in a fluid medium in motion. Reactants and products diffuse in the gas or liquid phases at the boundary of the solid and in the pore spaces of the aggregates. Catalyst efficiency is assessed in terms of three parameters: activity; selectivity; lifetime. The activity is the extent to which the catalyst influences the rate of change of the degree of advancement of the reaction, i.e. reactant conversion (per unit mass or per unit volume of catalyst) under specified conditions. The activity per unit volume is of practical importance in terms of process economics where a low catalyst bulk density reduces the necessary reactor volume and associated cost. The turnover frequency represents the specific rate and is defined as the number of molecules reacting per active site per unit time. The usefulness of turnover frequency values is dependent on the validity of the method used to measure (or estimate) the number of active sites (Gates, 1992; Somorjai, 1994). Very often a reactant or set of reactants may simultaneously undergo several parallel reactions, giving different products that can react further in consecutive reactions to yield secondary products. Selectivity is an important catalyst property, serving as a measure of the extent to which a particular catalyst promotes the formation of a ‘target’ product, i.e. the ability of the catalyst to direct conversion to a desired product. The productive lifetime of the catalyst is the period during which the catalyst delivers a product yield in excess or equal to that designated (Twigg, 1989).

6.4.3 Catalyst structure

Catalytic efficiency is influenced by four principal catalyst structural features which are interrelated: (a) the exposed area in contact with the fluid; (b) the intrinsic surface chemical reactivity; (c) surface topography – geometric and electronic features; and (d) occurrence of defects – vacancies, interstitials and dislocations. Commercial catalysts must possess sufficient mechanical strength to resist losses as a result of crushing (in packed bed operation) or attrition (in reactors involving vigorous agitation). High surface areas can be attained either by fabricating small particles or clusters where the surface-to-volume ratio of each particle is high, or by creating materials where the void surface area (pores) is high compared with the amount of bulk material. Many catalysts are porous solids with a high
surface area that is both ‘external’ and ‘internal’, the former represented by the envelope surrounding discrete particles. The internal surface comprises the walls of the pores/channels/cavities and the total surface area equals the sum of the external and internal areas. Gas adsorption methods, notably the Brunauer–Emmett–Teller (BET) approach, are widely used to determine surface areas (Ponec et al., 1974; Anderson, 1990). Porosity is a measure of the fraction of the bulk volume that is occupied by pore or void space. Pore size distribution is an important characteristic of porous catalysts where pores of diameter in excess of 50 nm are considered macro-pores, those less than 2 nm are termed micropores and pores of intermediate size are denoted mesopores (Lecloux, 1981; Gates, 1992). It must be stressed that a wide range of pore sizes, spanning both micro- and macro-porosity, is characteristic of standard solid catalysts. The pore size distribution is an important factor in controlling diffusion of reactants/products within any catalyst pore network and is an essential characteristic property of the catalyst. A distinction must then be drawn between the true catalyst density (solid mass to volume ratio excluding all pores and voids) and bulk or packing density. The location of the catalytically active component within the porous structure and the manner in which pores interconnect can have a profound effect on the accessibility of reactants to the catalytically active site, and to the removal of products.

The catalyst particle can be a complex entity composed of a porous solid serving as a support for one or more catalytically active phases. The latter may comprise clusters, thin surface mono- or multi-layers or small crystallites where interaction with the support can impact on surface reactivity. The major active component is typically expressed on a percentage weight basis (e.g. 10% w/w Pd/Al₂O₃) where the crystallographic form of the support (e.g. γ-Al₂O₃) should be given. Secondary components or additives can serve as promoters where this modification may be directed towards enhancing activity/selectivity, poison resistance or textural properties. The determination of the surface chemical composition and structural properties, as opposed to bulk characteristics, can call upon a range of complementary surface science techniques. The structures of catalyst surfaces are notoriously difficult to elucidate owing to the involvement of microscopic and even macroscopic regions with different compositions, phases and structures, each bearing a diversity of imperfections. Adsorption/desorption measurements provide indirect structural information while transmission electron microscopy is applicable for surface analysis at the nanoscale level. In terms of catalysis, the atomic scale structure is critical, i.e. the arrangement of atoms involved in chemical bonding with reactants. X-ray diffraction is applicable to measurement of crystallite sizes and identification of any crystalline phases that are present. Electron spectroscopies, notably Auger electron spectroscopy (AES), x-ray
photoelectron spectroscopy (XPS) and secondary ion mass spectroscopy (SIMS), facilitate measurement of the chemical composition of reactive surfaces. Instrumentation developments are now directed towards detection of finer detail, i.e. atomic spatial resolution, ever smaller energy resolution and shorter timescales. In those cases where experimental characterisation techniques are impractical, theoretical calculations (\textit{ab initio}, semi-empirical and force field methods) can be instrumental in gaining a better understanding of catalyst structure and the feasible transition states/reaction pathways.

Certain catalytic reactions proceed at the same rate regardless of the nature of the reactive surface and are deemed to be structure insensitive, whereas other reactions exhibit an appreciable structure sensitivity where the rate can vary by orders of magnitude from one crystal face to another (Gates, 1992). Masel (1996) has noted that all catalytic reactions exhibit some degree of structure sensitivity under certain reaction conditions. Heterogeneous catalysts cannot be regarded as representing a ‘model’ uniform reacting surface but display a distribution of interaction energetics associated with the different exposed crystal faces, occurrence of dislocations, defects and other disturbances (Boudart and Djéga-Mariadassou, 1984). The simplest surfaces can be regarded as ‘flat’ and deviations from this ideal arrangement include ‘ledges’, ‘kinks’, ‘adatoms’ and ‘vacancies’ (Lang and Kohn, 1970). The relative concentration of atoms in the ordered domain (flat surface) and in defects depends on surface preparation/pre-treatment. Variation in catalytic particle size can result in a change in the distribution of sites and the preponderance of a particular defect which can result in a structure-sensitive response.

6.4.4 Zeolites

Zeolites represent a commercially important branch of advanced ceramic catalytic materials that have now found use in waste polymer recycling applications. Zeolites are aluminosilicates that are structurally unique in having cavities or pores with molecular dimensions as part of their crystalline structure (Breck, 1974; van Bekkum, 1991). Zeolites occur naturally as minerals and are extensively mined in many parts of the world. The zeolite materials that find widespread use in the chemical industry are synthesised where the synthesis is controlled to produce a specific zeolite structure tailored for a particular application. The zeolite aluminosilicate framework is composed of oxygen tetrahedrons, each encasing either a Si or Al atom. The oxygen atoms can be shared by only two tetrahedra, and no two Al atoms can share the same oxygen atom, with the resultant restriction that the Al/O ratio \( \leq 1 \). The zeolites finding the greatest application on a commercial scale belong to the family of faujasites and include zeolite X
and zeolite Y. The framework structure of zeolites X and Y is shown in Fig. 6.7(a) and is based on a regular arrangement of truncated octahedral and sodalite cages to generate a high surface area microporous structure. Zeolite Y is synthesised by a gelling process, is characterized by a void volume fraction of 0.48, a Si/Al ratio of 2.43 and is thermally stable up to 1063 K (Bhatia, 1990). The geometrical crystalline features associated with zeolite Y are evident from the scanning electron micrograph (SEM) presented in Fig. 6.7(b). Zeolite crystal structures are complex three-dimensional frameworks with long-range crystalline order and pore sizes of sub-nano dimensions. Access to the intracrystalline Y zeolite sites is via an interconnecting, three-dimensional network of cavities, i.e. the accessible supercages of internal diameter 1.3 nm that are linked by shared rings of 12 tetrahedra (free diameter = 0.7–0.8 nm) and the less accessible sodalite units that are linked through adjoining rings of six tetrahedra which form the hexagonal prisms (free diameter = 0.20–0.25 nm). The size of the zeolite window is determined by the number of oxygens in the ring, as revealed in Table 6.2. This makes for a molecular ‘sieving’ effect where molecules can pass freely through the zeolite matrix or transport can be severely restricted or blocked depending on the relative dimensions of the

![Structure of faujasite and SEM micrograph showing the topographical features of Na-Y zeolite.](image-url)
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Table 6.2 Relationship between the number of ring oxygens and zeolite 'window' dimensions

<table>
<thead>
<tr>
<th>Number of ring oxygens</th>
<th>Window diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1.2</td>
</tr>
<tr>
<td>5</td>
<td>2.0</td>
</tr>
<tr>
<td>6</td>
<td>2.8</td>
</tr>
<tr>
<td>8</td>
<td>4.5</td>
</tr>
<tr>
<td>10</td>
<td>6.3</td>
</tr>
<tr>
<td>12</td>
<td>8.0</td>
</tr>
</tbody>
</table>

![Neutral sodium (charge) balanced zeolite framework.](image)

Zeolites can operate over a range of acid/alkaline conditions. As silicon is tetravalent and aluminium is trivalent, the zeolite framework has a net negative charge that is balanced by an exchangeable cation (typically Na⁺), as shown in Fig. 6.8. Zeolites have found widespread use in ion exchange as the indigenous charge balancing cations are not fixed rigidly to the hydrated aluminosilicate framework and are readily exchanged with metal cations in solution (Breck, 1974). In environmental remediation applications, both synthetic and naturally occurring zeolites have been used to remove a range of toxic heavy metals from water (Ouki and Kavanagh, 1997; Ahmed et al., 1998; Kim and Keane, 2000). Solution pH has a significant impact on zeolite exchange properties where a sufficiently low pH can cause structural damage while metal hydroxide precipitation/deposition may predominate at high pH (Kim et al., 2001). Zeolite addition to water is accompanied by an immediate solution pH increase as a result...
of a hydrolysis of the zeolite (Lutz et al., 1990), which in the case of zeolite Na–Y can be shown as

$$\text{Na–Y} + (\text{H}_2\text{O})_x \Leftrightarrow \text{H–Y} + (\text{H}_2\text{O})_{x-1} + \text{Na}^+ + \text{OH}^-$$

The ion exchange of divalent metal ($\text{M}^{2+}$) ions with Na-Y can be represented by the equilibrium (Breck, 1974):

$$\text{M}^{2+}_s + 2\text{Na}^+_z \leftrightarrow 2\text{Na}^+_s + \text{M}^{2+}_z$$

where $s$ and $z$ represent the solution and zeolite phases, respectively. The degree of divalent ion exchange is dependent on the zeolite composition (Si/Al ratio), size of the exchanging hydrated metal ions, metal ion concentrations and temperature (Keane, 1994). Metal ion exchange also serves as a synthetic route to supported metal catalysts where a reduction (in hydrogen) of the divalent metal exchanged zeolite generates a supported zero valent metal phase according to the equilibrium:

$$\text{M}^{2+}_z + \text{H}_2 \leftrightarrow \text{M}^0_2 + 2\text{H}^+_z$$

Zeolite supported transition metal catalysts have been used to promote a range of hydrogenation/dehydrogenation, hydroisomerization, dehydrocyclization and hydrogenolysis reactions (Coughlan and Keane, 1991; Stanislaus and Cooper, 1994; Meriaudeau and Naccache, 1997). Two surface hydroxyl groups (Brønsted acid sites) are generated for each reduced divalent metal and these impart a surface acidity that can be employed to promote catalytic transformations that require acid sites, e.g. alkylation and dehydration (Coughlan and Keane, 1990, 1992a; Park and Keane, 2001). Brønsted acidity can also be introduced through hydrolysis (as shown above) and by zeolite exchange with $\text{NH}_4^+$ followed by thermal treatment (Coughlan and Keane, 1992b; Bortnovsky et al., 2001). The ability of zeolites to preferentially sieve molecules can be put to good effect in catalytic applications in that the production of a chemical of particular size and/or shape may be preferentially promoted (Meisel et al., 1976). Where a reactant is sterically hindered in accessing the active sites located within the zeolite pore network, then the product resulting from that reactant will also be restricted. Alternatively, if a ‘bulky’ product is formed within the zeolitic cavities, its intracrystalline diffusional transport will also be restricted. The molecular sieving properties of zeolites, in consort with the dual functionality (metal and acid sites) of the zeolite surface place these materials in a unique category of highly efficient, selective and widely applicable catalysts.
6.4.5 Catalyst deactivation

It is typical that a heterogeneous catalytic unit operation exhibits a progressive drop in conversion with catalyst use. Catalyst deactivation as a function of time is often unavoidable and the deactivated catalyst must either be regenerated or replaced (Bartholomew, 1984). The causes of catalyst deactivation are numerous but they can be conveniently grouped into three general categories (Butt, 2000): sintering, poisoning and coking. Sintering refers to a diminution of active site dispersion and can apply to all phases present in the catalyst, i.e. active phases, modifiers and support. The overall effect of sintering is a reduction in active surface area per unit volume of catalyst and is normally the result of excessively high reaction temperatures (Wanke and Flynn, 1975). The presence of deactivating species in the reactant feed (as impurities) or formed during reactant conversion (transformation of an intermediary and/or product) can induce a partial or total loss of activity. Catalyst poisoning can be irreversible (true poisoning), reversible or transient (inhibition) or may involve fouling agents which induce a mechanical inhibition. The latter refers to non-covalent bonding (van der Waals interaction, hydrogen bonding, ionic interactions, etc.) that serve to physically impede access of reactants to the active sites. True poisoning involves strong chemical interaction with the active sites where catalytic activity cannot be recovered without drastic change in the operating conditions (Fitzharris et al., 1982; Butt and Peterson, 1988). The time-dependent loss of activity can be linked to a migration of active species into the catalyst pellet, morphological changes of surface crystallites of a given phase, change in the number of steps, kinks and vacancies on the surface and modifications to the surface/bulk composition ratios. Activity loss due to coke formation is typical of reactions involving hydrocarbons and is due to reactant or product degradation that produces a carbonaceous residue on the surface. Coke that accumulates on a catalyst may cause deactivation either by covering active sites or by occluding the pores in the catalyst, as shown in Fig. 6.9. Coke deposits can amount to 15–20% w/w of the catalyst, depending on the operating conditions and the nature of the catalyst and reactant(s) (Forzatti and Lietti, 1999). Moreover, carbon deposition on reactor tubes and heat exchanger surfaces can adversely affect the performance of an array of unit operations associated with catalytic processing. Such deposits invariably contain both carbon and hydrogen with H/C ratios varying from almost zero up to 2 (Bond, 1997). The carbonaceous byproduct deposits are a complex mixture of amorphous and graphitic structures (Espinat et al., 1990; Shimada et al., 2000). Considerable effort (use of promoters/catalyst regeneration) is expended to minimise carbon deposition and extend the productive lifetime of the catalyst (van Santen and Jansen, 1991; Bond, 1997; Thomas and Thomas, 1997). The catalyst regeneration
strategy depends on the cause(s) of deactivation (Peterson and Bell, 1987; Bhatia et al., 1989). Deactivation due to carbon deposition can be reversed by heating the spent catalyst in air/oxygen which serves to ‘burn off’ the carbon deposit. This oxidative (highly exothermic) treatment must be carefully controlled in order to avoid any possible sintering due to excessive high temperature fluctuations.

6.5 **Catalytic treatment of non-halogen containing polymer waste**

Feedstock recycling applied to waste plastics, sometimes known as chemical recycling or tertiary recycling has enormous potential to enhance waste recovery. This approach does not have the negative societal impact of incineration and the recovered materials may have a broader range of applications than mechanically recovered plastics (Hardman and Wilson, 1998). In the catalytic degradation of non-halogenated plastic waste, the majority of published studies have focused on polyolefins, notably high
density polyethylene (HDPE), low density polyethylene (LDPE), linear
low density polyethylene (LLDPE) and polypropylene. This is largely due
to the fact that these polymers make up the largest component (60–70%)
of municipal solid waste plastics (Lin et al., 1997). There have been a limited
number of studies (Nambu et al., 1987; de la Puente and Sedran, 1998;
Serrano et al., 2000; Ukei et al., 2000) describing the catalytic cracking of
polystyrene over a range of zeolite (HZSM-5, HMOR and zeolite Y),
SiO₂–Al₂O₃, BaO and sulphur promoted zirconia catalysts. In these studies,
the operating temperature (623–773 K) employed during the catalytic pro-
cessing was appreciably lower than that required for thermal cracking. In
the catalytic degradation of HDPE (over the temperature range 563–703 K),
the yield of volatile hydrocarbon product increased in the order: HZSM-5
> HY ≈ HMOR (Garforth et al., 1998). A two stage catalytic degradation
process involving amorphous SiO₂–Al₂O₃ and H-ZSM-5 zeolite has been
used to convert polyethylene into a gasoline fraction with a high octane
number (Uemichi et al., 1999). In a two-stage process involving degradation
of HPDE and polypropylene over a solid acid followed by hydrogenation
over a Pt catalyst, Walendziewski and Steininger (2001) obtained a 90% yield of gas and liquid fractions with boiling points less than 633 K.
Aguado et al. (2000) have achieved good selectivity (40–60%) to C₅–C₁₂ hydrocarbons at 40–60% conversion of polypropylene and polyethylene over β-
zeolite. Product distribution has been demonstrated to depend on zeolite
pore size and surface acidity where HZSM-5 preferably generated C₃–C₅ products compared with HY, which delivered a higher yield of C₃–C₈ (Negelein et al., 1998; Hesse et al., 2001). The molecular sieving or shape
selectivity properties of microporous zeolites can be used to exert some
control over product composition. While the studies conducted to date have
considered ‘fresh’ catalysts, there is some evidence (Ali et al., 2003) that
‘used’ zeolites are effective in the processing of HDPE, which is significant
in terms of the cost of the overall feedstock recycle operation.

As hydrocracking is an exothermic process (Scheirs, 1998) it presents
advantages over the endothermic pyrolytic options. Moreover, hydropro-
cessing can facilitate a reduction in aromatic content and transform hetero-
atoms (e.g. O, N and S) that are present in the plastic waste. Hydrocracking
operation involves a complex network of hydrogenolysis, hydrogenation,
β-scission and isomerisation reactions (Weitkamp, 1975). High hydrogen
pressures are typically employed to hydrogenate coke precursors and
limit poisoning by sulphur-containing compounds (van Veen, 2002).
Hydrocracking catalysts must be bi-functional, containing a metal function
(Ni, Pd, Pt, Co/Mo, Ni/Mo and Ni/W) to promote hydrogen mediated steps
and an acid function (see Section 6.4.4) to catalyse cracking (and isomerisa-
tion) steps. The balance of both functions is critical in that a strongly acidic
catalyst with a relatively weak metal function will preferentially produce
naphtha (light product) with a high degree of isomerisation, resulting in a high octane number. On the other hand, a weak acidic function in combination with a very active metal phase will lead to a high quality middle distillate product. Hydrocracking has been applied in a two-step process to treat the product of a first stage thermal or catalytic pyrolysis (Ali and Siddiqui, 2005; Joo and Guin, 1997). The available literature deals with a range of feeds: polyethylene, polypropylene, polystyrene and mixed plastics (Ding et al., 1997; Walendziewski, 2002; Hesse and White, 2004); municipal plastic waste (Feng et al., 1996; Walendziewski and Steininger, 2001); co-processing of plastics with coal (Feng et al., 1996; Luo and Curtis, 1996; Rothenberger et al., 1997; Wang and Chen, 2004); co-mixing of polymers with different refinery oils such as vacuum gas–oil (Ucar et al., 2002; Karagoz et al., 2003b; Cakici et al., 2004). Processing to date has been limited to batch (autoclave, 30–120 bar) treatment with volumes ranging from 20 cm$^3$ to 1 dm$^3$ and temperatures in the range 623–723 K. Luo and Curtis (1996) have demonstrated an appreciable dependence of product yield and selectivity on the nature of the catalyst. Ding and co-workers (1997) have obtained a liquid fraction from comingled plastics that approaches a boiling point response close to that of commercial premium gasoline. More recently, Metecan et al. (2005) obtained a product with a yield >85% (from the hydrocracking of HDPE) that exhibited the characteristics of a commercial naphtha. However, in the majority of these studies the catalyst has been poorly characterised, if at all. Consequently there is a dearth of information that provides an explicit link between catalyst structure and hydroprocessing activity and selectivity.

### 6.6 Catalytic treatment of halogenated polymers: focus on polyvinyl chloride

The catalytic processing of halogenated plastics has been conducted in laboratory scale batch (Uddin et al., 1999, 2002), semi-batch (Brebu et al., 2002) and fixed bed (Sakata et al., 2003) reactors under atmospheric pressure. These unit operations involved the use of hydrogen. Catalytic hydrogen mediated dehalogenation is an emerging methodology for a low energy treatment of a range of halogenated waste streams involving the selective cleavage of one or more C–X bonds, lowering toxicity and generating reusable raw material (Keane, 2003). A distinction should be drawn between hydrodehalogenation and dehydrohalogenation, the former involving hydrogenolysis of C–X bonds. The latter describes the internal elimination of HX where an external hydrogen supply is not necessary but can serve to limit catalyst deactivation (Tavoularis and Keane, 1999). Urbano and Marinas (2001) have noted that the ease of C–X bond scission decreases in
the order R–I > R–Br > R–Cl >> R–F, which matches the sequence of decreasing bond dissociation energies. In the treatment of polychlorinated reactants, a range of partially chlorinated products have been obtained where product composition depends on the nature of the catalyst and process conditions, i.e. temperature, concentration, residence time, etc. (Shin and Keane, 2000). Hydrogen mediated dehalogenation has been successfully promoted using supported Pd (Coq et al., 1986; Bodnariuk et al., 1989), Pt (Creyghton et al., 1995), Rh (Coq et al., 1986; Ukisu and Miyadera, 1997) and Ni (Shin and Keane, 1999; Shin et al., 1999; de Jong and Louw, 2004) catalysts. Based on three comprehensive reviews of the available dehalogenation literature (Lunin and Lokteva, 1996; Urbano and Marinas, 2001; Alonso et al., 2002), it is clear that Pd is the most active metal. However, Pd catalysts suffer from appreciable deactivation with time-on-stream (Armendia et al., 1999). Catalyst deactivation has been attributed to coke deposition (Creyghton et al., 1995), the formation of surface metal halides (Park et al., 2002; Keane, 2004; Murthy et al., 2004) and metal sintering (Ohtsuka, 1989).

Thermogravimetric analysis of PVC has established a two-stage decomposition: c.60% mass loss up to 693 K corresponding predominantly to the evolution of HCl and the release of low molecular weight hydrocarbons; a secondary higher temperature mass loss (c.20%) attributed to the release of more complex volatile hydrocarbon species, including aromatics (Jiminez et al., 1993; Chatterjee et al., 1994; Keane, 2007). Below c.623 K, dehydrochlorination involving free radical reactions results in the formation of C=C bonds accompanied by the near stoichiometric evolution of HCl (Murty et al., 1996), i.e.

$$(-\text{CH} - \text{CHCl}-)_n \to (-\text{HC} = \text{CH} - \text{CH} = \text{CH}-)_n + n\text{HCL}$$

Above 623 K the dechlorinated polymer undergoes further cracking and pyrolysis to linear and cyclic compounds while the aromatic to aliphatic hydrocarbon ratio is reversed above 803 K (Yassin and Sabaa, 1990; Marcella and Beltran, 1995). It has been demonstrated that the incorporation of an alumina-supported Pd catalyst (Keane and Patterson, 2005; Keane, 2007) resulted in a marked enhancement in degradation rate, an increase in the product liquid fraction, a decrease in the liquid phase Cl content (by a factor of over 500) and an increase in the gas phase C1–C4 hydrocarbon content with a higher overall alkane content (ethane/ethylene in excess of 20). Sakata and co-workers have conducted a series of thermal and catalytic degradation of polyethylene/PVC and polypropylene/PVC mixtures (Lingaiah et al., 2001a,b; Sakata et al., 2003; Bhaskar et al., 2006). They found that catalytic dechlorination over Fe-based catalysts is effective in removing the Cl content as HCl but long-term catalyst stability remains.
an unresolved issue. The full extent of the catalytic impact in terms of product distribution has yet to be irrefutably established but the results suggest that catalytic dechlorination can be a feasible route to a Cl-free hydrocarbon product.

6.7 Future trends and conclusions

While the multiple applications of synthetic polymers are of considerable societal benefit, a build up of polymeric waste can have a deleterious effect on the environment. Although global environmental systems are extremely resilient, there is a limit to the pollution burden that can be sustained. Landfill or incineration do not represent best practicable environmental options. Research in catalytic feedstock recycle of waste polymers is still at the development stage. In the case of polyolefins, it has been established that the use of a catalyst serves to significantly lower the requisite operating temperature, which is an important consideration in terms of energy usage. Solid acids, notably zeolites, are now established as effective polymer degradation agents where preliminary results have demonstrated that some control is possible over product composition by varying zeolite acidity and pore structure. An explicit relationship between zeolite structure and performance will require further fundamental research but this is essential in order to facilitate process optimisation. In dealing with PVC waste, the Cl content must be removed in a controlled fashion as part of an overall recycle operation. Supported metal mediated dechlorination has a decided role to play in generating a Cl-free product, i.e. ultimate production of a fuel oil from a starting waste PVC. Future work must be directed at extending the limited database of catalytic waste plastic processing to consider a wider range of reaction conditions and alternative catalytic materials with a full assessment of the final product distribution. Control over product composition and catalyst reuse are critical in order to implement an economically sustainable recycling unit operation.

6.8 Sources of further information and advice

A wide range of academic journals are available that cover all areas of catalysis research. The Journal of Catalysis publishes original and scholarly contributions in the fields of heterogeneous and homogeneous catalysis with a particular emphasis on studies that relate catalytic function to fundamental chemical processes. Applied Catalysis publishes papers on all aspects of catalysis that is of practical interest. The Journal of Molecular Catalysis deals with research articles that consider molecular and atomic aspects of catalytic activation and reaction mechanisms. Other journals devoted to catalysis research include: Catalysis Letters; Catalysis
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Communications; Catalysis Today; Topics in Catalysis. The North American Catalysis Society (NACS) has an official web site (http://www.nacatsoc.org) that provides a range of general and specific information on catalysis developments with useful catalysis-related links. The International Association of Catalysis Societies also has a web site (http://www.iacs-icc.org) where details of upcoming meetings/conferences are posted. The Royal Society of Chemistry maintains a site (http://www.rsc.org/chemistryworld) where the latest developments in chemical technologies, many involving catalysis, are presented in a very clear and informative manner. Useful contacts for further information on plastics production, consumption and recycling include: Association of Plastic Manufacturers in Europe (APME); British Plastics Federation; British Polyethylene Industries PLC; Department for the Environment, Food and Rural Affairs (Defra). Topical issues relating to the polymer industry receive a comprehensive treatment in the European Plastics News and Plastics & Rubber Weekly magazines. The ‘wasteonline’ web site (http://www.wasteonline.org.uk) provides a valuable plastics recycling information sheet that is regularly updated. A comprehensive treatment of waste plastic reuse is provided in ‘Plastics in the UK Economy’, which is available to download from: www.wasteonline.org.uk. The Recycled Products Guide (available at www.recycledproducts.org.uk) provides a listing of products made from recycled plastics. Legislation which is particularly relevant to waste plastic recycling is the 1994 European Union Directive on Packaging and Packaging Waste 94/62/EC (the Packaging Directive). Croner (see http://www.croner.co.uk) is a useful resource providing information on environmental management, waste minimisation and legislation compliance.

6.9 References


