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Review

Recycling of PET

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Abstract

The recycling of post-consumer PET (POSTC-PET) as a technology is a cross-disciplinary practice with many fields of science involved. These include polymer chemistry and physics, process engineering and manufacturing engineering. This paper presents a concise background of the current state of knowledge with respect to POSTC-PET recycling covering the disciplines mentioned above. In the first section of this paper, a brief background is presented about virgin PET synthesis, thermal transitions, processing and applications. The second section covers the PET recycling process with a focus on contamination and ways to increase the molecular weight of recycled PET (R-PET). It serves as an introduction to Section 3 where the chain extension process is described in detail. In Section 3, the current understanding of chain extenders, chain extension experimentation variables and equipment is reviewed. Reactive extrusion process is described in Section 4 with a special focus on system stability under chain extension conditions. Section 5 covers the effect of chain extension on R-PET thermal transitions and crystallinity. Section 6 presents the injection stretch blow moulding (ISBM) process as a possible application for R-PET with a focus on preform and bottle moulding. The last section gives a description of FT-IR technology to detect bottles' orientation and conformation changes.
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Keywords: PET; Reactive extrusion; ISBM; FT-IR

Contents

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1. Virgin PET

Virgin PET is considered as one of the most important engineering polymers in the past two decades due to rapid growth in its use. It is regarded as an excellent material for many applications and is widely used for making liquid containers (bottles). It has excellent tensile and impact strength, chemical resistance, clarity, processability, colour ability and reasonable thermal stability [1]. Many companies produce virgin PET globally giving it different trade names [2,3]. Some of the common trade names of commercially available PET are summarized in Table 1.

Commercial PET has a wide range of intrinsic viscosity [η] that varies from 0.45 to 1.2 dl g^{-1} with a polydispersity index generally equal to 2. The PET repeating unit is shown in Fig. 1. The PET chain is considered to be stiff above the glass transition temperature (T_g) un-

Table 1
The trade names of PET and their manufacturer

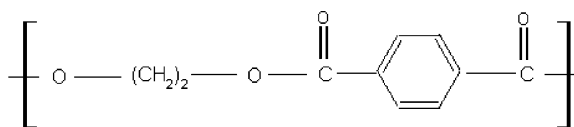| Trade name	Manufacturer
Arnite	DSM Engineering Plastics
Diolen	ENKA-Glazstoff
Eastapac	Eastman chemical company
Hostadur	Farbwerke Hoechst AG
Mylar	E. I. Du Pont de Nemours & Co., Inc.
Melinex	Imperial Chemical Industries Ltd.
Rynite	Du Pont de Nemours & Co., Inc.

Fig. 1. PET repeating unit.

like many other polymers. The low flexibility of the PET chain is a result of the nature of the short ethylene group and the presence of the *p*-phenylene group. This chain inflexibility significantly affects PET structure-related properties such as thermal transitions [3,4]. The standard physical and chemical properties of commercial PET are shown in Table 2.

1.1. PET synthesis

PET production process involves two different starting reactions. The first starting reaction is an esterification reaction where terephthalic acid (TPA) reacts with ethylene glycol (EG) at a temperature of between 240 °C and 260 °C and a pressure between 300 and 500 kPa. The second reaction is *trans*-esterification reaction where dimethyl terephthalate (DMT) is reacted with EG at 150 °C [5], 180 °C–210 °C [2], 140–220 °C and 100 kPa [6]. *trans*-Esterification is the much preferred

process due to easier purification (Fig. 2a) [2]. The output of both these processes is bis(hydroxyethyl) terephthalate (BHET). The pre-polymerisation step follows in which BHET is polymerised to a degree of polymerisation (DP) of up to 30 (Fig. 2b). Pre-polymerisation reactions conditions are 250–280 °C and 2–3 kPa [2,3]. The third stage is the polycondensation process where the DP is further increased to 100. The polycondensation process conditions are 280–290 °C [6], 270–285 °C [2] and 50–100 Pa. Up to this stage, PET is suitable for applications that do not require high molecular weight (MW) or [η] such as fibres and sheets. Solid state polymerisation (SSP) might be required in which a high MW PET is produced. SSP is used to increase the DP to 150, and also increasing MW. SSP operating conditions are 200–240 °C at 100 kPa and 5–25 h [6]. Bottle-grade PET that has an [η] of 0.7–0.81 dl g^{-1} is normally produced by SSP at 210 °C for around 15–20 h [7,8].

Virgin PET manufacturers have tended in recent years to produce PET co-polymer; such as isophthalic acid modified PET, rather than homopolymer PET. PET bottles are normally made from co-polymer PET because of its lower crystallinity, improved ductility, better process ability and better clarity [9]. Some of the most important PET co-polymers are shown in Fig. 3 [10].

1.2. Virgin PET thermal transitions and crystallisation

Commercial PET has a melting temperature (T_m) of between 255 and 265 °C and for more crystalline PET is 265 °C [5]. The T_g of virgin PET varies between 67 and 140 °C. The thermal transitions and crystallisation of virgin PET with a focus on reversing crystallisation and melting have been analysed by several researchers [11,12].

An interesting phenomenon was reported in which the virgin PET experiences multiple endothermic transition during thermal analysis [11–13]. It was reported

Table 2
Physical and chemical properties of PET

Property	Test method	Value (unit)	Reference
Molecular weight (of repeating unit)	–	192 (g mol^{-1})	–
Mark–Houwink parameters	–	$k = 3.72 \times 10^{-2}$ (ml g^{-1}) $a = 0.73$	[15]
Weight-average MW	–	30,000–80,000 (g mol^{-1})	[15]
Density	–	1.41 (g cm^{-3})	[15]
Glass transition temperature	DSC	69–115 (°C)	[3,2,15,16]
Melting Temperature	DSC	265 (°C)	[5,16]
Heat of fusion	DSC	166 (J/g)	[2]
Breaking strength	Tensile	50 (MPa)	[17]
Tensile strength (Young's modulus)		1700 (MPa)	[17]
Yield strain	Tensile	4 (%)	[17]
Impact strength	ASTM D256-86	90 (J m^{-1})	[17]
Water absorption (after 24 h)	–	0.5 (%)	[17]

(a)

(b)
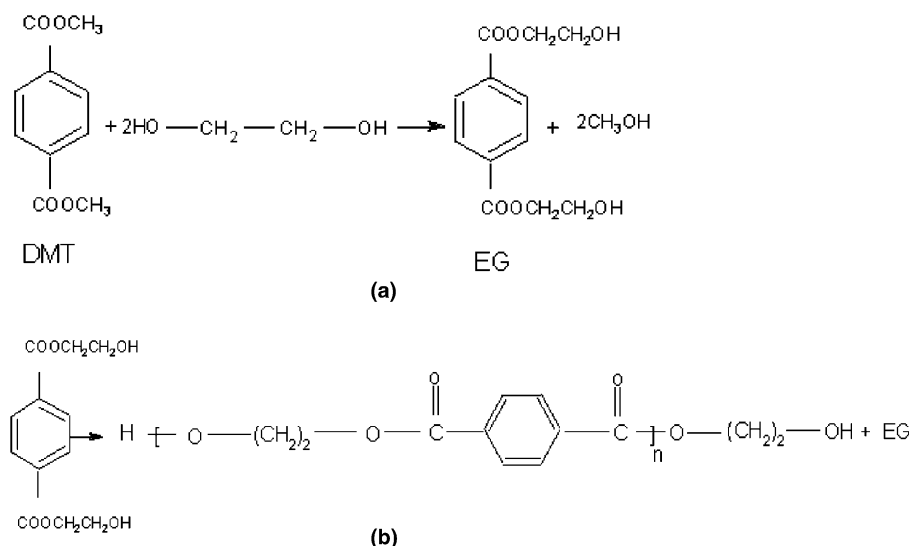
Fig. 2. PET synthesis reactions: (a) *trans*-esterification reaction and (b) condensation reaction.

Poly[(ethylene terephthalate)-co-(ethylene 2,6-naphthalate)] [PET/PEN]

Poly[(ethylene terephthalate)-co-(ethylene isophthalate)][PET/PEI]

Poly[(ethylene terephthalate)-co-(ethylene 2,5-bis(4-carboxyphenyl)1,3,4-oxadiazole)][PET/PEOD]
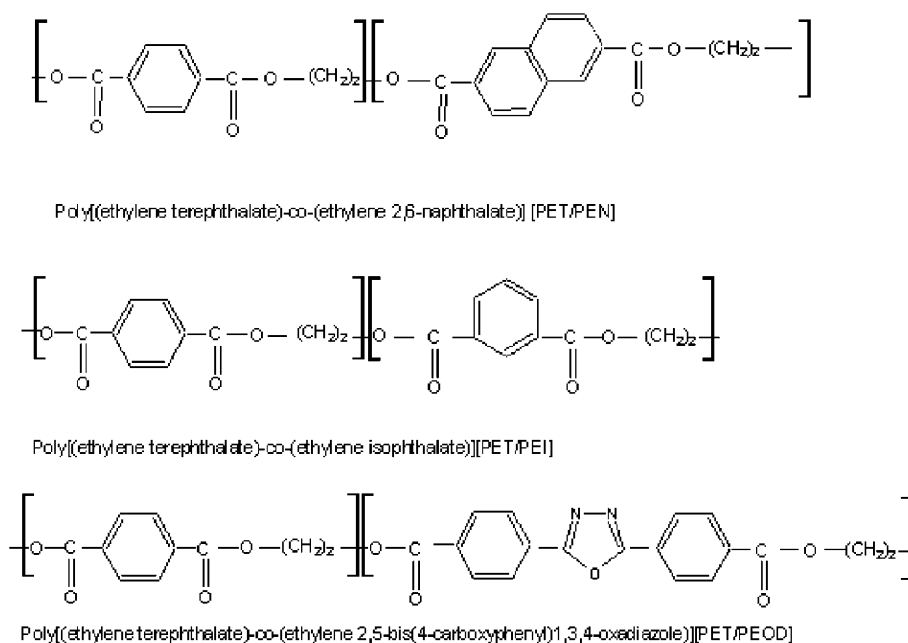
Fig. 3. Some of the most important PET co-polymers.

that this phenomenon is attributable to morphological and structural re-organization. As the temperature increases, better crystal structures are achieved because of the re-organization of the less perfect crystals [2].

Virgin PET is well known for having very slow crystallisation rate. The highest crystallisation rate takes place at 170 °C [5], or 190 °C [4]. Cooling PET rapidly from the melt to a temperature below T_g can produce an amorphous, transparent PET. Semi-crystalline PET can be obtained by heating the solid amorphous PET to a temperature above T_g where 30% crystallinity can be achieved [4].

The rate of crystallisation of virgin PET depends greatly on temperature and reaches its maximum at a temperature of 150–180 °C. The rate of crystallisation also depends on other factors such as MW, the presence of nucleating agents, the degree of chain orientation, the nature of the polymerisation catalyst used in the original production of PET and the thermal history [2].

1.3. PET applications and processing

PET is used broadly in products such as bottles, electrical and electronic instruments, automobiles products, house-wares, lighting products, power tools, material handling equipment, and sporting goods. [2]. PET films and fibres are the oldest applications of PET. Films are produced by biaxial orientation through heat and drawing. PET films are used in photographic applications, X-rays sheets and in food packaging [3]. PET films are also reported to be used in electrical and for recording tapes [5]. PET is also used as an electrical insulator. PET's insulating properties are regarded as good due to the severe restriction of the dipole orientation at room temperature that is well below the transition temperature [5]. PET fibres are another important application of PET and are produced by forcing molten PET through small holes in a die. Fibre strength is achieved by applying tension to align the chains through uniaxial stretching.

Virgin PET is produced at different specifications because different application requires different properties [9,14]. Examples of PET's $[\eta]$ with respect to the required application are shown in Table 3. PET granules can be processed in many ways depending on application and the final product requirements. The main PET processes are extrusion, injection moulding and blow moulding.

1.4. Extrusion

Extrusion is the oldest and simplest way of processing PET. The most common extrusion processes are extrusion moulding and extrusion to produce foam.

1.4.1. Extrusion moulding

Extrusion moulding is basically a process whereby molten PET is extruded into a mould where it sets to form the mould shape then is cut into moulding objects. PET extrusion moulding is normally used to produce large objects. PET is also easily extruded to produce films, sheeting, pipes and monofilament [2,18].

1.4.2. Extrusion to produce foam

Extrusion processes can be used to produce PET foam. Multifunctional modifiers are added to PET to achieve highly branched high MW PET enabling manu-facturers to produce PET foam by an extrusion process [7,19]. Some of the modifiers reported in the literature were pyromellitic dianhydride (PMDA) [20–23], 2,2′-bis(oxazoline) [24], triphenyl phosphate [25] and diimi-dodiepoxides [26].

1.5. Injection moulding

Pure PET has little value when injection moulded [5]. Injection moulded PET has poor mechanical properties due to the limited crystallisation, which is attributed to the high T_g that PET has, that can occur during cooling after injection moulding. Improvement has been made by many researchers and companies through the addition of nucleating agents and/or increasing mould temperatures to as high as 140 °C to promote crystallisation [18,27]. Examples of nucleating agents which improve crystallinity are 1,5-pentanediol and 1,8-octane-diol [28].

A detailed description of the PET injection moulding process was presented previously [5,29]. Injection moulding process control is reported by several researchers [30,31]. A schematic diagram showing the process parameters and their effect on the product quality is reported by Hurmuzlu and Nwokah [31]. The diagram (Fig. 4) is useful in understanding the injection moulding process variables and their interactions.

1.6. Blow moulding

PET has been used extensively in blow moulding applications to produce bottles. The blow moulding process starts with the injection of PET into a cold mould to produce an amorphous preform. With single stage injection blow moulding, the preform is transferred directly to an air-blowing unit where the preform is stretched and blown into a bottle mould. In two stage injection blow moulding, the preform is re-heated to around 10 °C above T_g and then blown into a bottle mould in a different air blowing unit. A clear and transparent pre-form has been known to be a good indication of successful injection blow moulding process [5,29].

2. Recycled PET

The POSTC-PET recycling industry started as a result of environmental pressure to improve waste management. The other aspect that acts as driving force for PET recycling industry is that PET products have a slow rate of natural decomposition [32]. PET is a non-degradable plastic in normal conditions as there is no known organism that can consume its relatively large molecules. Complicated and expensive procedures need to be operated in order for PET to degrade biologically [33].

Table 3
Examples of intrinsic viscosity for different PET applications

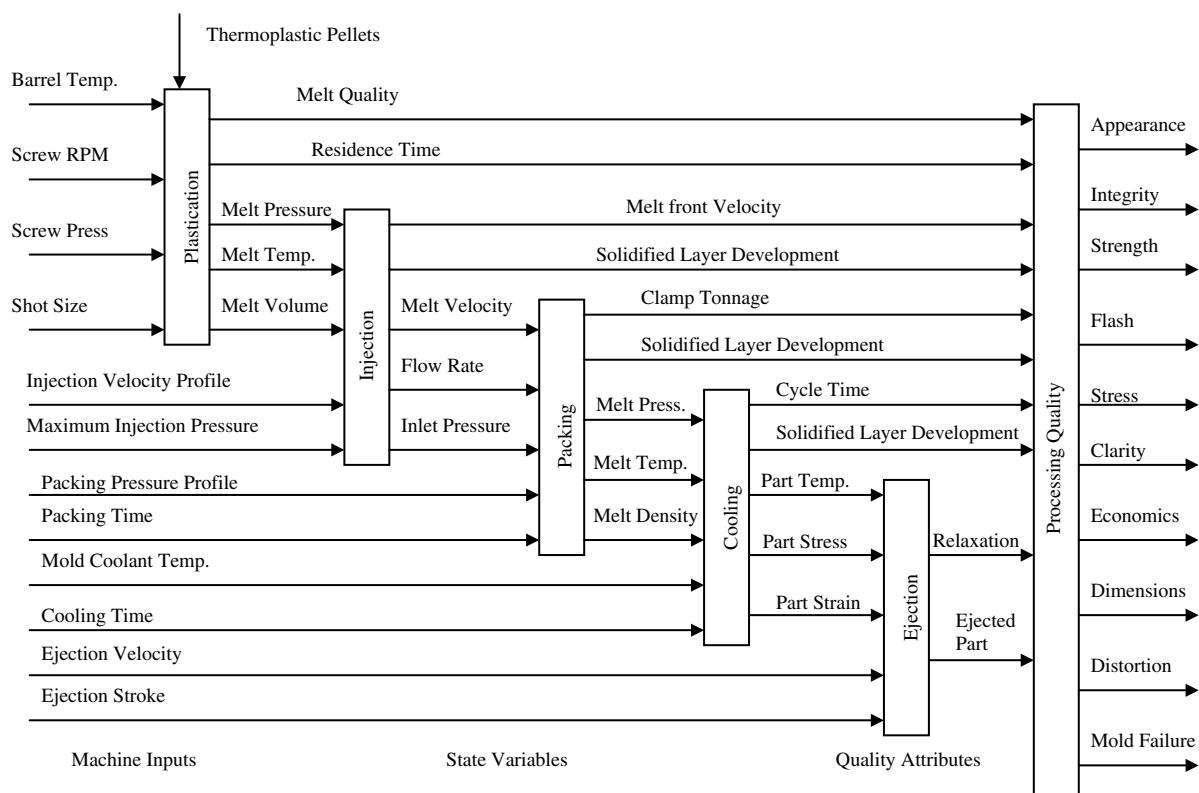| Application	$[\eta]$ (dl g^{-1})
Recording tape	0.60
Fibres	0.65
Carbonated drink bottles	0.73–0.8
Industrial tyre cord	0.85

Fig. 4. Injection moulding process variables.

Recycling processes are the best way to economically reduce PET waste [34–36]. On the other hand, as the price of virgin PET remains stable, new and cheaper technologies for recycling PET give an added value to the PET recycling industry by providing industry with relatively cheaper PET.

The first recycling effort of POSTC-PET bottles in the world was in 1977 [37]. The total consumption of PET in Australia for the year 2000 was 88,258 tonnes,

in which 28,113 tonnes were recovered demonstrating a recovery rate of about 32% [33].

Many researchers reported that in order to achieve successful PET recycling, PET flakes should meet certain minimum requirements [2,9,38]. Examples of the minimum requirements for the POSTC-PET flakes are summarized in Table 4. The major factor affecting the suitability of POSTC-PET flake for recycling is the level and nature of contaminants present in the flakes.

2.1. Contamination

Contamination of POSTC-PET is the major cause of deterioration of its physical and chemical properties during re-processing [39]. Minimizing the amount of these contaminants leads to better R-PET quality [40]. POSTC-PET is contaminated with many substances such as:

2.1.1. Acid producing contaminants
The most harmful acids to the POSTC-PET recycling process are acetic acid, which is produced by poly(vinyl acetate) closures degradation, rosin acid and abietic acid that are produced by adhesives and hydrochloric acid that is produced by PVC. The acids act as catalysts for

Table 4
Minimum requirements for POSTC-PET flakes to be re-processed

Property	Value
$[\eta]$	>0.7 dl g^{-1}
T_m	>240 °C
Water content	<0.02 wt.%
Flake size	0.4 mm < D < 8 mm
Dye content	<10 ppm
Yellowing index	<20
Metal content	<3 ppm
PVC content	<50 ppm
Polyolefin content	<10 ppm

the chain scission reactions during POSTC-PET melt processing [9,24,41]. Paci and La Mantia [42] investigated the influence of small amount of PVC during the melt processing of POSTC-PET. They reported that the presence of PVC (as little as 100 ppm) would increase POSTC-PET chain scission due to the catalytic effect of hydrogen chloride evolving during the degradation of PVC. The presence of PVC also results in discoloration of POSTC-PET during processing.

2.1.2. Water

Water reduces MW during POSTC-PET recycling through a hydrolysis reaction. Moisture contamination should be below 0.02% to avoid the MW reduction [9]. Most water content comes from the flake washing process but can be reduced substantially by proper drying.

2.1.3. Colouring contaminants

Fragments of coloured bottles and printed ink labels cause undesirable colours during processing. Enhancement of sorting and washing processes in bottle recycling may reduce colouring contaminants.

2.1.4. Acetaldehyde

Acetaldehyde is present in PET and POSTC-PET. It is a by-product of PET degradation reactions. The migration of acetaldehyde into food products from PET containers was a major concern in the early stages of developing the POSTC-PET recycling process. The high volatility of acetaldehyde means that it can be minimized by processing under vacuum or by drying [9]. Stabilizers such as (4-aminobenzoic acid, diphenylamine and 4,5-dihydroxybenzoic acid) are added to PET in order to minimize the amount of the generated acetaldehyde [43].

2.1.5. Other contaminants

The public use of PET bottles for storing other substances such as detergents, fuel, pesticides, etc. The remains of these substances could be a health hazard if traces of these substances remain after POSTC-PET recycling [44]. The increase of people's awareness of the danger of storing the materials inflicts to public health has minimized the amount of these contaminants significantly.

2.2. POSTC-PET conventional recycling processes

Two major processes have been applied in order to recycle POSTC-PET flakes. These processes are chemical recycling and mechanical recycling.

2.2.1. Chemical recycling

Chemical recycling (chemolysis) of POSTC-PET is achieved by total depolymerisation into monomers or partial depolymerisation into oligomers. The chemicals used for the depolymerisation of PET include water
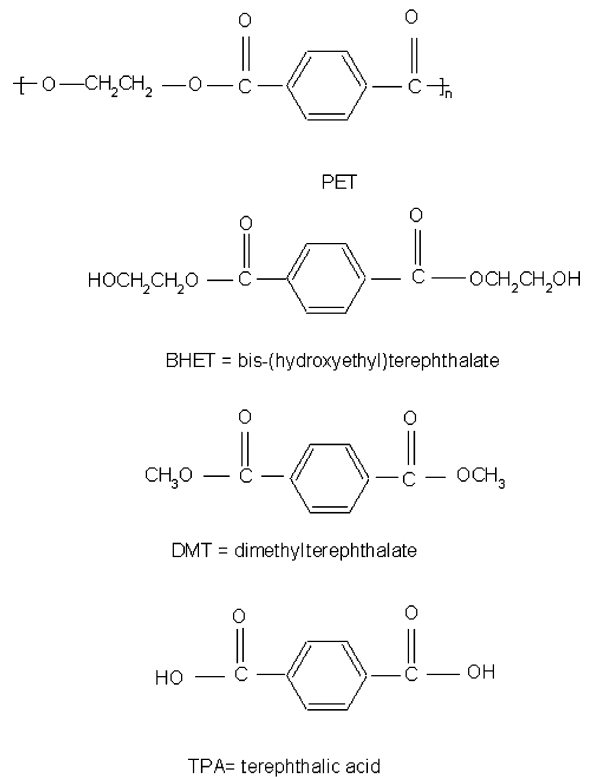
Fig. 5. Structural comparison between compounds resulting from PET depolymerisation process.

(hydrolysis), methanol (methanolysis) and EG (glycolysis) [36,45–52]. The structures of the compounds resulting from the depolymerisation of PET with comparison to the PET structure are shown in Fig. 5. The main disadvantage of PET chemolysis is its high cost [9].

2.2.2. Mechanical recycling

The mechanical recycling of POSTC-PET normally consists of contamination removal by sorting and washing, drying and melt processing. In this section the mechanical recycling of PET flakes originating from POSTC-bottles is described.

2.2.3. Contaminants removal

The removal of contaminants from POSTC-PET is a vital step in the mechanical recycling process of PET. Contaminant removal consists of several processes in which POSTC-PET bottles are sorted, ground and washed. The sorting process is basically separating PET bottles from PVC, polyethylene and other plastic containers. The sorting of PET bottles is an important and critical step. As discussed above, high levels of contamination by other materials causes great deterioration of POSTC-PET during processing.

PVC can be removed manually from PET bottle scrap before the grinding process; however, no more than 90% of the total PVC is typically manually removed [53]. While no 100% separation of PVC is reported yet, efficient separation of PVC from mixed PVC/PET bottles scrap can be achieved using methods based on the difference between the physical or chemical properties of PVC and PET. Gottesman [53] reported an automatic separation method based on the detection of chlorine atoms that help to identify PVC. Famechon [54] reported that 97.5% of PVC was removed using micronyl process which is a multistage grinding. Separation methods compete with each other on a cost basis; the fact that manual separation of PVC is becoming more expensive indicates that these separation techniques would be more feasible to use in the industry.

After sorting, POSTC-PET is ground into flakes in order to be easily reprocessed. PET flakes are washed following grinding. There are two ways in which POSTC-PET flakes are washed [9]:

(1) Aqueous washing which consist of two steps; a hot wash with 2% NaOH solution and a detergent at 80 °C followed by a cold wash with water only.
(2) Solvent washing for which tetrachloroethylene (TCE) has been reported to be suitable for washing PET flakes.

2.2.4. Drying

Drying is regarded as an essential step in POSTC-PET recycling. Minimizing the moisture content of POSTC-PET flakes reduces the hydrolytic degradation effect and leads to higher R-PET melt strength. Most POSTC-PET manufacturers use drying conditions ranging from 140 to 170 °C and 3 to 7 h [55]. In typical operating conditions, no more than 50 ppm water is allowed to be present in the PET flakes and this is normally achieved by using desiccated dryers operating at 170 °C for 6 h before feeding to the extruder [9].
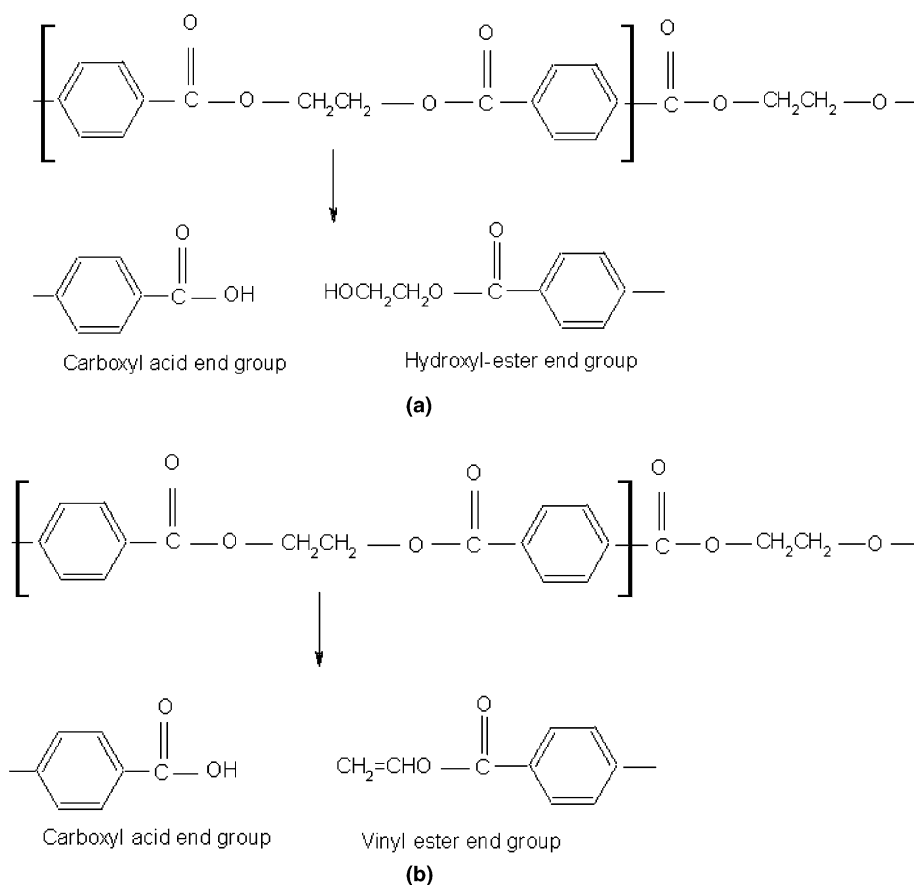

Fig. 6. Degradation reactions of PET: (a) hydrolysis reaction of PET and (b) thermal degradation reaction.

2.2.5. Melt processing

POSTC-PET flakes can be processed in a normal extrusion system into useful granules. However, due to the contaminants mentioned above that are present in POSTC-PET flakes, the produced granules have a low MW. Extrusion of PET flakes at 280 °C with the presence of above-mentioned contaminants reduces in MW due to degradation reactions.

The main advantage of the mechanical recycling of POSTC-PET is the fact that the process is relatively simple, environmentally friendly and requires low investment. The main disadvantage of mechanical recycling is the reduction of MW during processing, otherwise known as the reduction of [η]. A great sense of awareness of this problem by researchers and manufacturers was generated in the past two decades to find ways to maintain [η] during POSTC-PET processing.

2.3. Increasing recycled PET intrinsic viscosity

POSTC-PET undergoes a drop in MW when is recycled in a normal extrusion system. Thermal and hydrolytic degradation reactions during POSTC-PET melt processing are responsible for the reduction in MW or [η] of the PET [56]. The presence of water and PVC in the POSTC-PET flakes promotes PET chain scission during normal extrusion. At processing temperature (280 °C), hydrolysis reactions occur between water and PET resulting in shorter chains with acid and hydroxyl-ester end groups. The thermal cleavage of the PET ester bond also results in shorter PET chains with acid and vinyl ester end groups [6,14]. POSTC-PET hydrolysis and thermal degradation reactions are shown in Fig. 6.

Oligomers and volatile compounds are produced during PET processing above its melting temperature, which contribute to the depression of MW [57]. Scheirs [9] reported that cyclic and linear oligomeric compounds are formed during the reprocessing of PET as a result of thermal degradation reactions. He also showed that the oligomers content increased from 0.9 wt.% in virgin PET to 1.8–3.0 wt.% in R-PET. Examples of the most important cyclic and linear oligomeric compounds present in R-PET are shown in Fig. 7.

It can be seen from Figs. 6 and 7 that most of PET degradation products have low MW which depresses [η]. These products also serve as a catalyst to increase the rate of degradation reactions. Furthermore, as some of the degradation products have carboxyl ends, this increases the overall PET carboxyl content which leads to a decrease in PET thermal stability.

Overcoming the reduction of R-PET's MW or [η] has been the objective of many researchers [14,26,58]. Different methods and processes have been reported over the past two decades to restore or maintain MW or [η] during processing, which are outlined below.
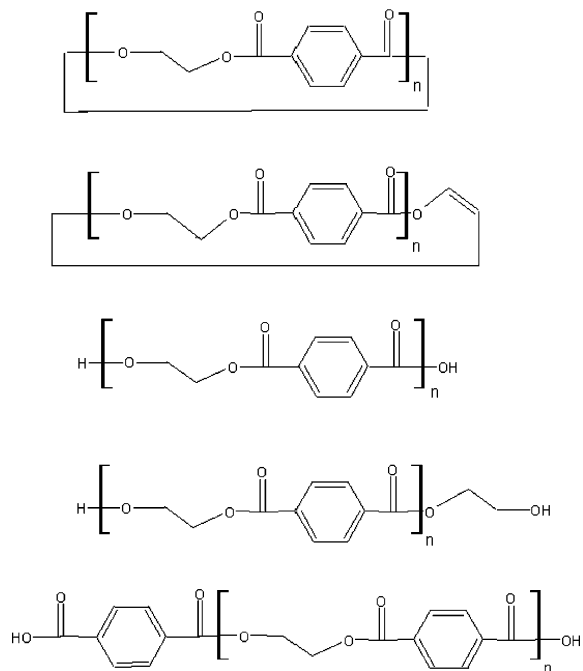

Fig. 7. Cyclic and linear oligomeric compounds present in R-PET during melt processing of POSTC-PET flakes.

2.3.1. Reprocessing under vacuum

The most recent PET recycling units are equipped with vacuum systems. All volatile substances present or produced while processing including water vapour are removed constantly during processing [59]. Volatile components further promote the degradation reactions and the removal of the volatile compounds during processing has recently been regarded as essential. Currently, intensive drying to remove moisture as well as vacuum degassing processing was introduced by Erema in their plastic recycling systems to minimize the effect of degradation reactions, resulting in higher R-PET [η] in comparison with normally extruded POSTC-PET [60].

2.3.2. Stabilizers

PET processing's stabilizers mainly have the function of reducing the effect of PVC contamination and are also associated with thermal stabilization. The majority of the PET process stabilizers are metal based such as butyl tin mercaptide, antimony mercaptide and lead phthalate [4]. Adding organic phosphate to PET during re-processing helps to stabilize it by decomposing hydroperoxide groups to non-radical products [9]. Scheirs [9] reported that bis(2,4-di-*tert*-butylphenyl) pentaerythritol diphosphite can prevent MW loss, inhibit yellowing reactions and reduce the production of acetaldehyde. The major disadvantage

of using stabilizers is the significant added cost to the PET recycling process.

2.3.3. Solid state polymerisation

The SSP is a process in which POSTC-PET is heated to above its T_g but below the T_m. Condensation reactions occur at a temperature range of between 200 and 240 °C, which is lower than the melt processing temperature (280 °C). Degradation reactions have little effect at the low temperature of processing leading to an increase in R-PET MW. SSP by-products are removed continuously by vacuum or by applying an inert gas stream [61].

Karayannidis et al. [62,63] investigated the use of SSP to increase the POSTC-PET's MW. They investigated the effect of reaction temperature and time on the resulted PET [η]. They reported that modified PET is produced with improved M_n after solid stating at 230 °C for 8 h. However, SSP is considered too slow and expensive to be applied on an industrial scale [64].

2.3.4. Chain extension

PET or POSTC-PET chain extension is a process where a di- or poly-functional low MW material is reacted with PET carboxyl and/or hydroxyl end groups to rejoin the broken chains that result from PET chain scissions during melt processing.

The mechanism of the PET chain extension reaction was introduced by Inata and Matsumura [65]. They suggested that for a 2,2′-bis(2-oxazoline) chain extender there are three types of reactions with PET:

(1) A blocking reaction where a molecule of chain extender reacts with one chain of PET.
(2) A coupling reaction where a molecule of chain extender joins two PET chains. This is the optimum target for the chain extension process.
(3) No reaction where the chain extender molecule fail to react.

The blocking reaction is an initiating step for coupling reactions and their rates are governed by the reaction conditions and chain extender concentration. One could expect that these three types of reaction apply only to di-functional chain extender or highly controlled reactions. Otherwise a branching reaction is inevitable. Branching and cross-linking does happen in chain extension process as is reported previously [26,66–68].

3. Chain extension process

Chain extension by the reactive extrusion process to overcome the drop of [η] was the attractive choice for many studies for several reasons. It is less expensive than SSP and easier to apply on an existing normal extrusion

system. There are many publications reported success of the chain extension process using virgin and POSTC-PET [20,24,64,65,67–72].

The majority of the chain extension research and experiments were done using low MW virgin PET in order to raise the [η] to the desired level [26,64]. An important aspect of the chain extension reaction is the effect of the PET end groups content.

3.1. End groups effect

The hydroxyl and carboxyl end groups content in R-PET and chain extended PET plays a vital role in increasing or decreasing the MW during processing [65]. It was reported that during POSTC-PET melt processing, a decrease in MW and an increase of carboxyl content was observed [24]. The carboxyl end groups are one of the main products of PET thermal degradation, thus the carboxyl content of R-PET is a good indication of the thermal degradation reactions' rate during melt processing [73].

Researchers [23,73,74] reported that PET MW decreases when carboxylic chain ends increase; they attributed the increase in PET carboxylic content to thermal degradation. Bikiaris and Karayannidis [73] reported that the oxidation of PET during processing is promoted by carboxyl end group content. The decrease in carboxylic groups in the chain extended PET increased the thermo oxidative stability of PET. Carboxyl end groups are consumed in a chain extension reaction during melt processing by an esterification reaction where it reacts with glycol end group PET as it shown in Fig. 8.

Inata and Matsumura [69] reported that the MW of chain extended PET could be determined by the carboxyl content as long as an equivalent amount of chain extender to the hydroxyl terminals of the initial PET is used.

All the above-mentioned research emphasises the importance of the end groups' content as an indicator of the degradation and chain extension rate when processing PET. Carboxyl content increase was associated with an increase in degradation rate as most degradation
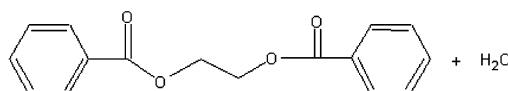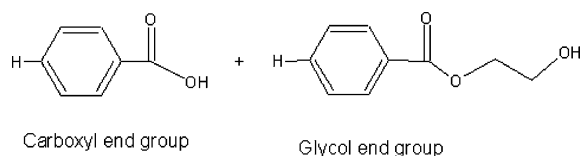

Fig. 8. The reaction of carboxyl end groups with glycol end group.

reaction products have carboxyl ends. Hydroxyl content decrease was associated with an increase of the chain extension reaction rate during processing. The sole purpose of PET chain extension process is to achieve linear coupling. However, the cross-linking or branching reaction is inevitable and needs to be minimized.

3.2. Cross-linking reaction

Cross-linking mechanisms were reported for POSTC-PET melt processing [42,75]. It was proposed that the cross-linking reaction was initiated by the formation of peroxy radicals; unstable hydroperoxides and free radicals were produced by the abstraction of the hydrogen from the polymer chain. The process ends when two radicals combine leading to the increase in the MW [42]. Inata et al. [76] reported that cross-linking of PET improve its thermal stability. However, it is essential in the POSTC-PET chain extension process to avoid heavy cross-linking. Heavy cross-linking leads to gel formation, which in turn will negatively affects the products' mechanical properties and thermal stability.

3.3. Chain extenders

Various chemicals have been used for the PET chain extension processes. Addition-type chain extenders generating no by-products are much preferred. Inata and Matsumura [20,65,69–72] extensively investigated the reactive blending of virgin PET with chain extenders in order to raise the $[\eta]$ of the PET. Their efforts concentrated on evaluating potential chain extenders. They showed that additive type di or poly functional chain extenders were the preferred chain extenders due to their higher reaction rates without generating by-products. Many addition type chain extenders were reported to be effective chain extenders for linear PET, such as diepoxides, bis-2-oxazolines and bis-5,6-dihydro-4h-1,3-oxazines [20,24,77,78].

Chain extenders can be classified according to the PET functional end group that they react with. The chain extenders that react with carboxyl end groups are effective, in addition to the chain lengthening, by reducing the overall carboxyl content leading to high hydrolytic and thermal stability which in turn maintains MW during melt processing [69]. Some examples of carboxyl-reactant chain extenders are 2,2′-bis(2-oxazoline), 2,2′-bis(5,6-dihydro-4h-1,3-oxazine), N,N′-hexamethylene-bis(2-carbonyl 1,2-oxazoline) [20,69]. The other type of chain extenders is hydroxyl-reactive chain extenders. They are more effective with low MW PET produced by melt polycondensation because the hydroxyl content predominates over the carboxyl end groups. The hydroxyl-reactive chain extenders will increase $[\eta]$ rapidly when reacting with PET that is produced by melt
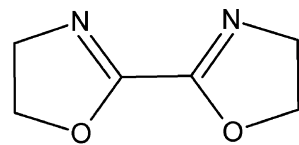
BO= 2,2′-bis(2-oxazoline)

Fig. 9. Chemical structure of BO chain extender.

polycondensation PET [69]. An example of hydroxyl-reactive chain extenders are 2,2′-bis(3,1-benzoxanin-4-one) [70].

Many researchers reported disadvantages associated with operating with some chain extenders. Cardi et al. [24] reported that undesired side reactions could take place when using bis(2-oxazoline) (BO) to chain extend PET due to the sensitivity of the oxazolinic ring to acidic compounds. Structure of bis(2-oxazoline) is shown in Fig. 9.

Torres et al. [58] reported that diisocyanates are more effective chain extenders than BO and diepoxides; however, they reported product discoloration when using diisocyanates. Use of bisepoxy compounds, bis(cyclic carboxylic anhydride) and diisocyanates as the addition type chain extender show unavoidable increase in branching and/or the development of less thermally stable linkages in the polymer chains. Nevertheless branching and cross-linking could be useful in the sense of increasing the MW, but after a certain limit, gel formation process within the polymer start to occur which is undesirable [20,65].

PMDA has previously been reported as an efficient chain extender or branching agent [21,22,68,79–82]. It is thermally stable, produces no side products on reaction with PET, is tetra functional, commercially available and economical. Khemani [22] showed that when PMDA with concentration of 0.2–0.3 wt.% was used with virgin PET at laboratory scale equipment, a significant increase in melt strength was obtained. Fig. 10 shows the structure of PMDA.

Khemani [21] reported a mechanism for the reaction of PMDA with PET end groups. Glycol transfer and
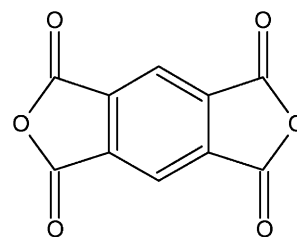
PMDA= Pyromellitic dianhydride

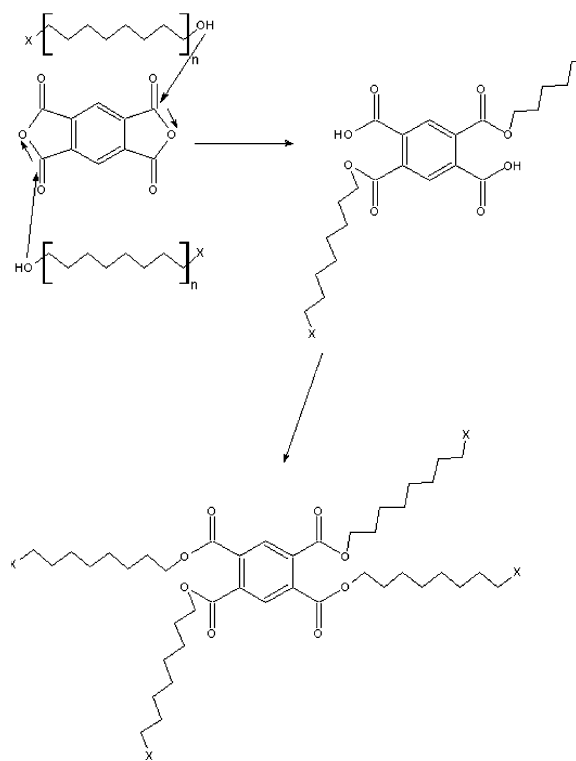Fig. 10. Structure of PMDA chain extender/branching agent.

Fig. 11. Branching reaction between PMDA and PET.

trans-esterification reactions are the results of direct reaction of the PET hydroxyl group with PMDA. Khemani [21] also proposed a branching reaction scheme between PMDA and PET as shown in Fig. 11. Two carboxyl groups are formed as a result of the initial linear coupling between the PMDA molecules and the PET hydroxyl end groups. The reaction between PMDA and PET might develop further in which all the PMDA functional groups are reacting in esterification and *trans*-esterification reactions resulting in branching or cross-linking structures [83]. Carr et al. [84] reported that polyester blends undergo *trans*-esterification reactions in the melt leading to branching and at later stage to cross-linking. The esterification of carboxyl end groups and the etherification of hydroxyl end groups reactions, by diepoxides, result in secondary hydroxyls that may react further with carboxyl or epoxy groups promoting the branching and cross-linking structures [66].

3.4. Chain extension process experimental variables

The influence of variables such as the chain extender concentration and the reaction time on the virgin and POSTC-PET chain extension process have been investigated extensively [20,22,24–26,65–72].

The chain extender concentration has been the main research parameter examined in the chain extension process by reactive blending process [26,66,85,86]. The theoretical amount of chain extender required was calculated according to the chain extension reaction stoichiometry and in ideal reaction conditions, a higher amount of chain extension than theoretically needed lead to heavy cross-linking reactions resulting in gel formation. In these studies, the reactive blending process residence time was relatively high (up to 10 min) [69]. Some chain extenders have the time, in addition to couple short chains, to develop dense branching reactions and cross-linking.

Starting from virgin PET having $[\eta]$ of 0.6–0.7 dl g^{-1}, researchers obtained PET with $[\eta]$ above 1 dl g^{-1} in the presence of chain extenders by reactive blending. By selecting the appropriate chain extender, controlling its amount and reaction time, it is possible to obtain PET with predetermined properties such as a specified degree of cross-linking [20,26,69].

All the above-mentioned publications for chain extension process dealt with virgin PET, the experiments were done using laboratory scale equipment and no optimisation methods for particular applications were used to identify optimum conditions.

Paci and La Mantia [41] reported that during POSTC-PET processing competition between degradation and chain extension reactions took place. Using nitrogen in the process promoted chain extension reactions producing R-PET with high MW. By using nitrogen purging during melt mixing they reported an increase in R-PET $[\eta]$ up to 0.88 dl g^{-1}. However, using nitrogen is regarded as not feasible for extrusion or reactive extrusion commercial applications due to the complications of installing the nitrogen purging equipment and also because of the cost of nitrogen consumed.

Several process variables were investigated in the chain extension process via reactive extrusion system such as shear rate, residence time and chain extender concentration. It was found that short reaction times and a decrease in moisture content encourage effective chain extension and restrain thermal and hydrolytic degradation [64,78]. These findings are very beneficial to the application of chain extension process in a normal production line of R-PET extrusion. POSTC-PET extrusion systems have short residence time and the system is normally equipped with vacuum lines to extract light components.

3.5. Chain extension process equipment

For chain extension experiments, various machines were used, such as single screw extruder [64], twin-screw extruder [79], a stainless steel custom-made laboratory scale reactor, and a medium-scale rheomixer [26,78,87]. The twin-screw extruder is well suited for use in chain

extension process due to better mixing and its stable mechanical processing.

4. Reactive extrusion process

Reactive extrusion processes facilitate polymer modifications greatly in the sense of providing a modified polymer with better specifications for different applications. Reactive extrusion is basically achieved by using an extruder as a reactor. For the POSTC-PET modification process, reactive extrusion has been attractive because of its advantages of combining a reactor and an extruder in one system. Many researchers used reactive extrusion systems to modify virgin PET [22–24,88]

and/or POSTC-PET [24,79] in order to achieve better chemical and rheological properties. When applying POSTC-PET chain extensions in a reactive extrusion system, process parameters such as the twin-screw extruder performance and stability are closely monitored to ensure successful operation. Akkapeddi and Gervasi [64] investigated a reactive extrusion system of virgin PET with added chain extenders. They obtained lower carboxylic content using different types of chain extenders.

Different models have been introduced to describe the reactive extrusion system. Janssen [89] introduced an interaction chart that presented the parameters affecting reactive extrusion as shown in Fig. 12. These parameters and conditions influencing the reactive
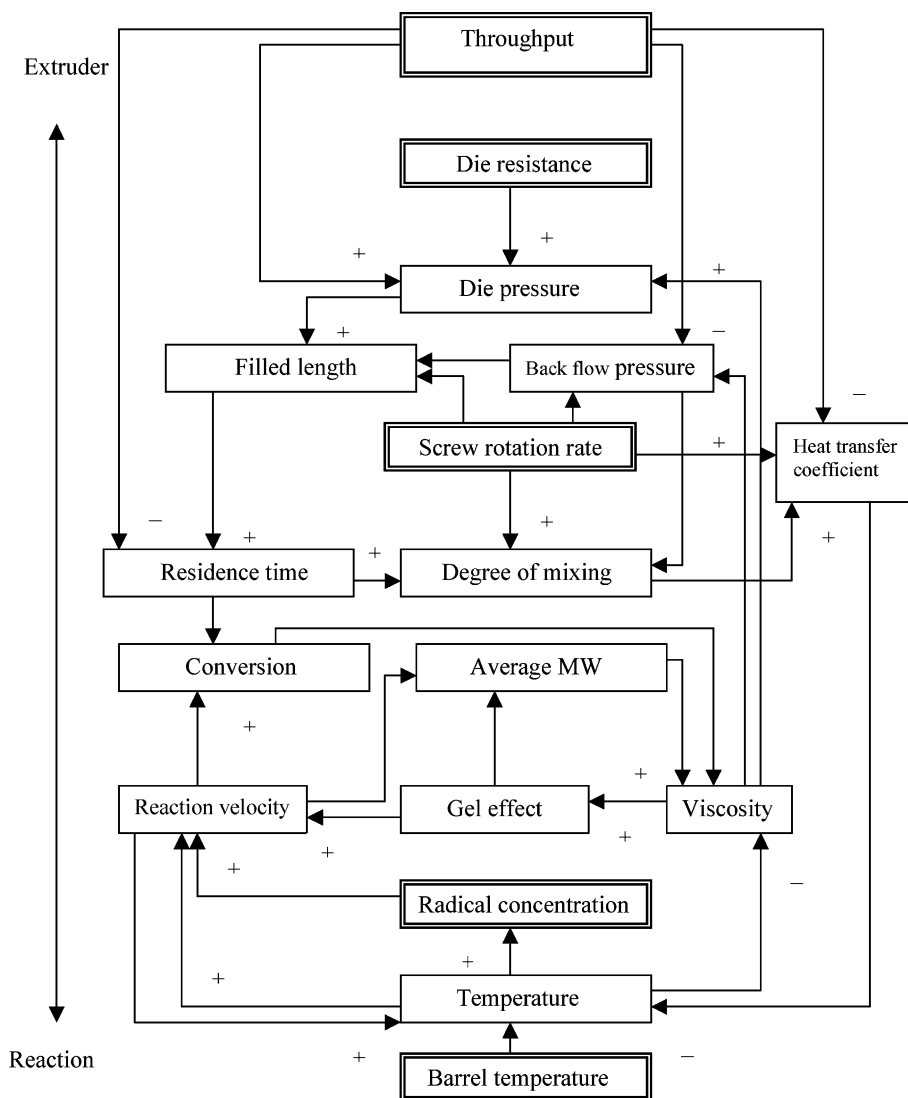

Fig. 12. Reactive extrusion process interaction chart in which (+) sign means leads to increase and (−) sign means leads to decrease.

extrusion process and its stability have been also described by several researchers [89–92]. Vergnes et al. [93] developed a model and software to characterize the flow in a co-rotating twin-screw extruder.

Fig. 12 shows the parameters (double lined boxes) that can be altered or varied in order to achieve successful operation at different reactive extrusion systems. These parameters of throughput (flow rate), die resistance, screw rotation rate, radial concentration and barrel temperatures are considered as variables for reactive extrusion systems investigations. In reactive extrusion process, the variables of flow rate, screw rotation rate and barrel temperature are the system control variables. For example, because of the increase in residence time, an increase in reaction conversion can be expected when the extruder screw speed is decreased [90].

Fig. 12 shows the possible feed back loops that govern the interaction and effect of these variables with other reactive extrusion process parameters and reaction properties [89]. Fluctuations in the above-mentioned variables are a major cause of thermal, hydrodynamic and chemical instabilities leading to disturbances in the reactive extruder operation. In an industrial size reactive extruder, a great emphasis is placed on controlling instabilities by providing stable operating conditions [29].

For the POSTC-PET reactive extrusion processes, single or twin-screw extruders can be used. Single screw extruders have the advantage over twin-screw extruders of lower capital cost which is the reason why they are used widely in the extrusion industry. Twin-screw extruders are well known for their high mixing ability and are used mainly in compounding and reactive polymer processes.

4.1. Single-screw extruder

Single-screw extruders are not the preferred choice for researchers to perform PET reactive extrusion experiments because of the relatively poor mixing ability. However, Aharoni et al. [25] reported a reactive extrusion process of PET and triphenylphosphite (TPP) using a single-screw extruder. Single-screw extruders have the advantage over twin-screw extruders of lower capital costs. Nevertheless, for designing commercial scale reactive extrusion systems, optimisation of mixing performance and capital cost should be considered.

4.2. Twin-screw extruder

The twin-screw extruder is a practical system for reactive extrusion applications due to the better mixing performance achieved in comparison with a single-screw extruder. Twin-screw extruders can have fully intermeshing, partially intermeshing or totally non-intermeshing flights. When the screws of a twin-screw extruder rotate in same direction the extruder is considered to be co-

rotating, otherwise it is counter-rotating. Co-rotating twin-screw extruders have an advantage over counter-rotating twin-screw extruders of a better ability to mix additives or reactants of a small particle size with PET [94].

Twin-screw extruder had been extensively applied to the PET reactive extrusion processes at laboratory scale [23,24,79,82] and most recently on industrial scale [68]. It is well known that the flow in the twin-screw extruder is very complicated and governed by a large number of parameters [93].

Backpressure or die pressure fluctuation is one of the serious problems in reactive extrusion systems. Many researchers reported the occurrence of pressure fluctuation problem in twin-screw extrusion systems [89–91]. Bulters and Elemans [91] reported also, that the screw design is an important parameter in the stability of reactive extrusion process. The degassing or vacuum system installed in reactive extrusion process has a disadvantage of possibly causing pressure fluctuations during operation [91]. These researchers were describing reactive extrusion process based on experiments on laboratory scale equipment.

A general model describing the flow in a twin-screw co rotating extruder was reported by Vergnes et al. [93]. A close examination of their method in generating the flow model reveals many assumptions and approximations; the use of the model in describing PET-PMDA reactive extrusion system is not practical.

The melting process and pressure generation and their mechanisms in twin-screw co-rotating extruders are complex. Kim and Gogos [92] attempt to explain melting behaviour and they concluded that melting behaviour is effected by screw design and operating conditions. Several researchers reported a description of mixing and pressure generating mechanisms in co-rotating twin-screw extruders [95,96].

Measuring the residence time distribution during reactive extrusion operation is important because of its influence on the chemical reactions behaviour during extrusion. Many researchers reported different methods for measuring (by ultraviolet and ultrasonic techniques), analysing and modelling residence time distribution in twin-screw extruders [97–100].

In conclusion, the process control of twin-screw extruders especially in reactive extrusion processes has to be taken into important consideration during the PET chain extension process.

4.3. Stability of reactive extrusion system

It has been reported that process stability is a decisive factor in the successful operating of the reactive extrusion system [89]. Janssen [89] described three different types of instabilities in a reactive extrusion system, thermal, hydrodynamic and chemical. Reactive extrusion

process instability is defined as a disturbance in one or more of the variables governing process control. Thermal instability is caused by a disturbance in the extruder barrel temperature that leads to fluctuation in the reaction temperature and in turn disturbs the barrel temperature even further. Hydrodynamic instability is caused by a disturbance in the die pressure that leads to an increase in the melt viscosity and in turn affects the reaction conversion, leading to further disturbance in the melt viscosity and the die pressure. Chemical instability happens when the reaction velocity increases at a local point causing an increase in melt viscosity and that will initiate hydrodynamic disturbance (Fig. 12). In POSTC-PET reactive extrusion systems, the initial chemical disturbances are caused by the local difference in chain extender concentrations leading to local difference in reaction conversions. Due to the high sensitivity of the POSTC-PET chain extender reactions, a completely stable operation is not expected. However, the reactive extrusion process is regarded as stable when the die pressure, temperature and flow rates are within the safe working conditions of the system. In other words, the system is stable when the fluctuations in die pressure or temperature or flow rate are within a medium value and below the hazardous operating pressure or temperature. Minimizing the disturbances in reactive extrusion barrel temperature, flow rate and vacuum pressure is vital to secure a stable operation.

5. The effect of chain extension on PET crystallinity and thermal transitions

The crystallinity and thermal transitions are of the most important properties of reactive extruded recycled (RER-PET) that are affected by chain extension process [67]. The increase in MW of chain extended R-PET alters the crystallisation rate and the crystallinity level and that in turn influences the RER-PET performance and properties including thermal transitions such as T_g, T_m and crystallisation temperature (T_c) [40,79, 101,102].

There are many techniques and instruments used in the literature to investigate the thermal transition and crystallinity of virgin PET, POSTC-PET, R-PET and modified PET. These techniques include differential scanning calorimetry (DSC) [103–109], TMDSC [110–115], dynamic material thermal analysis [116,117] and thermo mechanical analysis [118]. TMDSC has been used for the analysis of the melting and crystallisation of virgin PET extensively [119–124].

TMDSC is an improved DSC technique, in which a linear change of temperature for the measured sample is combined with sinusoidal modulation in heat flow. TMDSC theory and operating principles are extensively described in the literature [125–131]. The TMDSC instrument is capable of recording the heat capacity of the sample at the same time as recording the heat flow as a function of the modulation of the temperature [120,126,132,133].

TMDSC has many advantages over conventional DSC. TMDSC separates the reversing and non-reversing thermal transitions [132]. It demonstrates an increase in resolution without a loss in sensitivity. TMDSC separates the relaxation phenomena from the glass transition [132]. TMDSC allows the measurement of heat capacity and thermal conductivity directly. However, the approach developed to calculate initial crystallinity based on the difference between the reversing and non-reversing components is still in debate [134]. TMDSC provide more insight into the process dynamic behaviour of polymer samples than DSC. TMDSC provide not just overall quantitative information of processes like glass transition, crystallisation and melting but also an insight into their kinetics [12,126]. The understanding of chain mobility and its affect on phenomena such as crystallisation and melting is possible with the use of TMDSC because of the heat component separation [128,133].

The reversing heat flow component is the reversible component of the total heat flow while the non-reversing component (NR) represents all irreversible components of the total heat flow at the time and temperature of the experiment. The separation of these two components allows the study of thermal transitions in more detail.

5.1. Thermal transitions and crystallinity

There have been rigorous efforts by many researchers to understand the effects of the chain extension process on thermal transitions of virgin PET [65,78,118, 135,136]. By using DSC, the decrease in T_g, T_c, T_m values and crystallinity is observed after virgin PET has been chain extended by different chain extenders. Haralabakopoulos et al. [78] reported a decrease in PET thermal transition values when increasing the diepoxides chain extender concentration and reaction time. Bikiaris and Karayannidis [118] showed a decrease in T_m while there was no significant change in T_g when virgin PET had been chain extended by diepoxides. Nevertheless, Inata and Matsumura [65] reported that virgin PET chain extension processes did not have a serious effect on T_m values.

In these results mentioned above, various chain extenders have been used with different chain extender concentrations and this explains the degree of significance of the chain extension process on thermal transitions of virgin PET. It is generally expected that the increase in MW and [η] decrease the T_c and T_m values because of the decrease in the enthalpy of crystallisation and melting.

Crystallinity of PET strongly affects the end-use application and mainly depends on the molecular structure and crystallisation conditions [137]. The decrease in crystallinity is expected during chain extension processes due to the resultant chain entanglements and the difficulties in chain folding into a crystal structure due to the high degree of branching [79]. However, crystallisation at high temperatures increases due to the ease of chain disentanglement [135]. In a recent study, Torres et al., [40] reported that the impurities present in the chain extended R-PET could act as nucleating agents promoting crystallisation. Furthermore, Rosu et al. [138] reported that adding branched PET to linear PET also increases its crystallinity. Thus more information is needed to clarify the effect of the chain extension process on the crystallinity of R-PET.

5.2. Multiple melting peaks phenomena

Multiple melting peaks are observed in PET during DSC thermal analysis. Many researchers believe that the multiple melting peaks behaviour of PET is linked to partial melting and re-crystallisation and re-melting (mrr) [137,139–141]. Other researchers believe that the multiple melting peaks are attributable to the distribution of crystals with different lamellar thickness, and to the melting of different crystal structure [11,13, 142,143]. Wang et al. [142] reported an extensive investigation into the nature of secondary crystallisation in PET. They used three techniques of X-ray scattering, DSC and TMDSC. They concluded that the first melting peak is attributed to the melting of secondary crystals while the second melting peak is attributed to the melting of the primary crystals. This suggests that the primary and secondary crystals of PET have different melting enthalpies, which force double melting peaks. In a recent study, Lu and Hay [107] reported that increasing the heating rate will lead to minimize the multiple endothermic phenomena due to the rapid melting of crystals.

6. ISBM process

PET is widely used thermoplastic polyester in the bottling industry for its excellent properties of clarity, thermal stability, toughness and chemical resistance [144,145]. Biaxial orientation during the ISBM process gives PET bottles produced by this technique enhanced toughness and low gas permeability [5]. Bottle-blowing grade PET has an [η] of about 0.70–0.85 dl g^{-1} and is generally synthesized by SSP with DP of up to 150 [134,146]. There are two techniques used in making ISBM bottles. The first technique is a two-stage process; in the first stage a preform is produced by injection moulding then

later it is re-heated to the orientation temperature for stretching and blowing. The second technique involves one stage in which the injection moulding, stretching and blowing of preform are combined in single operation.

Many elements of the single stage ISBM process need to come together in order to achieve successful processing. These elements, such as orientation temperature and stretch ratio, characterize ISBM bottles' properties. Orientation temperature is the temperature at which the preform has to be deformed in order for the molecules to align during stretching. The mechanical and barrier properties of PET are much improved by molecular orientation [94].

In ISBM, biaxial PET molecular orientation is achieved by stretching the preform at a temperature between T_g and T_m. Biaxial stretching promotes orientation-induced crystallisation as well as producing molecular orientation. Molecular orientation and crystallisation are related to each other in which crystallisation is promoted by orientation. The degree of orientation and crystallisation affects individually and interactively a bottle mechanical, optical and barrier properties.

6.1. Preform moulding

In a single stage ISBM process, PET melt is injected into the preform mould at a temperature above 270 °C. During preform mould filling, orientation take place near the side walls with the melt flowing in a non-Newtonian manner, after the preform has been filled, it cools down during which it is thermally conditioned for the stretch blow moulding stage. Colour, clarity, concentricity, moisture waves, gas bubbles, and crystallinity haziness can indicate preform quality [1].

6.2. Bottle stretch blow moulding

The preform is loaded into the blow moulding station. The preform is then stretched axially by a stretching rod towards the base of the bottle mould; at the same time low-pressure air expands the preform in a radial direction. When the stretching rod reaches the base, high-pressure air is switched on forcing the preform against the bottle mould wall. The bottle mould wall is at about 10–15 °C, which allows the bottle to have maximum orientation and lowest thermal crystallisation [1]. ISBM process design aspects are described in details by [94,147,148].

6.3. ISBM of RER-PET

During the single stage ISBM process, RER-PET experience complex physical and chemical phenomena. Degradation and chain extension reactions compete

with each other during the melting stage. Different viscosity distribution is expected when the RER-PET is forced to flow through the extrusion chambers due to the shape of the screw and barrel geometry. Then RER-PET is injected at high pressure into a mould where it deforms to take the shape of the mould as preform, and then it is stretched by biaxial orientation to have the shape of a bottle, then cooled down and solidified. The nature and properties of the inlet material have great impact on the properties of the produced bottle.

PET has a maximum stretch ratio of about 16/1 [94]. When manufacturing bottles, stretching over this ratio cause the bottle to burst. The actual stretch ratio (axial and hoop) of a bottle depends on the bottle size and design. Typical stretch ratio for PET bottles at different sizes is found in the literature [1,144].

At a processing temperature of 280 °C, degradation reactions occur instantly upon feeding, during the injection stage, causing a drop in melt [η] and MW. However, during the same stage of the ISBM process, RER-PET undergoes further chain extension mainly between its active chain ends and the un-reacted PMDA molecules left from the previous reactive extrusion process. PMDA di- or tri-functionally reacted molecules have the chance also to react further to become tetra functional and produce branching [68]. Both chain extension and degradation reactions co-exist during RER-PET ISBM processing and degradation reactions would be dominant over the chain extension reaction especially with the absence of vacuum or purging systems to remove degradation products [41]. It is believed that during the injection stage of ISBM, the competition between chain extension and degradation reactions is influenced greatly by the RER-PET and PMDA concentrations [68]. The expected decrease in MW and [η] during the injection section of the ISBM process is another factor affecting bottle orientation in the following stretch-blow moulding.

The RER-PET and virgin PET blend melt is thermally quenched when injected from approximately 280 °C at the injection unit to the mould temperature of 15 °C. The resulted preforms are desired to be fully amorphous to achieve the highest orientation in the stretch- blow moulding stage. However, low level of crystallinity might form at high level of RER-PET concentration because of the presence of nucleating particles (contaminates) [41]. At the stretch blow moulding stage, the RER-PET is crystallized while in the rubbery state as a result of chain orientation caused by vertical stretching by rod and radial stretching by air. The stretched (oriented) chains initiate a crystal structure after reaching the lowest critical orientation level [149]. The orientation-induced crystallinity depends on many factors including the thermal crystallinity content, MW and the stretch and blowing mechanisms [150]. In turn, orientation-induced crystallinity strongly affects the bottles physical properties.

6.4. Bottle physical properties

The orientation, optical, mechanical and barrier properties of PET bottles produced by ISBM depend on many factors such as operating conditions, melt strength, MW, crystallinity and crystallisation conditions [1,137].

There have been concentrated efforts to investigate the effect of initial crystallisation and crystallisation conditions of virgin PET on the ISBM operation and bottles properties [1,135,137,145,149,151]. A decrease in crystallinity is expected during the POSTC-PET chain extension process due to chain entanglements and the difficulties in chain folding into a crystal structure due to the high degree of branching [135]. It is reported that high crystallinity is advantageous for the bottles' barrier performance and toughness [1,145,149], however, a slow crystallisation rate and low crystallinity are favourable for bottle clarity and low acetaldehyde formation [134,146]. Caldicott [1] mentioned that crystallinity in virgin PET promotes good physical properties and chemical resistance. Sakellarides [146] described a process to modify virgin PET with a co-monomer to slow the PET crystallisation rate with the purpose of improving bottle clarity and reducing the acetaldehyde formation. Bashir et al., [134] reported that high initial crystallinity should be avoided during SSP of bottle-grade PET, as that will force a higher T_m. In turn, higher T_m leads to higher injection moulding temperature that in turn will increase the acetaldehyde content that is undesirable.

The reduction of the bottles' weight to minimize cost was the objective of a study of several researchers [152,153]. Bottle barrier resistance and mechanical properties decrease with decreasing bottle weight (wall thickness). Bottle manufacturers balance between bottle weight and physical properties when designing bottle moulds.

The barrier properties of virgin PET bottles processed via ISBM have been studied extensively [149,154–156]. The permeability of a liquid or gas into a polymer depends on its diffusion coefficient. The diffusion coefficient depends to a large extent on the molecular size and shape of the permeates' molecules [155]. Large molecular size permeant with a complex structure leads to a lower diffusion coefficient resulting in lower permeability. Hansen [155] reported that the diffusion coefficient is concentration dependent and that the diffusion of a low MW liquid permeant becomes faster as the local concentration in the polymer become higher.

It was reported that 80–100% of CO_2 molecules are lost in PET bottles due to permeation and absorption [154]. Hartwig [154] reported that for virgin PET, CO_2 permeability decreases with increasing crystallinity; he

Table 5
Permeability of gases through PET

Gas	Permeability (cm day^{-1} 100 in^{-2} mil^{-1}) at 25 °C
CO_2	15–25
H_2	100
N_2	0.017–10
O_2	6–8

also explained that the lack of free volume in the crystalline structure prohibits CO_2 from migrating through the bottle wall. Mechanical properties and barrier resistance of PET bottle improves with more uniform thickness distribution and with thicker walls while clarity characteristics favour thinner walls [149]. Lin et al. [156] reported that the effect of crystallinity on O_2 and CO_2 permeability of PET bottles can not be understood in the usual two phase approach of amorphous and crystalline, they suggested a three phase model of crystalline, free amorphous and rigid amorphous to clarify the relationship between crystallinity and barrier properties. The permeability of gases through PET is shown in Table 5 [3].

In conclusion, thermal crystallinity is not a desired property [146]. The rate of crystallisation during the injection stage should be minimized in order to produce clear preforms, which in turn produces bottles with the desired clarity. However, crystallinity promoted by orientation is a desired property due to the advantages of increased bottles mechanical toughness and improved barrier properties [144,145,157]. It was reported that orientation crystals are so small that they do not scatter light, and thus will not affect the bottles clarity [144].

Moreover, orientation will break up thermally formed large crystals into units smaller than the wavelength of visible light [1]. Orientation patterns for biaxial oriented PET were described in detail by many researchers [150,157,158]. Also it was thought that the orientation and distribution of crystallites is the dominant factor in gas permeation behaviour [158].

Several researchers reported that modifiers were used in a blend with PET to enhance properties of bottles produced by ISBM. Liquid crystal polymer (LCP) was used as a PET modifier to improve bottle barrier resistance [117,159].

Many researchers investigated the influence of ISBM process variables on the virgin PET bottle properties [135,137,145,147,149,154,156]. Information on the bottle design and the factors affecting bottle properties are also reported by [1,160].

Researchers reported many insightful experimental tests to assess them in evaluating the performance of PET bottles. These tests include environmental stress cracking [144], burst pressure [1,152,161], clarity, top load [1,144,152,162], drop impact test [161], gas permeability [144,162,163] and liquid permeability [144].

7. Orientation and conformation of molecules of PET bottle

Chain orientation basically occurs when molecules align parallel to each other as a result of mechanical influences. In ISBM process, the mechanical influences are the vertical stretching rod and the radial blowing air. The orientation pattern in PET bottles is complex

Table 6
FT-IR spectrum that was studied by different researchers to investigate PET structural conformation

Wavenumber (cm^{-1})	Representation	Reference
845	Increase in intensity during crystallisation. *trans*-Conformation of the ethylene glycol segment	[165]
895	Decrease in intensity during crystallisation. *gauche*-Conformation of the ethylene glycol segment	[165]
898	The amount of amorphous content in PET. Wagging of the oxy-ethylene group and their *gauche* and *trans*-confirmation	[174,166]
973	Thermal crystallisation. Wagging of the oxy-ethylene group and their *gauche* and *trans*-confirmation	[174,166]
973	Increase in intensity during crystallisation. *trans*-Conformation of the ethylene glycol segment	[165]
1040	Decrease in intensity during crystallisation. *gauche*-Conformation of the ethylene glycol segment	[165]
1240–1330	Associated with parallel dichroism	[168]
1337	Increase in intensity during crystallisation. *trans*-Conformation of the ethylene glycol segment	[165]
1340	*trans*, Extended, crystalline. Wagging of the ethyl unit	[174,166]
1370	*gauche*, Relaxed, amorphous. Wagging of the ethyl unit. CH_2 wagging mode of the *gauche*-conformer	[165,174,166,169]
1410	Normalizing reference	[174]
1453	Decrease in intensity during crystallisation. *gauche*-Conformation of the ethylene glycol segment	[165]
1470	Increase in intensity during crystallisation. *trans*-Conformation of the ethylene glycol segment	[165]
1729	Associated with perpendicular dichroism	[168]

because of the nature of biaxial orientation that varies along the bottle surface [157]. Molecular conformation of PET has been studied by using infrared (IR) spectroscopy [164–166]. FT-IR instrument was used extensively in the investigations into orientations and conformation structure [157,167,168]. The conformation in the amorphous and crystalline phases of PET plays an important role in the structure–property relationship. Everall et al. [157] analysed PET bottle orientation using attenuated total reflection FT-IR. They concluded that PET bottles have complex orientation patterns strongly dependent on preform and mould design. They described strong orientation gradients associated with the bottles walls. The FT-IR spectrum that was studied by different researchers to investigate PET structural conformation is summarized in Table 6.

It is widely recognized that orientation-induced crystallinity (or crystallisation in the oriented form) is largely dependent on chain and molecular orientation [169]. Crystallinity and crystallisation rate have a major effect on bottles properties. The rate of crystallisation depends strongly on the degree of orientation [169]. The mechanism of orientation and its interaction with the draw ratio and crystallinity phase are very complex and several theories were developed recently for PET film [169,170]. Hence, the study of PET orientation is essential for the evaluation of PET bottles performance. Researchers investigated two molecular conformational characteristics including *trans* and *gauche* isomerism and dichroic ratio extensively as a source of giving insight on the orientation degree and mechanism of PET [168–170].

7.1. trans–gauche-Conformational changes

The crystallisation process in PET is reported to be complex. The *trans–gauche* isomerism in the ethylene glycol segments is reported to be associated with crystallinity in PET [165]. Several researchers reported that the *gauche*-conformation structure of the ethylene glycol group in PET transforms into *trans*-conformation structure during chain orientation [150,169,170]. It is also reported that high *trans*-conformation content is related to high degree of orientation [169]. Fig. 13 shows the *trans*-crystalline and *trans/gauche*-amorphous structure of PET [171].

The orientation mechanism of PET takes place in two stages [169–171]. In stage one and as orientation initiates, the amorphous phase which has a total *gauche*-conformer transforms into a mesomorphic amorphous phase which contains mainly *trans*-conformer and to less extent *gauche* conformer. Then as orientation reaches a critical degree [150,172], stage two begin with the initiation of the crystalline phase that consists of totally *trans*-conformer. As a result, at the finished orientation process, the three phases of amorphous, mesomorphic amorphous and crystalline exists at different content. The amounts or concentrations of the three phases are of great importance to the RER-PET bottle properties. The increase or decrease of *trans*-conformation affect the bottles barrier properties as for example it is reported that permeability occurs at higher rate in the *gauche*-amorphous phase than in the *trans*-crystalline phase [135,144,171].

7.2. Dichroism

Chains dichroism by FT-IR can be defined as the ratio between the FT-IR absorption of IR light polarized in parallel direction over the FT-IR absorbance on the perpendicular direction. The theory and measurements of polymer chain dichroism are described by [173]. The dichroic ratio was studied extensively for PET films and it was used as a measure of chain orientation [167,168]. The dichroic ratio can be calculated from Eq. (1) [169].

$$\text{Dichroic ratio } D = A_{\text{para}}/A_{\text{perp}} \quad (1)$$

where A is the absorbance of the selected band peak that shows response to chain dichroism. Some of the absorbance bands that are reported in literature that are shown in Table 6.
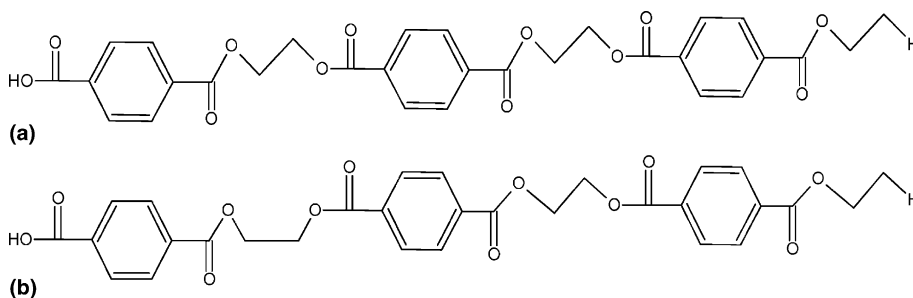

Fig. 13. Ethylene glycol group at different conformational structures: (a) *trans*-crystalline structure and (b) *trans/gauche*-amorphous structure.

8. Conclusions and further research

In addition to the environmental incentive, recycling of PET as an industry is getting its driving force from the increasing value and applications of virgin and modified PET. Publications review as reported above indicates that many scientific findings were made in the field of recycling of PET. Particular focus in this review was on publications exploring different recycling technologies with emphasis on industrial applications. The review spotlighted the use of chain extenders to modify POSTC-PET in a reactive extrusion process and towards an advanced application such as ISBM. The most favourable operating conditions that have been found in laboratory instruments including chain extender concentration, residence time, instrument type, and reaction temperature and rate represent the knowledge base for developing the PET recycling further towards feasibility. Furthermore, information on modified PET and chain extenders characteristics is of great advantage to PET recyclers enabling them to select best chemicals, conditions and equipment to suite their objectives.

Despite the immense amount of research regarding the PET recycling processes, many aspects of research are still unexplored. Some of the suggestions for future research in this field include:

(1) Investigating the direct feeding of chain extenders into POSTC-PET advanced applications such as ISBM which will reduce the numbers of thermal history cycles of POSTC-PET and conserve energy by combining reactive extrusion and application processes in one step.

(2) Investigating viscosity distribution inside the reactive extruder which is an important study that gives insight on the chain extender and POSTC-PET reaction mechanism.

(3) Free volume investigation of modified PET and virgin PET bottles because of the further insight to the knowledge of gas and liquid permeation mechanisms through chain extended PET and virgin PET blends' bottles.

(4) Optimising the ISBM process parameters that can further extend the success of using modified PET and virgin PET blends for producing ISBM bottles. ISBM parameters such as blow up ratio, temperature profile and injection pressure could be optimised for processing chain extended PET blends to further improve properties of bottles.

(5) The study of networking mechanism during the chain extension process. The insight gained by the network developing while chain extension might lead to better understanding of a chain extender and POSTC-PET reaction mechanism.

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