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## Additives for the Modification of Poly(Ethylene Terephthalate) to Produce Engineering-Grade Polymers

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### 1 INTRODUCTION

Glass-filled, toughened poly(ethylene terephthalate) (PET) resins can be readily moulded into highly impact-resistant structural parts for appliances and automotive components. The PET-based compounds are also suitable for construction (e.g. as structural members), equipment housings (e.g. printer and copier parts), agricultural applications (e.g. mower and tractor engine covers), materials handling (e.g. pallets and trays), furniture (e.g. office chair bases), as well as electrical and electronic applications.

PET may be considered a low-cost raw material for the production of engineering compounds due to its widespread availability from recycled beverage bottles. Its abundant availability and good molecular weight make it an excellent precursor for the production of toughened compounds that can in many cases compete directly with toughened and glass-filled nylons at a considerable cost advantage.

PET however, has numerous shortcomings from the perspective of an injection moulding compound. Unmodified PET is generally not useful as an injection moulding resin because of its slow crystallization rate and the tendency to embrittle upon crystallization. For these reasons, PET has not traditionally

found application in injection moulding processes. Unmodified PET can be injection moulded without difficulty only when relatively low mould temperatures (15–40 °C) are employed. Furthermore, the amorphous parts so formed tend to crystallize during heat treatment (annealing) and the resultant polymer is quite brittle. However, the abundant supply of both virgin and recycled PET has led to the development of strategies designed to overcome specific deficiencies through proper formulation. A variety of formulants can be added to PET resin to produce a formulated, engineering-grade thermoplastic. PET was not originally considered as an injection moulding material because of high moisture sensitivity, poor impact strength, excessive warpage when glass-fibre filled and slow rate of crystallization which slows the moulding cycle. However, it has a higher modulus, heat distortion temperature and gloss than poly(butylene terephthalate) (PBT). Such properties can only be fully realized if mouldings are crystalline.

As can be seen from Table 14.1, the primary drawbacks of PET apart from its hygroscopicity are its slow crystallization rate, the low glass transition temperature and relatively low impact strength. Formulation and compounding of PET can correct these shortcomings, enhance other properties, and tailor performance properties to meet specifications. The properties of PET can be modified and enhanced to such an extent that it can then be used in durable products such as appliance housings, electronics, furniture, transportation, and building and construction. Such PET resins have superior mechanical, thermal, electrical, chemical and environmental properties to conventional bottle-grade PET resins. These so-called engineering resins possess a balance of properties tailored to each durable application.

Unmodified, bottle-grade PET resin begins to soften and become rubbery at 80 °C. This makes the direct use of unmodified PET in engineered applications not feasible. For PET to be used in durable products it must be made highly crystalline and needs to be reinforced with glass fibres or mineral reinforcements.

**Table 14.1** Additives used in engineering-grade PET to overcome specific shortcoming of the base resin

Property deficiency	Remedy
Hygroscopicity	Internal desiccants
Slow to crystallize	Nucleating agents, plasticizers
Uneven crystal size	Nucleating agents
Low glass transition temperature	Glass fibres
Brittle fracture behaviour	Impact modifiers
Notch sensitivity	Impact modifiers
Drop in IV during extrusion	Chain extenders
Oxidation during extrusion	Stabilizers
Hydrolysis	Hydrolysis repair additives
Autocatalytic acid-catalyzed hydrolysis	Carboxyl scavengers
Warpage	Mineral fillers

Glass-filled PET has good load-bearing characteristics and low creep, with a coefficient of thermal expansion being similar to that of brass or aluminium.

PET is a semicrystalline polymer which, depending on fabrication conditions, can have a molecular structure that is amorphous, crystalline or semicrystalline. High crystallinity is desirable in products that require high temperature stability, dimensional stability and stiffness. Crystallinity can be induced in strapping, sheet and stretch blow moulded bottles by mechanical orientation. In the case of injection mouldings, however, crystallinity needs to be induced by chemical crystallization and precisely controlled to develop certain targeted properties in the finished product. Crystallinity in PET can be induced by using nucleating agents on which crystals can grow, in combination with a crystal growth promoter or accelerator.

Unmodified PET is too slow to crystallize to allow practical moulding cycles. Relatively recent advances in nucleation chemistry have allowed the development of specific PET moulding grades such as Rynite™ and Petra™ (by DuPont and Honeywell, respectively). Such PET engineering resins are high molecular weight, high performance materials used for a wide range of engineering applications. Their high crystallinity and low melt viscosity means that they are ideally suited for injection moulding of complex parts which require high strength, good dimensional stability, and insulation properties.

The rheological properties of conventional PET resins are also not particularly well suited for extrusion foaming with physical blowing agents and as a result modified resins with higher melt viscosity and melt strength/‘elasticity’ are often used. In contrast to the commonly used polystyrene and low-density polyethylene (LDPE) resins, extrusion foaming of PET is quite challenging. Most commercial PET resins of relatively low molecular weight (MW) and narrow molecular weight distribution (MWD) have rheological properties at processing temperatures that are not conducive to foaming. Modified PET resins with improved rheology and melt strength for applications such as foaming, extrusion blow moulding, or simply for upgrading low-intrinsic-viscosity materials, can be produced through chain extension/branching reactions with di- or polyfunctional reagents such as chain extenders.

## 2 CHAIN EXTENDERS

Chain extenders (or coupling agents) can serve to reverse the MW damage caused by hydrolysis of polyesters or can modify the rheology of the polymer to increase its melt strength. Chain extenders have at least two functional groups capable of addition reactions with the terminal hydroxyl (OH) or carboxyl (COOH) groups of the polyester resin. In principle, any bifunctional (or higher functionality) chemical that reacts fast with the end groups of polycondensates may be used for chain extension or coupling. However, in practice most compounds suffer from severe side reactions or produce undesirable byproducts which limit their applicability.

Raising the molecular weight (or intrinsic viscosity or IV) of PET is usually performed by solid-state polycondensation ('solid-stating'). Conventional solid-stating is generally performed in tumble driers under high vacuum and high temperatures for extended periods of time (12–20 h). Solid-stating is characterized by very high capital costs and high production costs (since it is a time-intensive batch process). Chain extenders, on the other hand, can be simply added to the polymer during extrusion (single- or twin screw-extrusion or compounding). Furthermore, chain extenders enable the production of a whole range of viscosities, starting with only one single base resin. The chain extender couples two equal end groups in a statistical manner, in a similar process to what happens during post-condensation. However, the reaction occurs in minutes rather than hours and also chain extension does not change the MWD compared with solid-stated polyesters. Thus the main advantages of chain extension compared with a post-condensation process are lower system costs, faster reaction and more flexibility, without the need for any extra investments.

'Traditional' chain extenders for PET are compounds such as bisanhydrides, bisoxazolines, bisepoxides, etc., which react with either –OH or –COOH end groups, or both. Careful use of the correct concentrations of chain extender can allow one to tailor the IV of PET without the need for solid-stating. Chain extenders are thus very useful for building molecular weight during melt processing. Terms such as 'reactive extrusion' and 'reactive chain coupling' are used to describe the processing of polyesters such as PET with chain extenders. The latter can upgrade PET by increasing the intrinsic viscosity of bottle-grade PET, for example, from ~0.8 dL/g to greater than 1.0 dL/g. The use of chain extenders during PET compounding with modifiers and glass fibres needs to be carefully controlled since as the molecular weight of PET increases, the extent of fibre breakage and shear-induced heating during extrusion also increase.

There is a wide range of chain extenders commercially available for PET (Table 14.2). Bifunctional chain extenders promote linear chain extension while tri- and tetra-functional chain extenders promote chain branching. Such reactive compounds are also known as 'repair additives' since they can reverse the molecular weight loss of hydrolytically damaged PET.

Bifunctional molecules such as diepoxides, diisocyanates, dianhydrides or bis(oxazoline)s have been shown to increase the molecular weight of PET [1, 2] by reacting with its terminal groups. Triphenyl phosphite [3, 4], as well as diimidodiepoxides [5], have also proved to react efficiently with PET while promoting molecular weight enhancement.

The most common chain extenders are the dianhydrides (also known as tetracarboxylic dianhydrides). The most common of these is pyromellitic dianhydride (PMDA). The latter can be used in synergistic combinations with hindered phenolic aromatic phosphates such as IRGANOX 1425 manufactured by Ciba Geigy [6–8]. The hindered phenolic aromatic phosphate is used at levels of 0.1–2.5 wt%. The hindered phenolic aromatic phosphate is an advantageous co-synergist since it

**Table 14.2** Chain extenders used to couple PET chains via reactive extension of end groups

Compound	Tradename	Manufacturer	Addition rate (wt%)
Pyromellitic dianhydride	PMDA	Nippon Shokubai Allco Chemical	0.05–2% and preferably around 0.15%–0.25% <sup>a</sup>
Trimellitic anhydride	TMA	–	–
Phenylenebisoaxazoline	PBO	Mikuni (Japan)	0.4–1.5, and preferably 0.4–0.6
Carbonyl bis(1-caprolactam)	Allinco CBC	DSM	–
Diepoxide bisphenol A-diglycidyl ether	Epon 1009 <sup>b</sup>	Shell	0.6
Diepoxide bisphenol A-diglycidyl ether	Epon 828 <sup>b</sup>	Shell	0.6
Tetraepoxide tetraglycidyl diaminodiphenylmethane resins (TGDDM)	MY721	Ciba SC	0.4–0.6
Triphenylphosphite	TPP	Various	0.2–0.8

<sup>a</sup> Note: Excess can lead to undesirable molecular branching and cross-linking. Chain branching can severely hamper the crystallization capability of PET and this may lead to a loss in performance properties.

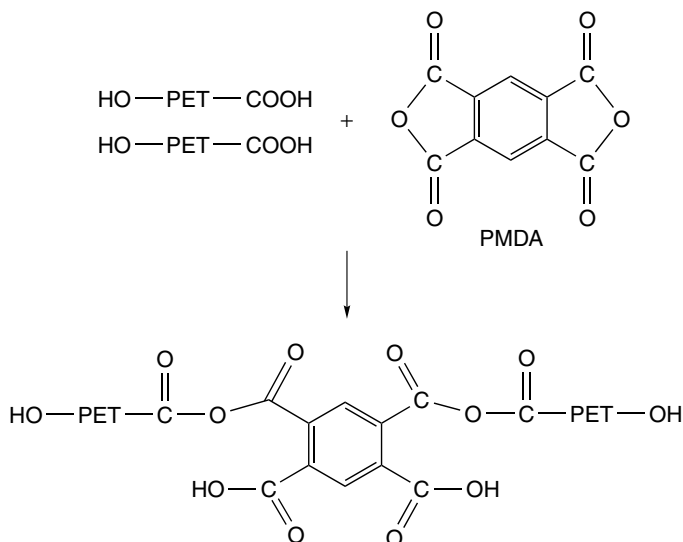
<sup>b</sup> Bisphenol A diglycidyl ether – prepared by a condensation reaction between epichlorohydrin and bisphenol A.

serves both as a solid-state-polymerization catalyst and a heat stabilizer to protect the PET from oxidation during solid-state polymerization.

Another highly effect chain extender is trimellitic anhydride (TMA) which gives rise to branching of the PET structure. Note that the multifunctional epoxies (see Table 14.2) react quickly with the terminal carboxylic acid groups of PET but can also react with the film former and the silane coupling agent on glass fibre reinforcements.

## 2.1 PYROMELLITIC DIANHYDRIDE

Pyromellitic dianhydride (PMDA) is generally used in PET at concentrations ranging from 0.05 to 2%. Reactive extrusion of PET with PMDA has been reported by Incarnato *et al.* [9]. These authors used PMDA to increase the molecular weight of PET industrial scraps sourced from a PET processing plant. They found that concentrations of PMDA between 0.50 and 0.75% promote chain extension reactions that lead to an increase of MW, a broadening of the MWD and branching phenomena which modify the PET scrap in such a way that makes



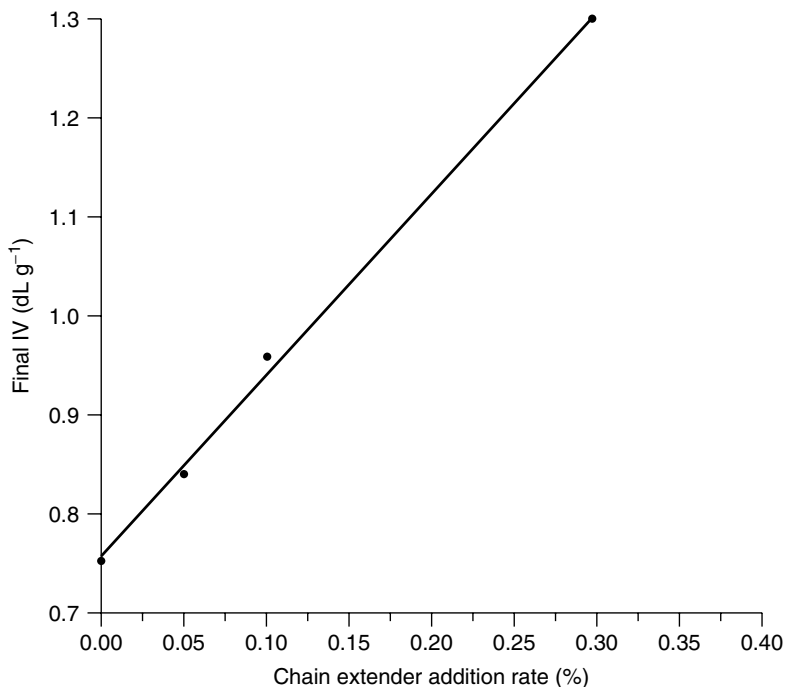
**Figure 14.1** Reaction of pyromellitic dianhydride (PMDA) chain extender with PET end groups (hydroxyl and carboxylic acid groups) to give chain extension and branching of PET

it suitable for film blowing and blow moulding processes. The reaction between PMDA and PET is shown in Figure 14.1. Pentaerythritol can be added as a synergist.

A dramatic improvement in the performance of PMDA in chain extension of PET is possible if the PMDA is added to the extruder in a concentrate using a polycarbonate (PC) carrier [10]. The reason being that if PMDA is compounded in a PET carrier resin then a premature reaction results leading to ultra-high MW PET and gel problems. Alternatively, if PMDA is compounded in a polyolefin carrier then degradation of the polyolefin occurs; whereas, when PMDA is compounded in a polycarbonate carrier there is no premature reaction because PC contains no acid end groups (rather,  $-\text{OH}$  end groups instead). Furthermore, PC is quite miscible with PET.

Aromatic carboxylic dianhydride chain extenders (e.g. PMDA) are a low-cost way of converting recycled PET flakes into high-IV crystalline pellets that can be used in high-value applications (e.g. bottles, strapping, foam, engineering alloys/compounds, etc.) (see Figure 14.2). PMDA is an effective chain extension additive for thermoplastic polyesters such as PET and PBT. It is suitable for the following applications:

- Enhancement of the intrinsic viscosity of PET and PBT
- Reactive extrusion of PET and PBT



**Figure 14.2** Effect of PMDA addition on the IV of PET bottle flake after extrusion at 280 °C

- Melt strength enhancement of PET and PBT for the production of blown polyester foams
- As a melt viscosity and melt-strength-enhancing additive for modifying PET for film blowing and extrusion blow moulding applications
- Tensile strength enhancement of PET and PBT for strapping applications without the need for solid-state polycondensation
- Upgrading of recycled PET flake to resin suitable for bottling applications (>0.80 dL/g)
- As an additive to reduce the time necessary for solid-phase polymerization of PET and PBT resins
- To increase the elongational viscosity of PET and PBT resins by facilitating extended and branched architectures

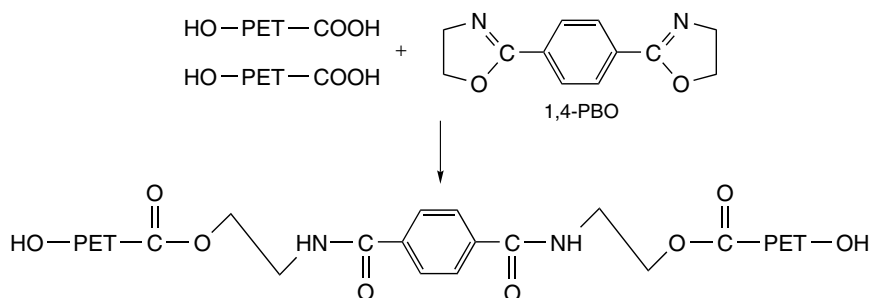
One of the main commercial uses of PMDA is to improve the melt strength of PET to allow it to be foamed. Unmodified PET cannot be foamed properly because its inherently low melt strength causes the cells to collapse and coalesce.

## 2.2 PHENYLENEBISOXAZOLINE

Both 1,3-phenylenebisoxazoline (1,3-PBO) and 1,4-phenylenebisoxazoline (1,4-PBO) are effective chain extenders for PET *via* the mechanism shown in Figure 14.3. PBO chain-extends PET by coupling together two terminal carboxylic acid groups. Effective use concentrations of PBO for PET are in the range 0.5–1.5 wt% and these can give an IV increase for PET of 0.2 IV units – that is, from 0.7 to 0.9 dL/g. The precise IV enhancement will depend on the carboxyl equivalent of the PET. Typical reaction conditions are 240 °C for 3 min. PBO also acts as a carboxyl group scavenger and in doing so increases the hydrolytic stability of the resultant PET. A concentration of 0.5 % PBO in PET can reduce the carboxyl content from 45 to 20 mmol/kg.

The product of the coupling reaction is an esteramide and no volatiles are emitted during the ring-opening reaction. The reaction is largely completed within the processing time (i.e. 3–5 min). The increase in viscosity can be adjusted by the amount of PBO. In practice, about 0.5 wt% is used. A 0.5 parts per hundred (phr) addition level of PBO in PET generally gives an intrinsic viscosity increase of about 0.2 dL/g. PBO can be used in combination with other chain extenders such as carbonyl bis(1-caprolactam) (CBC).

PBO is a very reactive compound towards PET containing carboxyl end groups but not hydroxyl end groups. Karayannidis [11] studied the effect of a PBO chain extender on the IV increase of PET during extrusion. Interestingly, these authors observed enhanced results when phthalic anhydride was added to the initial sample, before the addition of PBO. This technique succeeded in increasing the carboxyl groups by reacting phthalic anhydride with the terminal hydroxyl groups of the PET. After this initial modification of the PET sample, PBO was proved to be an even more effective chain extender. It was found that when using recycled PET with an IV of 0.78, a PET grade could be prepared having an IV



**Figure 14.3** Reaction of 1,4-PBO chain extender with PET end groups (carboxylic acid groups) to give linear chain extension of PET (leading to a polyamide–polyester); 1,4-PBO, 1,4-phenylenebisoxazoline



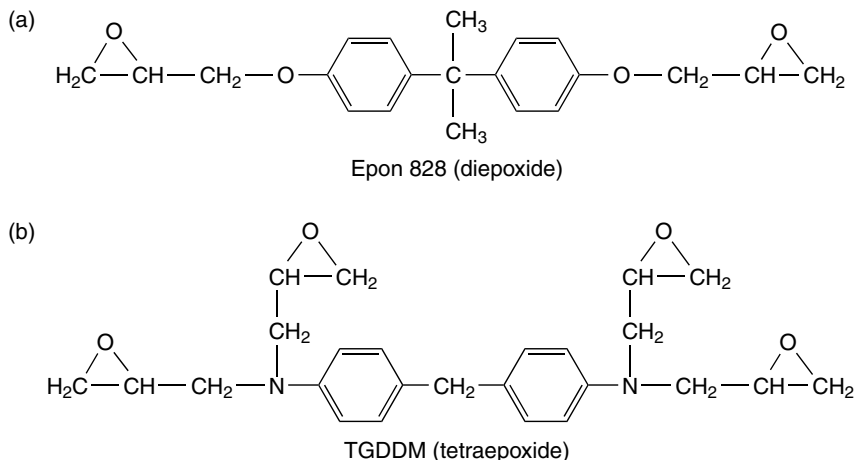
of 0.85 (or number-average molecular weight ( $M_n$ ) of 25 600) within about 5 min when using PBO as the chain extender.

### 2.3 DIEPOXIDE CHAIN EXTENDERS

Figure 14.4(a) shows the structure for a common diepoxide chain extender. Haralabakopoulos *et al.* [12] have reported that the molecular weight of PET increases *via* chain extension reactions with commercially available diepoxides. Low concentrations of extender and short reaction times generally favoured chain extension. In addition, purging with nitrogen resulted in chain extended polymers having the highest values of intrinsic viscosity (e.g. 0.82 dL/g).

PET chain-extended with a diepoxide as chain extender can exhibit varying degrees of branching and cross-linking depending on the level of chain extender used [13, 14]. The branched and cross-linked PETs exhibit significant improvement in tensile properties.

Bikiaris and Karayannidis [5] have investigated the use of diimidodiepoxides as chain extenders for PET resins. Starting with a PET having an IV of 0.60 dL/g and a carboxyl content (CC) of 42 eq/10<sup>6</sup> g, they obtained PET with an IV of 1.16 dL/g and a CC below 5 eq/10<sup>6</sup> g. The typical reaction condition for the coupling of PET was heating with the chain extender under an argon atmosphere above its melting temperature (280 °C) for several minutes.



**Figure 14.4** Chemical structures of two common epoxy chain extenders for PET: (a) a diepoxide, e.g. Shell Epon 828, based on bisphenol A diglycidyl ether; (b) a tetraepoxide, e.g. Ciba MY721, based on tetraglycidyl diaminodiphenyl methane (TGDDM)

## 2.4 TETRAEPOXIDE CHAIN EXTENDERS

Figure 14.4(b) shows the structure for a common tetraepoxide chain extender. Reactive processing of recycled PET with a tetrafunctional epoxy additive induces randomly branched molecules which gives rise to a corresponding increase in elongational melt viscosity. This enables the PET to be foamed and allows the production of closed-cell foams [15, 16]. The tetrafunctional tetraglycidyl diamino diphenyl methane (TGDDM) (CIBA SC, MY721) is particularly efficient [17].

The use of multifunctional epoxy-based modifiers to increase the melt strength of PET has been investigated in detail by Japon *et al.* [15, 16], with the aim of producing PET foams by an extrusion process. TGDDM resin was selected for the investigation of the modifier concentration effect on the reaction conversion. Using a stoichiometric concentration of TGDDM, the molecular weight distribution of modified PET, as determined by gel permeation chromatography, showed an eightfold increase of the *Z*-average molecular weight and the presence of branched molecules of very large mass. The resulting intrinsic viscosity of the modified PET was 1.13 dL/g.

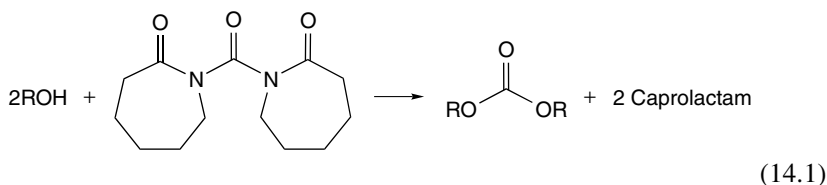
The chain extension of polyesters in the melt using a high-reactivity diepoxy, diglycidyl tetrahydrophthalate, has been studied in detail by Guo [18]. The diepoxy reacts with the hydroxyl and carboxyl end groups of polyesters such as PET at a very fast reaction rate and a relatively high temperature. The melt flow index of the chain extended polyesters dramatically decreased as the diepoxy was added to the polyester. In addition, the notched Izod impact strength and elongation-at-break of the chain extended polyesters was also found to increase. The chain extended polyesters are also more stable thermally. Compared with the conventional solid post-polycondensation method, this approach is a simpler and cheaper technique for obtaining high-molecular-weight polyester resins.

## 2.5 PHOSPHITES CHAIN EXTENSION PROMOTERS

The molecular weight and polydispersity of the recycled PET melt processed with organic phosphites was studied by Nascimento and Dias [19]. Some of the phosphites act as chain extending catalysts, so increasing the polymer's molecular weight. Superior chain extension results were obtained with triarylphosphites, while dialkyl- and trialkylphosphites promoted PET degradation. The study showed that triphenylphosphite was the best chain extender used in this study. The occurrence of transesterification reactions in PET/PEN blends prepared in the presence of triphenylphosphite (TPP) was investigated by Dias and Silva [20]. When PEN was processed with TPP, which is a known chain extender for PET, chain extension reactions also took place. Although transesterification inhibition was expected, this type of reaction was not suppressed by TPP.

## 2.6 CARBONYL BIS(1-CAPROLACTAM)

One of the newest chain extenders for PET is carbonyl bis(1-caprolactam) (CBC). The latter is a free-flowing white powder with a melting point of approximately 115°C. CBC reacts with terminal hydroxyl functional groups on the PET chains during the processing of polyesters forming carbonate, urethane and urea linkages, according to the following reaction [21]:



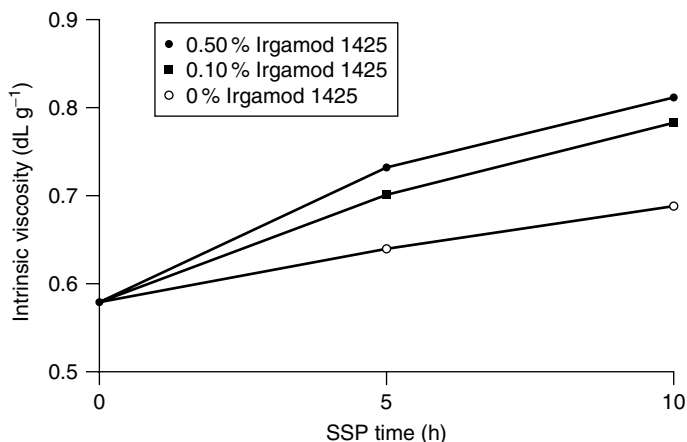
where R is the PET molecular chain.

During this reaction, some caprolactam is also liberated. The reaction is largely completed within the processing time (typically 3–5 min). The increase in intrinsic viscosity of PET can be adjusted by the amount of CBC. In practice, about 0.5 wt% of CBC is typically used. CBC is commercially available under the trade-name ALLINCO<sup>®</sup> (DSM, Geleen, The Netherlands). ALLINCO<sup>®</sup> is one of the most effective chain extender systems available for PET [21, 22]. CBC is often used in combination with PBO for an enhanced chain extension effect. Typically, the relative viscosity of PET is increased from 1.6 to 2.0 with a stoichiometric amount of CBC + PBO (ca. 1.2 wt%) in a single-screw extruder at 300°C.

## 3 SOLID-STATING ACCELERATORS

PET is a material that finds widespread use for soft drink and beverage bottle applications. For injection or blow moulding applications, high-molecular-weight PET  $M_n > 30\,000$  is required. While PET with  $M_n$  of 15 000 – ~25 000 can be achieved by a standard melt-polymerization process, the high-molecular-weight PET grades require a solid-state polymerization process. Commercial solid-state polymerization process systems are usually composed of a crystallizer and a polymerization reactor. First, melt-polymerized chips are fed into the crystallizer unit and crystallized to the extent of about 40%. In a second step, the crystallized chips are fed into a polymerization reactor vessel and then polymerized in the solid state at a temperature of around 220°C.

Solid-state polycondensation (SSP) is thus a technique applied to thermoplastic polyesters to raise their molecular weight or IV. During solid-state polycondensation, the polymer is heated above the glass transition temperature and below the melt temperature of the polymer either under an inert gas or under vacuum. Increasing the intrinsic viscosity requires a residence time of up to 12 h under vacuum or under inert gas, at temperatures from 180 to 240°C.



**Figure 14.5** Effect of a commercial solid-stating accelerator (Irgamod 1425) on the rate of intrinsic viscosity enhancement of PET (data obtained from Ciba Specialty Chemicals)

Solid-state polycondensation of thermoplastic polyesters such as PET is therefore both time-consuming and energy-intensive. Recently, additives have been developed to accelerate this process [23, 24]. Such additives enable PET with a very high IV to be produced at reduced residence times in the solid-state reactor, with enhanced outputs and at a reduced cost. Such additives accelerate the IV enhancement of PET at low cost. One such SSP accelerator is Irgamod 1425 which when used in PET at levels of between 0.1–0.5 wt% gives an SSP acceleration of approximately 50% (see Figure 14.5).

Typically, an IV enhancement of 0.10 dL/g requires 10 h of solid-stating. In the presence of an SSP accelerator, this time is reduced to just 5 h. Irgamod 1425 also contributes to reduced yellowing of the PET resin. For instance, 0.1 wt% can lead to a drop in *b* value (yellowness) from 1.1. to –2.9. Such SSP accelerators are based on sterically hindered hydroxyphenylalkylphosphonates such as calcium bis-ethyl-3,5-di-*t*-butyl-4-hydroxyphosphonate. Pfaendner *et al.* [24] details the use of Irganox 1425 (CAS 65140-91-2)<sup>1</sup> to accelerate the solid-stating of PET.

#### 4 IMPACT MODIFIERS (TOUGHENERS)

Impact modifiers for PET are generally elastomeric compounds that increase impact strength and elongation while usually decreasing modulus. An effective way to enhance the impact strength and to induce a brittle/ductile transition of the fracture mode, is by the dispersion of a rubber phase within the PET matrix. The

<sup>1</sup> Chemical Abstracts Service (CAS) Registry Number.

main role of the rubber particles is to induce an overall deformation mechanism rather than a localized phenomenon, thereby strongly increasing the amount of dissipated fracture energy. The effectiveness of rubber modification is found to be highly dependent on the following:

- the rubber and compatibilizer type
- the rubber content
- the rubber particle size
- the interparticle distance

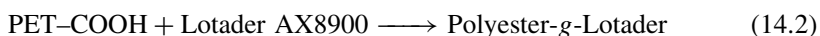
The basic mechanism of toughening is one of void formation and shear band formation (cavitation) when stress is applied.

#### 4.1 REACTIVE IMPACT MODIFIERS

In order to obtain a finely sized dispersed phase in the PET matrix, the use of reactive compatibilization has been found to be important. Small dispersed rubber particles and a small interparticle distance are necessary to induce high toughness. For effective rubber toughening of PET, it is important that the rubber domains be less than  $3\ \mu\text{m}$  in diameter (and preferably less than  $1\ \mu\text{m}$ ) and that the interparticle distance be between 50–300 nm.

Reactive impact modifiers are preferred for toughening of PET since these form a stable dispersed phase by grafting to the PET matrix. Non-reactive elastomers can be dispersed into PET by intensive compounding but may coalesce downstream in the compounder. Reactive impact modifiers have functionalized end groups. Functionalization serves two purposes – first, to bond the impact modifier to the polymer matrix, and secondly to modify the interfacial energy between the polymer matrix and the impact modifier for enhanced dispersion. Some examples of commercially available reactive impact modifiers for PET are shown in Table 14.3. An example of a *non-reactive* elastomer that can be used in combination with *reactive* impact modifiers is ethylene methyl acrylate (EMA), such as the Optema™ EMA range of ethylene methyl acrylates manufactured by the Exxon-Mobil Chemical Company (see Section 4.2).

Functionalized (reactive) elastomers such as Lotader AX8900 (see Figure 14.6) are excellent toughening agents for PET as they improve interfacial adhesion and importantly, reduce interfacial tension, thus allowing the formation of smaller rubber particles (Figure 14.7). Furthermore, a grafting of the elastomer to the PET matrix occurs according to the following reaction:



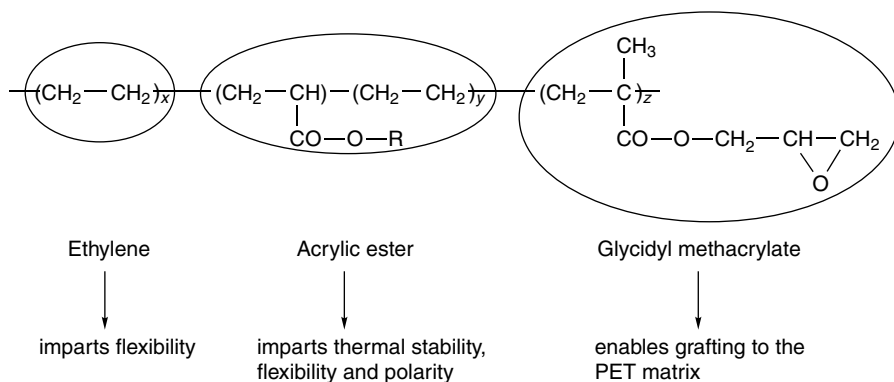
The chemical reaction between glycidyl methacrylate (GMA) end groups on the reactive elastomer and the carboxylic acid end groups of PET is shown in

**Table 14.3** Commercial reactive impact modifiers for PET

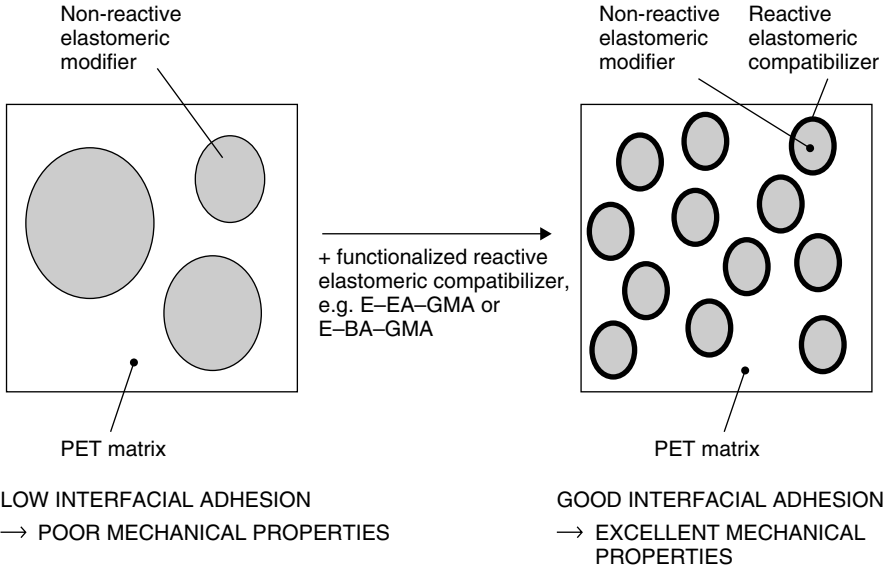
Elastomeric toughener <sup>a</sup>	Tradename	Manufacturer
E-EA-GMA (67:25:8) (ethylene-ethyl acrylate-glycidyl methacrylate terpolymer)	Lotader AX8900 <sup>b</sup>	Atofina
E-EA-GMA (68:24:8) (ethylene-ethyl acrylate-glycidyl methacrylate terpolymer)	Lotader 8860 Lotader 8840	Atofina
E-BA-GMA (63:31:6) (ethylene-butyl acrylate-glycidyl methacrylate terpolymer)	Elvaloy PTW	DuPont
E-VA-MA (ethylene-vinyl acetate copolymer, functionalized with maleic anhydride)	Exxelor VA1803	Exxon
SEBS-MA (styrene-ethylene butylene-styrene terpolymer, functionalized with maleic anhydride)	Tuftec M1943 Kraton G1652 Kraton FG1921X	Asahi Kasei Company Kraton

<sup>a</sup> Note: GMA is essentially an epoxy functionality.

<sup>b</sup> Lotader AX8900 is often used in combination with a non-reactive elastomeric toughener such as Lotryl (ethylene ethyl acrylate (EEA)). For example, a 30:70 blend of these two tougheners is a highly effective impact modifying system for PET.



**Figure 14.6** Simplified structure for random ethylene-acrylic ester-glycidyl methacrylate terpolymers which are effective rubber tougheners for PET compounds. The ethylene-acrylic ester segments provide elastomeric properties while the glycidyl methacrylate functionalities enable reactive grafting to the PET matrix via the hydroxyl and carboxyl chain ends of the latter



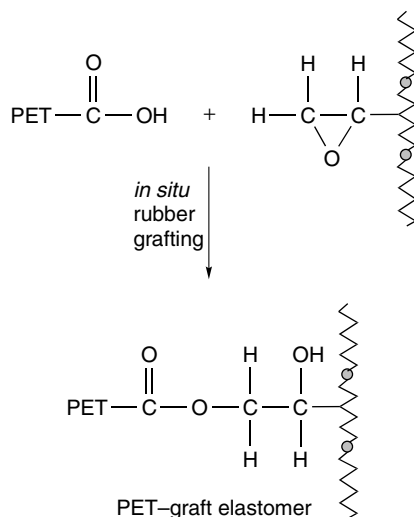
**Figure 14.7** Schematic highlighting the microstructure of rubber-toughened PET and performance improvements when non-reactive elastomers are blended with reactive elastomers (adapted from Atofina literature entitled 'Lotader® and Lotryl®')

Figure 14.8. This reaction is critical in ensuring the reactive elastomeric toughener becomes grafted to the PET matrix and forms smaller, uniform domains of a rubber dispersed phase.

Reactive tougheners such as Lotader GMA AX8900, AX8920 and AX8930 exhibit high reactivity with PET and induce a fine and homogeneous dispersion of rubber domains throughout the PET matrix. Figure 14.9 clearly illustrates the superior toughening effect afforded by reactive tougheners as opposed to non-reactive tougheners.

Figure 14.10 shows the microstructure of PET containing 20% of a reactive toughener (Lotader AX8900). The rubber domains have been selectively removed by solvent to provide contrast enhancement. Note that the scale bar is 5 μm long and that the rubber domains are consistently smaller than 1 μm. This fine morphology enables the production of 'supertough' PET with notched Izod impact strengths exceeding 700 J/m.

Elastomers with reactive end groups such as maleic anhydride (MA) or glycidyl methacrylate (GMA) are preferred for toughening PET. The reason that they are so effective is that they form a graft copolymer by reaction with the PET hydroxyl and carboxyl end groups (as shown below). The graft copolymer then acts as an emulsifier to decrease the interfacial tension and reduce the tendency



**Figure 14.8** Grafting reactions between PET end groups and glycidyl-methacrylate-containing rubber tougheners. This reaction is critical in ensuring that the reactive elastomeric toughener becomes grafted to the PET matrix and forms smaller, uniform domains of a rubber dispersed phase

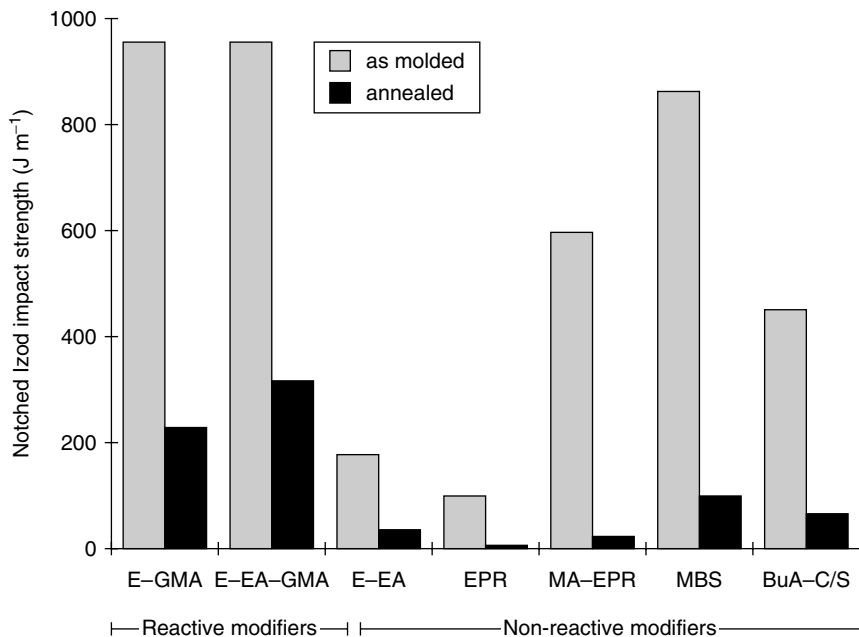
of the dispersed rubber particles to coalesce during processing. Furthermore in the solid state the graft copolymer promotes adhesion between the phases and facilitates cavitation in a triaxial stress state.

The use of maleic-anhydride-functionalized styrene-ethylene butylene-styrene (SEBS) elastomers (e.g. Kraton G1652 and Kraton FG1921X) to toughen PET has been reported by Tanrattanakul *et al.* [25]. Interestingly, particles of functionalized SEBS were primarily spherical in injection moulded blends, while in the unfunctionalized SBS blends the particles were highly elongated. The functionalized SEBS-PET blends exhibit far superior impact strengths compared to the unfunctionalized blends. It was found that the improvement in impact strength with the functionalized elastomers was related to a decrease in the rubber domain particle size. As little as 1% SEBS-*g*-MA in PET can increase the fracture strain by more than ten times. The graft copolymer acts as an emulsifier to decrease interfacial tension and reduce the tendency of dispersed particles to coalesce, and also importantly promotes adhesion between the phases in the blend.

#### 4.2 NON-REACTIVE IMPACT MODIFIERS (CO-MODIFIERS)

Most non-reactive (unfunctionalized) elastomeric impact modifiers such as general purpose rubbers, are not highly effective at toughening polyesters because they are unable to adequately interact with the polyester matrix so as to achieve



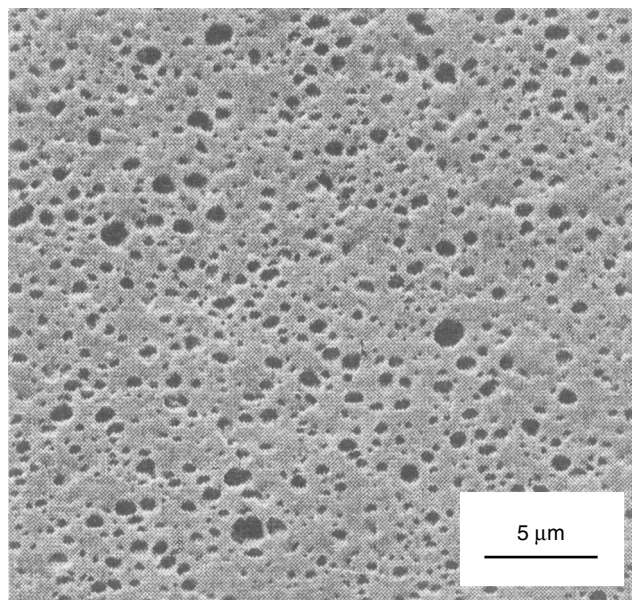


**Figure 14.9** Effect of various impact modifiers (25 wt%) on the notched Izod impact strength of recycled PET (as moulded and annealed at 150 °C for 16 h): E-GMA, glycidyl-methacrylate-functionalized ethylene copolymer; E-EA-GMA, ethylene-ethyl acrylate-glycidyl methacrylate (72/20/8) terpolymer; E-EA, ethylene-ethyl acrylate; EPR, ethylene propylene rubber; MA-GPR, maleic anhydride grafted ethylene propylene rubber; MBS, poly(methyl methacrylate)-*g*-poly(butadiene/styrene); BuA-C/S, poly(butyl acrylate-*g*-poly(methyl methacrylate) core/shell rubber. Data taken from Akkapeddi *et al.* [26]

optimally sized dispersed phases and strong interfacial bonding. Non-reactive elastomeric tougheners based on random ethylene-acrylic ester copolymers are effective impact modifiers for PET compounds however, if appropriate compatibilizing polymers are used. Some examples of these systems are shown in Table 14.4. Figure 14.11 shows the effect of blending a mixture of reactive and non-reactive ethylene copolymers (E-EA-GMA + EEA = 20 %) on the notched Izod impact strength of PET.

#### 4.2.1 Core-Shell Elastomers

MBS (methyl methacrylate-butadiene-styrene) graft copolymers are known as one of the most efficient non-reactive impact modifiers for PET and also poly(vinyl chloride) (PVC). MBS is used commercially as an effective impact modifier for PET recycle [27]. Typical MBS rubber particles contain an elastomeric core of

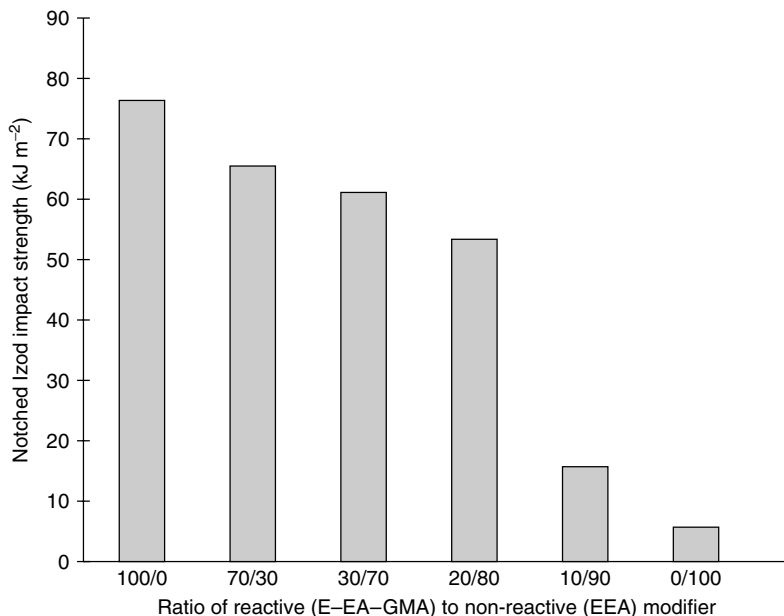


**Figure 14.10** Electron micrograph of PET + 20 % E–EA–GMA (reactive toughener – Lotader AX8900) showing the size and distribution of the rubber particles (note the 5  $\mu\text{m}$  scale bar). The rubber domains have been selectively etched out by solvent to provide contrast enhancement

**Table 14.4** Commercial non-reactive impact modifiers for PET

Compound	Tradename	Supplier
EMA (ethylene–methyl acrylate copolymer)	Optema™ EMA	Atofina Exxon-Mobil
EEA (ethylene–ethyl acrylate copolymer) <sup>a</sup>	Lotryl EEA	Union Carbide
EBA (ethylene–butyl acrylate copolymer)	Lotryl	Atofina
MBS (poly(methyl methacrylate)- <i>g</i> -poly(butadiene/styrene) graft copolymer)	Paraloid EXL	Rohm & Haas
Core/shell acrylate	Durastrength 400	Atofina

<sup>a</sup> E–EA–GMA (see Table 14.3) and EEA are often used in combination as a toughening system. The optimum blend ratio of reactive elastomers:non-reactive elastomers (e.g. Lotader:Lotryl) is 30/70. Since the E–EA–GMA terpolymer and EEA copolymer are mutually miscible, when blended together with PET the mixture acts as a single elastomeric phase, which is interfacially grafted to the PET continuous phase.



**Figure 14.11** Variation of the notched Izod impact strength of PET containing 20% of an elastomeric toughening system as a function of the ratio of reactive to non-reactive modifier. It can be seen that the 30:70 reactive:non-reactive mixture provides the optimum balance. The reactive modifier acts more as a compatibilizer in this system. Note: units for impact strength ( $\text{kJ m}^{-2}$ ) can be converted to  $\text{J m}^{-1}$  by multiplying by 10

styrene-*co*-butadiene random copolymer and a glassy shell composed of styrene and methyl methacrylate. MBS impact modifiers such as Paraloid EXL (Rohm & Haas) are effective tougheners for PET resins, especially those used for crystalline PET (CPET) applications which require low-temperature impact. The dispersion of small rubber 'core-shell' particles afforded by MBS tougheners provides PET with an excellent level of toughness, without strongly affecting other mechanical or thermal properties. The unique core-shell structure is obtained by copolymerization of a hard shell around a soft rubber core. This structure provides excellent impact properties to the PET due to the presence of the soft rubber core, without strongly affecting the matrix rigidity by virtue of the hard outer shell. In addition, since the core-shell structure is produced by emulsion copolymerization it provides a well-defined particle size which in turn leads to a well-controlled blend morphology. Grades of Paraloid EXL intended for PET modification include EXL 3300 and EXL 5375. Another impact modifier for PET is the core-shell modifier marketed under the trademark EXL 2330. Such impact modifiers are generally added at levels of around 10 wt%.

The PARALOID EXL range also includes PARALOID EXL 2314, an acrylic impact modifier with reactive functionality for PET impact modification.

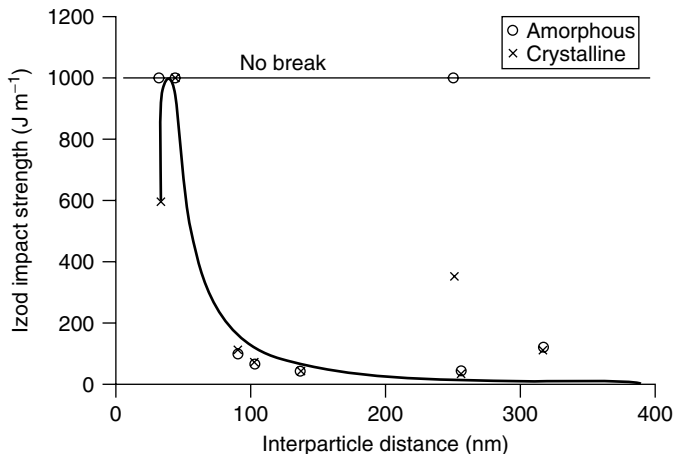
### 4.3 THEORY OF IMPACT MODIFICATION OF PET

The following equation relates the interparticle distance ( $ID$ ) to the volume fraction of the impact modifier ( $\phi$ ) and the weight-average particle size ( $dW$ ) [28]:

$$\bullet ID = [(\pi/6\phi)1/3 - 1]dW \quad (14.2)$$

Figure 14.12 shows that the impact strength increases sharply as the interparticle distance is reduced. The toughness increases as the interparticle distance decreases to a critical size, but becomes lower again as the distance becomes too small. It can be seen that the critical interparticle distance for PET is 50 nm.

Pecorini and Calvert [28] attribute the role of small particles and a small interparticle distance to inducing high toughness in PET by promoting massive shear yielding in the matrix. Their study showed that the non-reactive impact modifier gives a system in which the rubber phase is not well dispersed. It was shown that this is not effective in toughening PET at levels of either 10 or 20%. The



**Figure 14.12** Notched Izod impact strength data (on crystallized PET) for samples of toughened polymer as a function of the ratio of interparticle distance: O, amorphous; x, crystalline [28]. Reprinted with permission from Pecorini, T. J. and Calvert, D., in *Toughening of Plastics – Advances in Modelling and Experiments*, Pearson, R. A., Sue, H.-J. and Yee, A. F. (Eds), ACS Symposium Series, 759, American Chemical Society, Washington, DC, 2000, Ch. 9, pp. 141–158. Copyright (2000) American Chemical Society

**Table 14.5** Effect of impact modifier type, particle size and interparticle distance on the impact strength and elongation of PET

Property	Non-reactive modifier <sup>a</sup>	Non-reactive modifier <sup>a</sup>	Reactive modifier <sup>b</sup>	Reactive modifier <sup>b</sup>
Content (wt%)	10	20	10	20
Particle size ( $\mu\text{m}$ )	0.45	0.53	0.16	0.13
$ID^c$ ( $\mu\text{m}$ )	0.25	0.14	0.09	0.03
Izod impact strength (J/m)	35	45	118	659
Elongation at break (%)	8	7	16	65

<sup>a</sup> Non-reactive impact modifier (copolymer of ethylene and methyl acrylate).

<sup>b</sup> Reactive impact modifier (terpolymer of ethylene, methyl acrylate and glycidyl methacrylate).

<sup>c</sup> Interparticle distance, i.e. the average distance between particles of impact modifier in the PET matrix.

reactive impact modifier, on the other hand, gives far superior impact strengths and can produce a material with 'supertoughness' (Table 14.5).

## 5 NUCLEATING AGENTS

One of the primary limitations of PET is related to its slow rate of crystallization from the melt. A consequence of this is that relatively long cycle times are required to provide crystallinity in PET. When this is achieved, it is often accompanied by opacity and brittleness, due to the relatively large size of crystallites formed by thermal crystallization. Crystallinity itself is often desirable in moulded parts, due to the higher thermal and mechanical stability associated with it. Crystallinity is especially desirable when parts are intended to be subjected to elevated temperatures since if the PET components are amorphous they will anneal at temperatures above 80 °C.

It is well known that PBT crystallizes much faster than PET and hence PBT is the preferred polyester resin for injection moulding. Unmodified PET cannot be injection moulded to give crystalline parts with economical cycle times. Because PET is an intrinsically slow-crystallizing polymer, nucleating agents are often used to increase the rate of crystallization. In fact, in order to use PET in injection moulding applications, nucleating agents are essential.

Quick cooling of the PET melt results in the formation of small spherulites but the crystallinity, however, remains low because the polymer is practically 'frozen' in its amorphous state. Slow cooling of the PET, on the other hand, leads to a high degree of crystallinity; however, the spherulites grow to a large size at which optimum mechanical properties are not attained. In addition, an uneven spherulite size distribution results. Achieving a high degree of crystallinity and small spherulites in PET simultaneously requires the use of nucleating agents and crystallization promoters. While inorganic nucleating agents such as talc are

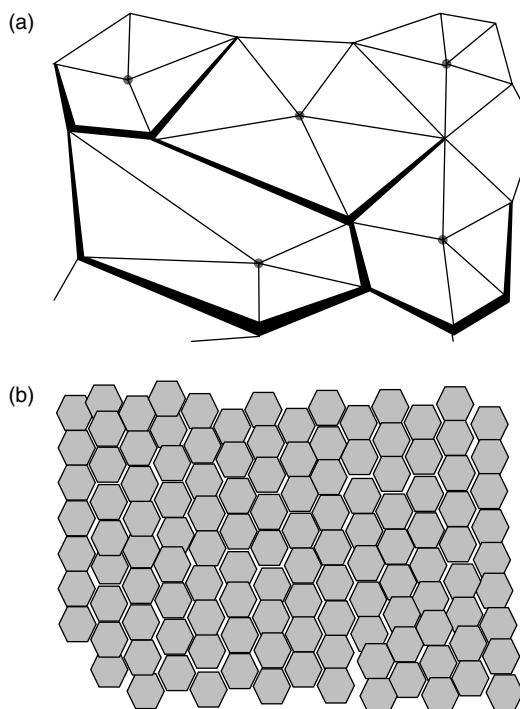
somewhat effective in nucleating PET, it has been found that alkali metal salts of high-molecular-weight carboxylic acids are far more effective. The reason for this is that compared to inorganic nucleating agents which reside in the PET as discrete particles, the organic salts can be distributed throughout the PET matrix at a smaller scale and more homogeneously.

Nucleating agents in PET serve two main functions, as follows:

- To induce a small and regular crystalline structure (Figure 14.13).
- To suppress large crystal growth which causes brittleness.

Additional functions of the nucleating system include the following:

- To decrease demoulding time (i.e. decrease cycle time for the part).
- To allow the material to crystallize at a uniform rate in the mould which tends to result in lower moulded-in stresses.



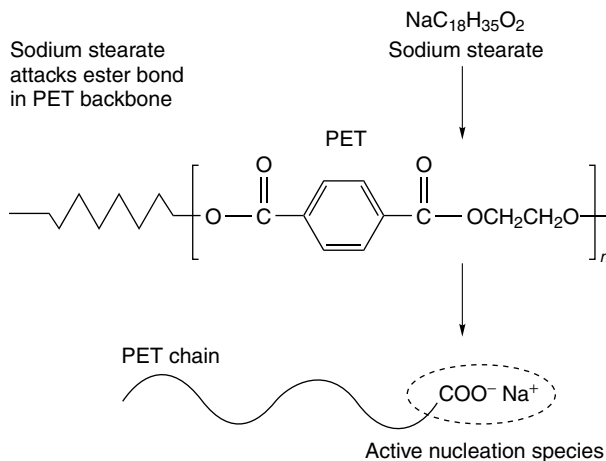
**Figure 14.13** Effect of a nucleating agent on the spherulitic morphology of PET. (a) Without a nucleator, PET forms large and irregular crystallites. Mouldings are brittle since low-molecular-weight material are concentrated at the crystal boundaries. (b) With a chemical nucleating agent, PET gives a much more regular spherulitic microstructure and this translates to improved mechanical properties

- To override any effect that particulate impurities or polyolefin contamination would have in modifying the crystallization behaviour of recycled PET.

As mentioned above, PET can be nucleated physically (by heterogeneous particulates, e.g. talc particles) and chemically (by a chemical reaction). PET grades for injection moulding are usually chemically nucleated – that is, nucleating agents take part in a chemical reaction with the polymer which leads to the formation of an *in situ* nucleating species. PET is generally chemically nucleated by certain sodium salts such as sodium stearate. The high nucleation efficiency of sodium stearate is not due to the additive itself, but to the products created by reaction with PET. The precise mechanism of this type of nucleation in PET has been identified by Legras *et al.* [29–31]. Sodium stearate reacts with the ester linkages of the PET, creating sodium carboxylate chain ends (Figure 14.14). These have been shown to be effective nucleating species.

While this is an effective nucleation mechanism for PET, the efficiency of this system is not stable and decreases significantly with melt mixing (compounding) time. This instability is due to a disproportionation reaction in which the sodium chain ends react with each other to give disodium terephthalate. The subsequent decrease in ionic chain end concentration is directly linked to the loss in nucleation efficiency.

The main factors determining the efficiency of sodium salts of organic acids as nucleating agents for PET are alkalinity, solubility and thermal stability. These are widely varying for different families of products and a compromise has to be made between these properties. The more soluble and the more stable, then the



**Figure 14.14** Sodium stearate is an efficient nucleating agent for PET since it scissions an ester bond and creates an ionic chain end which acts as the primary nucleation site. The disadvantage of this form of nucleation is that it leads to a reduction in the molecular weight of the polymer

more salt will react with PET. The counterion also has an influence but sodium usually offers the best compromise between reactivity for the nucleophilic attack of PET and thermal stability of the nucleating agent. The active nuclei are the platelet-like ionic chain ends. The size (and probably the crystal habit) of the nucleating molecules may also be considered as there seems to be an optimum corresponding to an optimal size of the platelet-like ionic chain ends aggregates which are thought to be the active nuclei [32].

It is not only sodium salts of monocarboxylic acids that are effective nucleating agents for PET; lithium, calcium and barium salts of monocarboxylic acids have also been found to impart nucleation ability [33].

Since chemical nucleating agents actively scission PET chains as part of their action, a drop in PET intrinsic viscosity can result. One strategy to offset this accompanying molecular weight reduction is to use both a nucleating agent and a chain extender in combination.

Due to both the limited thermal stability of sodium stearate during melt mixing and the molecular weight reduction accompanying chemical nucleation, another type of nucleating action is also employed. This is based on incorporating into the polymer a small percentage of melt-compatible resin which already contains sodium carboxylate chain ends rather than creating them *in situ*. Such ionomers have negatively charged acid groups which have been partially neutralized with sodium ions (see Figure 14.15). The nucleating system for commercial PET injection moulding compounds is thus typically based on a three-component package comprising the following:

- (i) sodium stearate (chemical nucleating agent)
- (ii) sodium ionomer (melt-miscible nucleating agent)
- (iii) poly(ether ester) (plasticizer to facilitate chain folding)

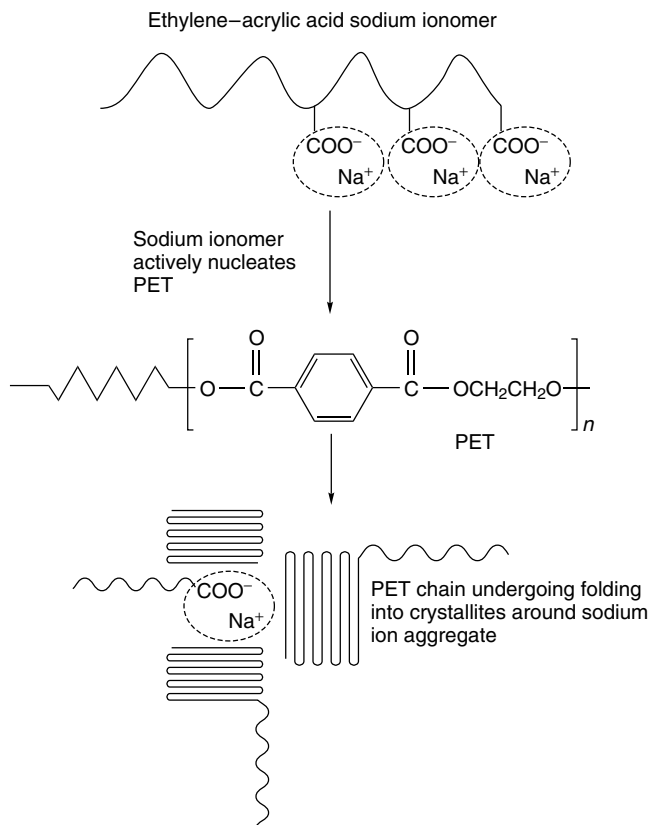
The use of nucleating agents in PET is not only intended for increasing the rate of crystallization and the crystallization temperature but also for forming a more homogeneous morphology, that is, a more uniform spherulite distribution.

Nucleating agents in PET also allow faster demoulding times, that is, the injection moulded part can be ejected from the mould more quickly or at a higher temperature.

Sodium ionomers are commercially recognized as the most effective nucleating agents for PET compounds. The typical use rate of sodium ionomer-based nucleating agents is 3–4 wt%. The sodium salt of poly(ethylene-*co*-methacrylic acid) is a particularly effective nucleating agent for PET.

Some examples of common nucleating agents used for PET are shown in Table 14.6. Aclyn ionomers (by Honeywell – formally Allied Signal) have proven to be highly efficient nucleating agents for PET and do not cause loss of MW. Use levels as low as 0.25 % promote rapid crystallization of PET. Such nucleators are particularly suited to thermoforming of PET trays where increased production rates can be achieved. Specifically, Aclyn 285 is particularly effective for lowering the crystallization onset temperature for PET, as shown in Table 14.7.





**Figure 14.15** Mechanism of PET nucleation by sodium ionomers. A particular advantage of such compounds is that they provide active nucleation sites without molecular chain scission

Sodium-neutralized salts of montanic acid (e.g. Licomont NaV) are also effective nucleators for PET. Montanic wax consists of a mixture of straight-chain, saturated carboxylic acids with chain lengths in the range of 26 to 34 carbon atoms. The low volatility and high thermal stability of montanic acid waxes makes them a suitable nucleating agent for engineering plastics such as PET and PBT.

Phyllosilicates are clay-related compounds with a sheet structure such as talc, mica, kaolin, etc. for which the nucleation mechanism of PET is known to be heterogeneous, although still uncertain.

Nanoclay particles by virtue of their particulate nature are emerging as effective heterogeneous nucleating agents for polyesters. The nanoclay particles in PET/montmorillonite nanocomposites impart to PET a higher crystallization rate without the need for expensive nucleating agents.

**Table 14.6** Commercial nucleating agents for PET

Nucleating agent	Tradename	Manufacturer
E-AA-Na <sup>+</sup> (ethylene-acrylic acid sodium ionomer)	Aclyn 285	Honeywell
E-MAA-Na <sup>+</sup> (ethylene-methacrylic acid sodium ionomer)	Surlyn 8920 <sup>a</sup>	DuPont
Sodium-neutralized salt of montanic acid wax	Licomont NaV101	Clariant
Sodium carboxylate salts (e.g. sodium stearate) <sup>b</sup>	–	SunAce
Sodium benzoate	–	Various
Sodium chlorobenzoate <sup>c</sup>	–	Aldrich

<sup>a</sup> Copolymer of ethylene and 15 wt% of methacrylic acid neutralized with 60% sodium cations.

<sup>b</sup> Typical use rate is 1.2% (can cause chain scission of PET chains).

<sup>c</sup> Sodium chlorobenzoate reacts with PET and leads to a loss of molecular weight. Furthermore, the effectiveness of sodium chlorobenzoate is time-dependent, i.e. the effectiveness of a given amount of sodium chlorobenzoate is dependent on the processing time in the polymer melt.

**Table 14.7** PET crystallization data (after 10 s exposure at 177 °C)

Nucleating agent	Nucleating agent concentration (%)	$T_{ch}^a$ (°C)	$T_{cc}^b$ (°C)	Crystallinity (%)
None	0	144	179	9
Aclyn 285	0.25	132	201	33
Aclyn 285	0.50	130	204	33
Aclyn 285	1.00	129	204	30

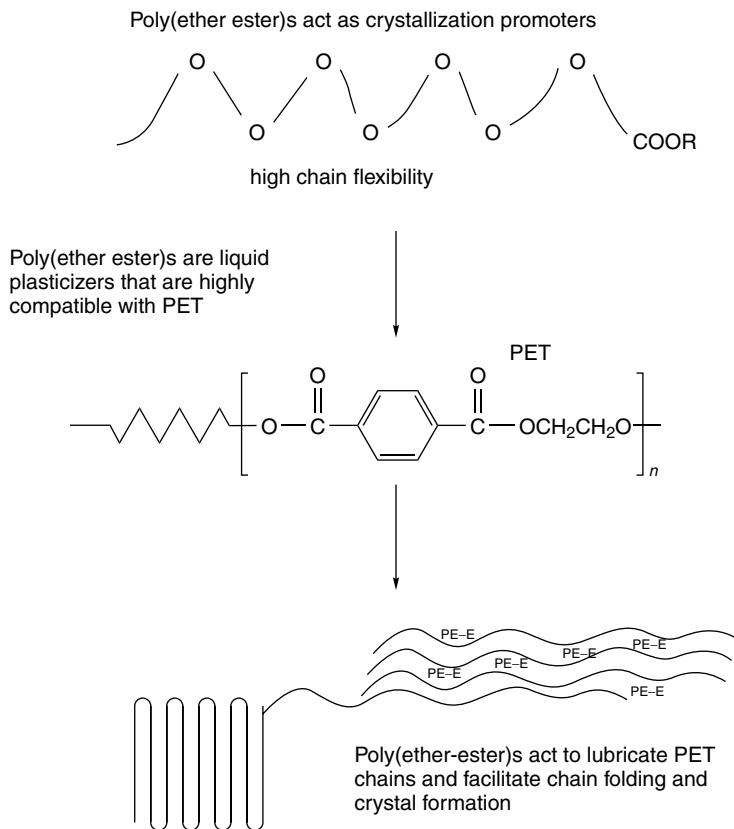
<sup>a</sup> Temperature of hot crystallization.

<sup>b</sup> Temperature of cold crystallization.

Newer nucleators include pyrrole-based salts which seem to produce chemical nucleation with a minimal molecular weight reduction.

## 6 NUCLEATION/CRYSTALLIZATION PROMOTERS

To facilitate and accelerate folding and crystallization of polymer chains, internal plasticizers are often added to PET to serve as crystallation promoters. Such additives are usually based on poly(ether ester)s. These plasticizers are liquids that are typically added at levels of 2–4 wt%. They reduce cycle time in injection moulding operations by increasing the rate of crystalline formation. They also plasticize the resin and act as processing aids by virtue of their lubricating action in the melt. On a molecular level, these plasticizers reduce the intermolecular



**Figure 14.16** Mechanism by which poly(ether ester)s function as crystallization promoters. Such materials internally lubricate and plasticize the PET molecular chains, thus allowing reptation (i.e. chain folding) to occur more quickly

forces between the PET chains and allow the latter to slip past one another more easily (Figure 14.16).

Nucleation promoters are essentially plasticizers that have a high MW and low volatility which are compatible with polyesters and internally lubricate the polymer chains. They act by increasing the rate of crystallite formation once the nucleation agent has provided a nucleation site. Generally, these nucleation promoters/plasticizers belong to the poly(ether ester) family. These compounds provide the free volume in the PET molecules for essentially complete crystallization during the short mould-dwell time and at acceptably low mould temperatures. Such compounds reside between adjacent polymer chains and thereby aid crystal growth during nucleation. Some examples of common nucleation promoters/plasticizers for PET are shown in Table 14.8.

**Table 14.8** Commercial nucleation promoters/plasticizers for PET

Promoter Plasticizer	Tradename	Manufacturer
PEG-400-diethylhexanoate	Tegmer 809	CP Hall
PEG-4-dilaurate	Uniplex 810	Unitex Chemical
Neopentyl glycol dibenzoate	Uniplex 512	Unitex Chemical
Triethylene glycol dibenzoate <sup>a</sup>	Benzoflex S-358	Velsicol Chemical Corporation

<sup>a</sup> Further details given in Iida *et al.* [33].

Other less common nucleation promoters/plasticizers for PET include *N*-ethyl-toluenesulfonamide and trioctyl trimellitate.

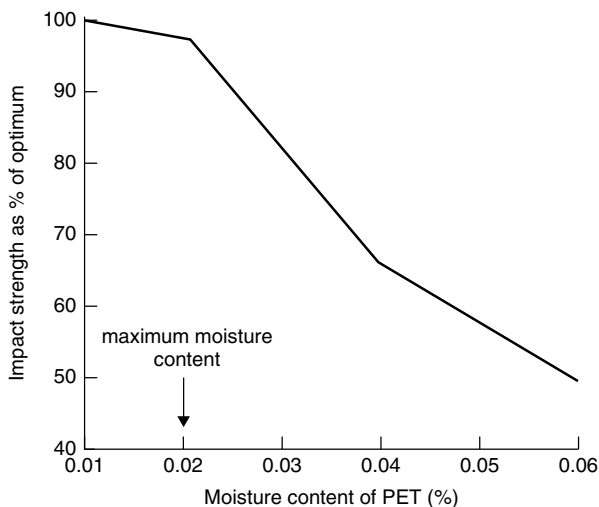
An important requirement for liquid plasticizers intended for use in PET is that they have good high temperature stability and low volatility on account of PET's relatively high processing temperature (i.e. 280–300 °C). Furthermore, temperature stability is important since some additives that are stable during the processing of PBT may degrade in PET. Another important characteristic for additives for PET is that they have low acid and hydroxyl values since PET is susceptible to both acid- and alkali-catalyzed degradation.

## 7 ANTI-HYDROLYSIS ADDITIVES

PET resin contains ester bonds which are susceptible to hydrolysis at elevated temperatures in the presence of moisture. The hydrolysis reaction leads to molecular chain scission at the ester bond. As the polymer chains shorten, the molecular weight decreases such that the melt viscosity and intrinsic viscosity also drop. The concentration of carboxyl end groups also increases. The hydrolysis reaction rate begins to become significant at temperatures of 160 °C and above. Since PET is generally processed at temperatures of between 270 and 300 °C, it is apparent that the rate of hydrolysis can become appreciable. At 250 °C the rate of hydrolysis of PET is some 10,000 × that which occurs at 115 °C. Suppressing hydrolysis is especially critical for reprocessing of recycled PET. The effect of residual moisture on the notched Izod impact strengths of PET compounds is shown in Figure 14.17.

Anti-hydrolysis additives for PET are moisture scavengers that sacrificially react with moisture during melt processing or in service, thereby minimizing hydrolysis of the polyester. Anti-hydrolysis additives for PET and PBT chemically react with free moisture during extrusion. These additives can be based on carbodiimide (HN–C–NH). Commercially available polycarbodiimide additives include Stabaxol™ P (Rhein Chemie Rheinau GmbH, Mannheim, Germany) and Carbodilite™ (Nisshinbo Industries, Inc., Chiba-Shi Chiba, Japan).

Hydrolysis during melt processing can be suppressed significantly by the addition of such anti-hydrolysis additives. This enables the IV to be maintained across



**Figure 14.17** Relationship between notched impact strength of PET compounds and their moisture content. The plot emphasizes the need for proper drying of PET resin to reduce the moisture content to below 200 ppm before melt processing. Intensive drying procedures are time-consuming and costly and therefore internal desiccants are often used

melt processing operations. Improvements in tensile strength and impact strength have also been reported with the carbodiimide-mediated coupling of PET.

Such hydrolysis stabilizers act as acid- and water-scavengers, converting and neutralizing both water and acids into non-reactive urea structures. Addition rates of 0.5 wt% polycarbodiimide to PET can maintain its IV across melt processing even with only partial pre-drying of the PET. Polycarbodiimides also react with the terminal acid groups of PET and decrease the initial acid value of the polyester resin. Imashiro *et al.* [34] have described adding a carbodiimide compound to recycled PET such that the intrinsic viscosity and strength of the polyester resin during processing is maintained.

Stabaxol KE 7646 is a grade claimed for maintaining the intrinsic viscosity of recycled PET during melt processing. Such additives expand the possibilities for applications of recycled PET resin into new fields.

Polycarbodiimides are also used as additives to provide long-term hydrolytic stability to polyester components in service in moist and humid environments (e.g. glass-filled PET in dishwasher applications).

Heitz *et al.* [35] (BASF) describe the use of polycarbodiimide as an additive to produce hydrolysis-resistant PBT. Further patents describe glass-fiber-reinforced mixtures of PBT with an aromatic polycarbodiimide having improved impact strength [36], and mixtures of PBT with an aromatic polycarbodiimide having improved melt strength and intrinsic viscosity [37].

Stabaxol™ P is used normally as a hydrolysis stabilizer in non-food polyester applications. One of the main applications is the stabilization of monofilament. An additional advantage of Stabaxol™ P is that it also works as a viscosity modifier. Stabaxol™ P has no FDA approval, and this means that it can be used only for technical applications.

Some examples of common anti-hydrolysis agents for PET are presented in Table 14.9. Desiccant additives can be used in PET and PBT to control moisture evolution during melt processing of polyesters. Such additives are generally based on a treated calcium oxide which reacts chemically with any moisture present in the polymer during extrusion. The moisture scavenging process results in a calcium hydroxide residue that remains as uniformly distributed, inert particles (5 µm diameter) in the polymer (essentially it becomes a chalk filler). These additives are available as a masterbatch (e.g. Colloids Ltd, Merseyside, UK). This masterbatch is based on a selected grade of calcium oxide (60 wt%) in a low-density polyethylene carrier (melt flow index (MFI) of 5 g/10 min).

The addition rate of the Dessicante® masterbatch is typically 1.0–3.0%. Approximately 1% addition of the PE 48/10/96 masterbatch will remove 0.1% of water from the polymer during the extrusion or compounding process.

## 8 REINFORCEMENTS

The reinforcing nature of inorganic fillers is dependant on both their aspect ratio (length to thickness ratio) and the interfacial shear strength that they develop in the PET matrix (a function of the type of surface treatment) (Table 14.10). Glass fibre reinforcement increases the flexural modulus, tensile strength and heat distortion temperature (HDT), while reducing the elongation at break. Bottle-grade recycled PET can be upgraded into engineering-grade PET for injection moulding through the addition of glass fibre reinforcement. The addition of glass fibre is used to upgrade the properties of PET recycle from soft-drink bottles into injection moulding applications [38].

**Table 14.9** Commercial anti-hydrolysis agents for PET

Compound	Tradename	Manufacturer
Polycarbodiimide	Stabaxol KE 7646 <sup>a</sup>	Rhein Chemie
Carbodiimide	Carbodilite E <sup>b</sup>	Nisshinbo Industries
Treated calcium oxide (Caloxol®)	Dessicante® PE 48/10/96	Colloids Ltd

<sup>a</sup> Stabaxol KE 7646 (Rhein Chemie, Mannheim, Germany) is a masterbatch based on PET plus an aromatic polycarbodiimide.

<sup>b</sup> Carbodilite E is a masterbatch of 10 wt% carbodiimide in a PET carrier resin.

**Table 14.10** Commercial reinforcing agents for PET

Reinforcement	Aspect ratio	Tradenames
Glass fibre (chopped strand)	300:1 (typical dimensions, 10 $\mu\text{m}$ $\times$ 3 mm)	PPG 3540 <sup>a</sup> Vetrotex 952 Saint Gobain Owens Corning 183F
Wollastonite (calcium silicate)	16:1	Nyco
Montmorillonite <sup>b</sup> (layered silicate nanoclay)	1000:1	Cloisite 93A Cloisite 30B (Southern Clay Products)
Mica	30:1	Muscovite-type mica (supplied by KMG); phlogopite-type mica (supplied by Suzorite, Inc.)
Talc	30:1	Various

<sup>a</sup> The glass fibre, PPG 3540, is a polyurethane-sized glass fibre manufactured by PPG Industries, Inc. The surface treatment on the glass fibre promotes good adhesion between the fibre and the polymer.

<sup>b</sup> Note: montmorillonite is surface treated with octadecylammonium or dioctadecyldimethylammonium ions.

Wollastonite is a relatively inexpensive reinforcing filler and extending agent for thermoplastic polyesters. This material can be used to give PET some 'body' in profile extrusion and to prevent sagging. Certain grades of wollastonite (such as that supplied by Wolkem India Limited from the Wolkem's mines in Rajasthan, India) have an aspect ratio of up to 20:1. Wollastonite reinforcing agents are an ideal partial replacement for glass fibres for the reinforcement of polyesters such as PBT. With a loading of 30 % wollastonite, PBT attains a HDT (at 18.5 kg/cm<sup>2</sup>) of 180 °C. Improvements in other mechanical properties, such as tensile strength, flexural strength, flexural modulus, and notched and un-notched impact strengths, are also achieved.

Nanoclays (nanophase layered silicates) give improvements in tensile modulus and tensile strength of PET at levels of only 1 wt% compared with say 10 % conventional fillers or analogously at loadings of 3 wt% compared with 30 % glass fibre (Table 14.11). The major benefit of nanoclay reinforcements is mechanical property improvement with minimal density (i.e. weight) increase. This is particularly advantageous for plastic components for automotive applications. Another benefit conferred by nanoclays is flame retardancy due to the tortuous path that hot combustion gases evolving from the polymer must take to reach the flame zone. Nanoclay particles in PET also increase the onset temperature for thermal degradation, decrease the heat output during burning, form protective char layers, and overall, impart self-extinguishing characteristics.

**Table 14.11** Property improvements of PET that are observed after the addition of 3 % nanoclay

Property	Improvement with nanoclay (%)
Elastic modulus	90 % higher
Tensile strength	55 % higher
Impact strength	22 % higher
Thermal expansion coefficient	52 % lower
Heat distortion temperature	123 % higher
Water uptake	41 % lower

## 9 FLAME RETARDANTS

Approximately 40 % of the thermoplastic polyester resin that is sold (excluding PET packaging resins) is flame-retarded. PET used for switches, sockets and other applications where the material is in direct contact with live parts of electronic and electrical appliances are required to be flame retardant.

PET can be made flame retardant (FR-PET) by halogenated additives in combination with synergists such as antimony compounds (which impart no flame inhibition by themselves). During combustion, volatile antimony trihalide is formed in the condensed phase and transported to the gas phase. Failure of this flame retardant in PET compounds can occur, however, due to the formation of stable metal halides such as the following:

- in the presence of calcium carbonate—stable calcium bromide forms
- in the presence of fumed silica—stable silicon bromide forms

This renders the halogen unavailable for reaction with the antimony compound, and therefore neither the halogen nor the antimony are transported into the flame zone during combustion.

The following examples demonstrate common pitfalls encountered when flame-retarding PET compounds:

- An antagonism can occur between phosphorus flame retardants and antimony compounds when used in combination.
- Phosphate esters hydrolyze easily, thus precluding their use in PET.
- Aluminium trihydrate (ATH) decomposes, absorbing energy from the flame and evolving water vapour which blankets and smothers the flame. The resulting water vapour at 230 °C can cause ‘massive’ hydrolysis of PET.
- Antimony oxide flame retardants act as depolymerization agents for PET. Instead, sodium antimonate is the synergist of choice.
- Brominated flame retardants can induce degradation namely, acid-catalyzed hydrolysis of PET.

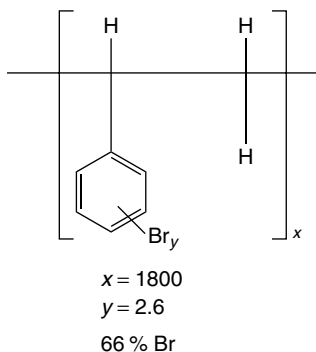


- Magnesium hydroxide is very basic (high pH) and will degrade PET and PBT if it is used as a flame retardant [39].

Generally, flame retardants for engineering PET compositions are based on bromine-containing compounds (such as brominated polycarbonate, decabromodiphenyl oxide, brominated acrylic, brominated polystyrene, etc.). Such compounds are available commercially (such as from the Ethyl Chemical Corporation, Great Lakes Chemical Corporation, Dead Sea Bromine Company, etc.) In addition, the flame-retardant package generally contains a synergist, typically sodium antimonate. PET may also be flame-retarded with diarylphosphonate, melamine cyanurate or red phosphorus.

The two main brominated flame retardants used commercially in PET are PyroChek 68PB (see Figure 14.18) and Saytex HP-7010 (Albemarle). Both of these flame retardants are based on brominated polystyrene. While there are similarities between these flame retardants, they are not equivalents. There are quality and performance differences between these two products as they use different raw materials (i.e. polystyrenes) and the process for bromination is different. Saytex HP-7010 has better thermal stability and colour control than does PyroCheck 68PB. However, if higher flow characteristics are a necessary property of the FR-PET, then Pyrocheck 68PB would be the product of choice. Sodium antimonate is the appropriate synergist in PET since it is more stable at the higher processing temperatures required of PET and does not cause depolymerization of this polyesters.

The loading level required of these flame retardants for a 30% glass-filled PET is in the range of 12 to 13% for a 94V-0 rating. The antimony synergist should be used at the 4 to 6% range. The quality differences of Saytex 7010 and Pyrocheck 68PB are such that an acid neutralizer should also be a part of the formulation, e.g. an inorganic-type stabilizer (e.g. talcite or DHT-4C). Saytex 7010 would require about 300ppm, while Pyrocheck 68PB would need about



**Figure 14.18** The chemical structure of PyroChek 68PB (Albermarle Corporation), a highly effective flame retardant for PET

**Table 14.12** Commercial flame retardants for PET

Flame retardant	Tradename	Manufacturer
Brominated polystyrene	PyroChek 68PB	Albemarle Corporation
Brominated polystyrene	Saytex HP-7010	Albemarle Corporation
Sodium antimonate	Thermoguard FR sodium antimonate	OxyChem
Melamine polyphosphate	Melapur 200	DSM
Antidripping PTFE	Teflon 60 Hostaflon 9202	DuPont Hoechst

2000 ppm of such a stabilizer. The acid neutralizer helps with colour control, melt viscosity control and reduced equipment corrosion [40].

PET requires special flame-retardant chemistry since the antimony oxide synergist that is normally used in combination with brominated flame retardants causes de-esterification of the PET chain and concomitant molecular weight loss. In place of antimony oxide, PET requires a sodium antimonate synergist. Another problem with antimony trioxide is that it decreases the thermal stability of the brominated flame retardant which then produces hydrobromic acid which degrades the PET.

PET can achieve a UL94 V-0 rating at 0.8 mm when using 13–15 % Pyrocheck 68PB and 4–7 % sodium antimonate. For example, Pyrocheck 68PB is used in Rynite by DuPont. Sodium antimonate ( $\text{NaSbO}_3$ ) (Thermoguard FR) is a fine white powder used as the antimony source to flame-retard selected polymers as well as for pigment applications. Since Thermoguard FR has a basic pH, it is the antimony synergist recommended to flame-retard acid-sensitive polymers and polyesters such as PET and PBT.

As the glass content of PET goes down, the polymer content goes up and therefore the requirement will be for additional flame retardant. In addition to the required flame-retardant loading with reduced filler, there will generally be an increase in the dripping during the burn test, such as UL94. This generally is controlled by the addition of an anti-drip agent such as Teflon at loadings of 0.5 to 1.0 wt%. The addition of 1 % of anti-drip Teflon 60, or Hostaflon 9202 or 1665, is usually used. Control of dripping will be necessary to obtain the 94V-0 rating.

Some examples of common flame retardants used for PET are shown in Table 14.12.

## 10 POLYMERIC MODIFIERS FOR PET

PET can be blended with PBT or polycarbonate (PC) to make blends or alloys. Polycarbonate is a high  $T_g$  (150 °C) ductile, high-impact-strength polymer but has rather poor solvent resistance because of its amorphous nature. PET/PC blends have therefore proved advantageous because they combine the solvent-resistance

**Table 14.13** Common polymeric modifiers for PET

Polymer	Effect on PET properties
PC	Better impact strength
PBT	Better crystallization
Phenoxy resin	Improve impact strength and heat distortion temperature

advantages of PET with the high  $T_g$  and toughness advantages of PC. Blends of PET and PC are phase-separated systems that exhibit partial miscibility in the absence of significant ester interchange. In blends containing >40% PET, the continuous phase (matrix) is PET-rich, while the dispersed phase (domains) is PC-rich. This partial miscibility is responsible for the self-compatibilizing nature of the blend, hence resulting in good delaminating resistance and tensile strength. However, despite the good ductility of this blend and drop-weight impact strength, the notched Izod impact strength of this blend is still quite low (<60 J/m). For this reason, an elastomeric toughener is invariably needed to improve the notch sensitivity of PET/PC blends [26].

Phenoxy resins can also be used for the modification of PET and PBT. Phenoxy resins such as Paphen™ PKFE (Inchem Corporation) are polyhydroxyether materials with pendant hydroxyl groups that can react with the PET. Paphen™ phenoxy resins are reactive modifiers that can modify and upgrade brittle polymers. Such resins contain 6% of secondary hydroxyl groups. The latter serve as reactive sites for reaction with polyesters, polyamides, polycarbonates, epoxies and phenolics.

PET undergoes transesterification with the phenoxy polymer (actually it is an oligomer). The transesterification is a bonding reaction between the pendant hydroxyl (OH) groups on the phenoxy resin repeat unit and the terminal acid (COOH) groups on the polyester chains. The result is that individual PET polymer chains become coupled together (thus increasing the molecular weight) and also that the thermally stable phenoxy backbone is inserted into the PET structure. This is claimed to upgrade the mechanical properties of polyesters and to enhance their structural integrity.

The effects that the most commonly used polymeric modifiers have on the properties of PET are shown in Table 14.13.

## 11 SPECIALTY ADDITIVES

### 11.1 MELT STRENGTH ENHANCERS

Polycondensation polymers such as PET are characterized by low melt viscosities and low melt strengths. Furthermore, with PET there is a marked shear liquefaction

during the processing of the polymer melt – accordingly, PET exhibits low melt elasticity. These attributes are the opposite of those required for good foamability of polymers. Therefore, the production of foam from PET can only be achieved by structural modification of the polymer to improve its melt strength and melt elasticity. Melt strength enhancers are generally based on chain extenders (see Section 2).

The Eastman Chemical Company (Kingsport, TN) produces a reactive additive masterbatch, Eastolite<sup>®</sup> E3031-92AA, which increases the melt strength of PET to help facilitate foaming. The pyromellitic dianhydride additive attaches itself to the ends of the PET molecules, forming ‘pseudo-star molecules’ by adding chain length and branches. Starting with PET resin with an intrinsic viscosity of 0.80 dl/g, the addition of the melt-strength-enhancing additive raises the intrinsic viscosity to 1.2 dl/g and significantly increases the melt strength so that stable PET foaming can occur. Another melt strength enhancer is Eastapak MSE 14438 which is based on a PETG copolyester.

### 11.2 CARBOXYL ACID SCAVENGERS

The carboxyl end group (CEG) content of PET is an indicator of the number of acid groups on the ends of the PET chain. The CEG content of the PET has an influence on the hydrolysis resistance of the polymer. The lower the value, then the higher the hydrolysis resistance. Phenylenebisoxazoline (PBO) is an effective carboxyl acid scavenger for PET where it reacts with acid end groups and in doing so couples the PET chains, thus increasing the polymer molecular weight. Polycarbodiimides also react with terminal acid groups of PBT and lowers its acid value.

### 11.3 TRANSESTERIFICATION INHIBITORS

Transesterification of PET/PC blends can lead to copious gas evolution (carbon dioxide). To suppress transesterification of binary polyesters, inhibitors such as inorganic phosphates can be added.

### 11.4 GLOSS ENHANCERS

Gloss enhancers are additives that when added to PET or PBT produce a glossy surface finish that is similar to that of acrylonitrile–butadiene–styrene (ABS) terpolymer. Such additives include AC wax, such as AC316 (Honeywell).<sup>1</sup> These waxes have limited compatibility with PET and ‘bloom’ to the surface to give a

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<sup>1</sup> AC<sup>®</sup> waxes are a range of low-molecular-weight polyethylene performance products available from Honeywell (formerly from Allied Chemicals). Further details are available on the web site: [<http://www.acperformanceproducts.com/index.html>].

high gloss surface. These wax-based additives also function as a mould release and external lubricant. AC316 can also nucleate PET in applications such as thermoformed PET trays where they enable faster processing speeds. AC400A wax, based on an ethylene–vinyl acetate copolymer, is effective as a gloss enhancer for PET resins at dosages of 0.3–1.0 %. The vinyl acetate portion gives some compatibility with PET while still providing external lubrication.

### 11.5 ALLOYING (COUPLING) AGENTS

Alloying agents can compatibilize polyester blends, thus producing alloys with enhanced mechanical properties. Such alloying agents can be based on titanate or zirconate compounds (e.g. Kenreact Lica-12 by Kenrich). For example, a titanate alloying agent can compatibilize an unusual mix of 80 % continuous-phase recycled PET with 20 % recycled polycarbonate (see Table 14.14). Such an organotitanate (manufactured by Kenrich Petrochemicals Inc.) at a concentration of 1 % can improve the elongation to break and impact strength of polyesters.

### 11.6 PROCESSING STABILIZERS

Phosphite processing stabilizers are used in PET to maintain the IV, suppress yellowing and overall to reduce thermo-oxidative degradation.

For processing and thermal stabilization of PET the following stabilizers are recommended – Irganox HP 2215, Irganox B 561, Irganox 1425, and in selected cases, Irganox 1222 (Irganox is a trademark of Ciba Specialty Chemicals).

Certain organophosphorus compounds can be used to melt-stabilize PET. Stabilizers such as 3,5-di-*t*-butyl-4-hydroxybenzyl diethyl phosphate (Irganox 1222) and triphenylphosphate lead to a reduction in the concentration of terminal carboxyl groups of PET, thus giving improved hydrolytic stability.

**Table 14.14** Effect of a titanate alloying agent (Kenrich Lica-12) on a 80/20 PET/PC blend (data obtained from Kenrich Petrochemicals Ltd)

Property	Unmodified PET/PC	PET/PC +0.2 % alloying agent	PET/PC +0.5 % alloying agent
Notched Izod impact (lb ft/in)	0.832	0.819	0.80
Deflection temperature (°C)	151	165	172
Melt flow rate (285 °C, 2.16 kg) (g/10 min)	37	48	84
Tensile strength (psi)	7 085	8 137	8 405
Elongation (%)	10	93	68
Tensile modulus (psi)	189 140	348 800	330 449

## 12 TECHNOLOGY OF COMMERCIAL PET ENGINEERING POLYMERS

Engineering-grade PET finds widespread use in numerous load-bearing applications, as demonstrated in Table 14.15.

The principal commercial grades of engineering-grade PET are shown in Table 14.16.

### 12.1 RYNITE™

Rynite by DuPont is a toughened PET based on Elvaloy PTW as the impact modifier [42]. Elvaloy PTW is an ethylene terpolymer containing epoxy functional groups based on glycidyl methacrylate (GMA). This terpolymer exhibits excellent adhesion to the PET matrix because of its epoxy functionality. In addition, it confers excellent low-temperature properties due to its low glass transition temperature which is a function of the *n*-butyl acrylate component. While Elvaloy PTW markedly improves the notched impact strength of PET it does detract from PET's flexural modulus (i.e. stiffness), tensile strength and extruder residence time (due to the higher viscosity).

The formulation for Rynite™ from DuPont is described in United States Patent 4 753 980 [41]. This disclosure discusses the use of an ethylene terpolymer such

**Table 14.15** Typical applications for engineering-grade PET

Sector	Specific applications
Automotive	Distributor housings, coil housings, rotors, ignition system components, electrical system components, grill opening retainers, mirror housings, windshield wiper components, headlight bezels, HVAC <sup>a</sup> vent doors, cowl vents
Consumer electronics and appliances	Motor housings and internal components, corn poppers, coffee makers, hair curlers and dryers
Furniture	Arm rests, seat shells and bases

<sup>a</sup> Heating, ventilating and air-conditioning.

**Table 14.16** Commercially available engineering-grade PET resins

Tradename	Manufacturer
Rynite	DuPont
Petra	Honeywell
Impet	Ticona GmbH
Eco Vylopet	Toyoda Gosei Company

as ethylene–methacrylate–glycidyl methacrylate to toughen PET. The critical point highlighted in this patent is that the dispersed elastomeric phase must have an average particle size of less than  $3\ \mu\text{m}$  to confer effective toughening. A typical toughened PET composition claimed in this DuPont patent is as follows:

- (a) 20 % of E–BA–GMA (Elvaloy with 63 % of ethylene, 31 % of *n*-butyl acrylate (BA) and 6 % of glycidyl methacrylate (GMA)) was first compounded with 80 % of PET.
- (b) 60 % of this compounded blend was then mixed with 30 % of coupled glass fibre, 3.8 % of Surlyn 8920 (sodium-neutralized ethylene–methacrylic acid copolymer), 0.6 % of an epoxy compound (e.g. Epon 1009 by Shell – a condensation product of epichlorohydrin and bisphenol A), 4 % of Uniplex 512 (by Unitex Chemical – the dibenzoate of neopentyl glycol) and 0.4 % of a phenolic antioxidant. This blend is then extruded through a single screw extruder.

## 12.2 *PETRA*<sup>™</sup>

The formulation for Petra<sup>™</sup> from Honeywell (formerly Allied Signal) is described in United States Patent 5 723 520 [42]. This disclosure concerns the preparation of toughened PET composites by first pre-reacting the PET with a copolymer of ethylene and a glycidyl acrylate or methacrylate and then subsequently blending with a nucleating agent (such as the sodium salt of a carboxylic acid, e.g. sodium stearate) to increase the crystallization rate of the polyester. Glass fibers or reinforcing fillers are then added to provide rigidity and heat distortion resistance. The compositions exhibit a good balance of toughness, rigidity and gasoline resistance, and are particularly useful for automotive structural parts such as inner door frames, panels, reinforcements, bumper beams, window surrounds, and other metal-replacement applications. These glass-filled PET (GF-PET) compounds possess flexural modulus values from about 1000 to about 15 000 MPa (in accordance with ASTM D-790) and a notched Izod impact strength of at least about 70 J/m (in accordance with ASTM D-256).

## 12.3 *IMPET*<sup>™</sup>

The formulation for Impet from Ticona (a Division of the Hoechst Celanese Corporation) is described in United States Patent 6 020 414 [43]. The latter discloses toughened PET formulations based on an ethylene–alkyl acrylate copolymer and an ethylene–alkyl methacrylate copolymer. The crux of this patent is to use a combination of an elastomeric terpolymer functionalized with glycidyl acrylate or glycidyl methacrylate and an alkyl acrylate or alkyl methacrylate (the latter forming the major part of the combination – up to 40 wt%). For instance,

a typical formulation is based on PET plus 4 wt% of the terpolymer ethylene–methyl acrylate–glycidyl methacrylate (E–MA–GMA) plus about 16 wt% of the total composition of ethylene–methyl acrylate (EMA) and 15 % of glass fibre. Suitable commercially available terpolymers include ethylene–methyl acrylate–glycidyl methacrylate formulations sold under the tradenames of Lotader™ AX8900, AX8920, AX8660, AX8850 and AX8870 (from Atofina).

### **13 COMPOUNDING PRINCIPLES FOR PREPARING ENGINEERING-GRADE PET RESINS**

The compounding of toughened PET formulations is generally carried out on a twin-screw extruder with down-stream glass feeding capability. Many such compounders are commercially available (such as, for example, the Werner Pfleiderer twin-screw extruder). The extruder may be fed with the resin and additives at the main hopper while the glass is fed downstream. The melt temperature is maintained in the range 260–300 °C. The material is compounded and then pelletized. Vacuum venting is generally performed at the first two vents to remove volatiles such as moisture, carbon dioxide, ethylene glycol, etc. The compounder should be configured with at least two sets of kneading blocks and reverse bushings to give adequate high-shear regions for effective dispersion of the rubber toughener. The geometry of the screws should be set up to give the best combination of dispersive and distributive mixing. The reason for this being that for effective rubber toughening of PET, the rubber domains must have a particle size of less than 3 μm.

A twin-screw extruder is generally preferred for producing rubber-toughened, glass-filled PET compounds for injection moulding applications. The PET and impact modifier are added at the throat while the glass reinforcement is added downstream. The size of the rubber domains will depend on the amount of energy and the capability of the equipment used for dispersion.

It is important to avoid a potential interaction between the reactive impact modifiers (i.e. those with GMA end group functionalities) and the coupling agent on the glass fibre reinforcement. For this reason, it is important to add the glass fibre to the compounder downstream, by which time the reactive toughener will have grafted to the PET matrix. It is believed that the reactive toughener can inhibit the silane reaction with the PET.

### **14 COMMERCIAL GLASS-FILLED AND TOUGHENED PET GRADES**

Literature citations report that untoughened, crystallized PET mouldings are quite brittle, particularly under conditions of stress concentration such as when sharply



Table 14.17 Commercial grades of glass-filled PET

Grade	Izod impact strength (J/m)	Comments
Petra 110 BK-112	55	15 % GF
Petra 110	70	15 % GF
Rynite 520	70	20 % GF
Rynite 530	85	30 % GF
Petra 140 BK-112	90	45 % GF
Petra 130	95	30 % GF
Petra 130 BK-112	95	30 % GF
Petra 7030	95	30 % GF
Rynite 545	106	45 % GF
Petra 140	110	45 % GF
Petra 132 BK-112	120	Impact-modified; 30 % GF
Rynite 408	120	Impact-modified; 30 % GF
Rynite 415HP	130	Impact-modified; 15 % GF

notched. Such mouldings have low notched Izod impact strengths (30–50 J/m) [26]; whereas toughened PET has Izod values of 70–120 J/m, while ‘supertoughened’ PET exhibits Izod impact values of 300–1000 J/m. Indeed, PET with 20 % reactive impact modifier can give NB (no break) results in the ASTM D-256 Izod impact test.

Table 14.17 summarizes the impact strength of commercial GF-PET resins for comparative purposes.

## 15 ‘SUPERTOUGH’ PET

The notched Izod impact strength of PET at room temperature is only 45 J/m. ‘Supertough’ PET with notched impact strengths up to 1000 J/m can be prepared by melt blending PET with 20 wt% of a reactive elastomeric terpolymer (e.g. E–MA–GMA). Pecorini and Calvert [28] have attributed this supertoughness phenomenon to two distinct toughening mechanisms, as follows:

- Massive shear yielding in the matrix when the dispersed particles are less than 200  $\mu\text{m}$  in size.
- Multiple crazing in the matrix when the particle size of the dispersed particles is larger.

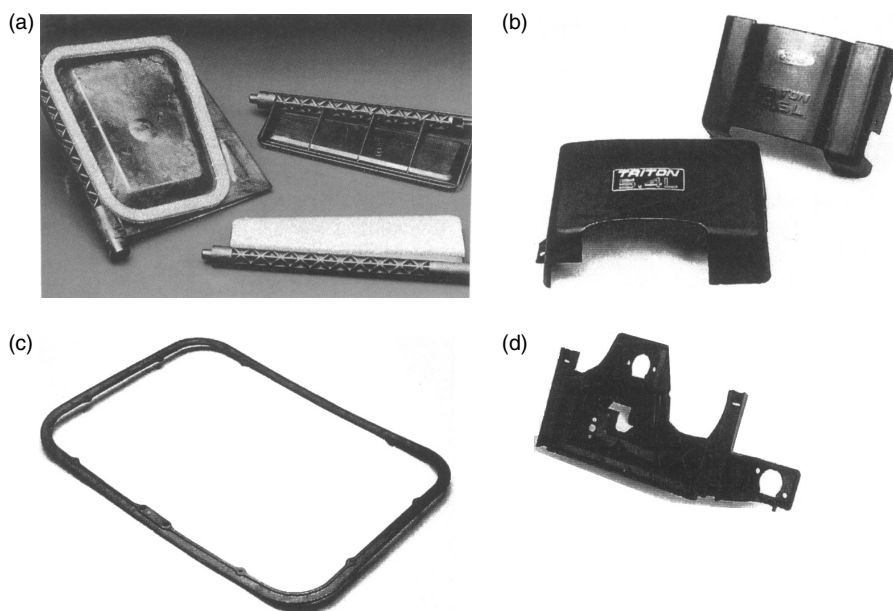
These authors found that to achieve supertoughness in PET by shear yielding, a reactive modifier is superior to a non-reactive rubber modifier and that a dispersed particle size and interparticle distance of 200 and 50 nm, respectively, are

required. Alternatively, supertoughness can also be achieved through a mechanism of multiple crazing when a dispersed particle size of  $1\ \mu\text{m}$  is achieved.

## 16 AUTOMOTIVE APPLICATIONS FOR MODIFIED PET

Some typical automotive applications for reinforced and toughened PET are illustrated in Figure 14.19.

Recently, Mitsubishi Motors have produced a  $1900\text{ cm}^2$  engine cover injection moulded from glass-fibre-reinforced recycled PET. This polymer material is said to have properties similar to the polyamide normally used for engine covers. Recycled PET in its conventional form has low impact strength, and so a 'strength-enhancing additive' (a rubber toughener) is employed in a design that is 10 to 30% thicker in cross-section than conventional polyamide. The resulting component has an Izod impact strength superior to polyamide. The material, called ECO VYLOPET is based on recycled PET and was developed jointly by the Toyoda Gosei Company, Ltd and the Mitsubishi Motors Corporation. Both



**Figure 14.19** Typical automotive applications made from glass-filled recycled PET compounds: (a) heating and air conditioning door duct vents for Ford's Taurus, Mercury Sable and Lincoln Continental models; (b) engine covers for Ford's Taurus, Mercury Sable and Lincoln Continental models; (c) fixed window surround for the Ford Excursion model; (d) headlamp retainer for GM's Montana, Yukon and Sierra trucks

the latter and the Toyota Motors Corporation use this material to produce their automobile engine covers.

A variant of the Impet Hi 430 PET grade (Ticona, USA) is being used in the Chrysler Corporation Composite Concept Vehicle (CCV). The polyester parts for the CCV body are the largest components ever moulded in an engineering thermoplastic. The new Plymouth Pronto Spyder concept sports car uses another variant of the new PET formulation in its moulded car body. Impet Hi 430 PET resin contains only 15 % glass and is easy to injection mould. At  $-20^{\circ}\text{C}$ , for example, the material exhibits a 40 % higher notched impact strength ( $8.8\text{ kJ/m}^2$ ) than conventional glass-reinforced PET resins. Ticona's compounding technology has given traditionally brittle PET more ductile failure modes and greater impact strength for these demanding structural applications.

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