The effect of cleaning and tooth whitening agents on the mechanical properties of two thermoplastic orthodontic retainer materials.

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Abstract

Thermoplastic retainers are removable appliances used to prevent teeth from moving after orthodontic treatment.

The aim of this study was to investigate the effect of cleaning agents, whitening gel and uniaxial tensile cyclic loading on the mechanical and thermal properties of thermoplastic orthodontic retainer materials.

The materials chosen were: Essix ACE (polyethylene terephthalate) and Essix C+ (polypropylene). Double-edge notched tension specimens were produced for tensile strength testing and un-notched specimens for creep testing. Differential scanning calorimetry was used to understand the glass transition temperature and degree of crystallization of each material. Materials were tested initially dry and then following an immersion protocol in the relevant cleaning and whitening solutions (distilled water, sodium hypochlorite, Retainer Brite and whitening gel).

Essix ACE demonstrated superior mechanical properties compared to Essix C+ in terms of tensile strength and creep. The use of cleaning agents or whitening gel in the short-term did not negatively affect the mechanical properties of either material.

Synopsis

Thermoplastic retainers are a form of removable appliance used to prevent teeth from moving from their corrected position after orthodontic treatment. It is the most common form of orthodontic retainer used in a number of countries worldwide. Polyethylene and polypropylene and copolymers of these materials are used to fabricate thermoplastic retainers, which are subject to a number of cleaning agents on a daily basis. Furthermore, there has been recent anecdotal evidence that thermoplastic retainers are being used as a carrier for whitening gel. Consequently, it is important to understand the effects cleaning and whitening agents may have on the mechanical properties and ultimately the effectiveness of thermoplastic retainers. The aim of this study was to investigate the effect of cleaning agents, whitening gel and uniaxial tensile cyclic loading on the mechanical and thermal properties of thermoplastic orthodontic retainer materials.

Two orthodontic retainer materials were chosen for this investigation: Essix ACE, (amorphous non-crystallizing polyethylene terephthalate) and Essix C+ (polypropylene), both manufactured by Dentsply Raintree Essix, Florida, USA. Dumb-bell shaped specimens (98 x 37 mm) of each material were fabricated using a thermal forming method for each test group from an acrylic template. Double-edge notched tension specimens were produced for tensile strength testing and un-notched specimens used for creep testing. Differential scanning calorimetry was also used to understand the glass transition temperature and crystallinity of each material type. For each characterisation, technique both materials were initially tested dry and then following an immersion protocol in relevant cleaning and whitening solutions (distilled water, sodium hypochlorite, Retainer Brite and whitening).

A significant difference was observed in the tensile strength and the degree of creep between the two materials. Essix ACE exhibited a significantly higher tensile strength and lower creep than Essix C+. Immersion of the materials in distilled water, sodium hypochlorite, ‘Retainer

Brite' and whitening gel had no significant effect on the tensile strength for either material ($p>0.05$). The immersion regime had no effect on the degree of creep shown by Essix ACE, although immersion of Essix C+ in distilled water and Retainer Brite significantly reduced creep ($p<0.05$). Uniaxial cyclic loading did not affect the tensile strength of dry Essix ACE or Essix C+. The combination of uniaxial cyclic loading and the immersion regimen reduced the tensile strength of Essix ACE significantly but did not affect the tensile strength of Essix C+. Immersion of Essix ACE in distilled water significantly reduced its glass transition temperature. The degree of crystallization of polypropylene was unaffected by the immersion regimen.

Conclusions: Essix ACE demonstrated superior mechanical properties compared to Essix C+ in terms of tensile strength and creep. The use of cleaning agents or whitening gel in the short-term does not negatively affect the mechanical properties of either material. Clinically, Essix ACE can be considered the preferred material for use in the fabrication of thermoplastic retainers.

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Abbreviations used

PET	Polyethylene terephthalate
PP	Polypropylene
VFR	Vacuum-formed retainer
DSC	Differential scanning calorimetry

Chapter one: Literature review and aims of the study

1.1 Introduction

After completion of orthodontic treatment and the removal of orthodontic appliances, there is a tendency for teeth to move from their corrected positions towards their original position and for the irregularity of the teeth to increase again (Little, 1990). If these tooth movements occur relatively quickly following orthodontic treatment, they are known as relapse. When tooth movement occurs more gradually over a number of years, it is referred to as physiological age related changes, owing to continued growth throughout life. Relapse, as defined by the British Standards Institute is the "return, following correction, of the features of the original malocclusion" (British Standards Institute, 1983). Stability is a desirable and principal aim of orthodontic treatment as a lack of stability can lead to a compromise of ideal function and aesthetics. The main determinants of post treatment stability are thought to be growth, degree of initial crowding and patient compliance (Melrose and Millet, 1998). Retention is the phase of orthodontic treatment that aims to maintain the teeth in their corrected position, which involves the use of appliances (retainers), or other adjunctive procedures, to prevent unfavourable tooth movement. Evidence shows that significant deterioration of the corrected malocclusion and incisor alignment can occur within four weeks following the removal of fixed appliances when no retainers are used (Lyotard et al., 2010). In the longer term, evidence shows that the stability of lower incisor alignment is variable and unpredictable: a follow up of 31 cases, 10 years after orthodontic treatment, found that less than 30 % maintained satisfactory alignment while at 20 years post treatment only 10 % had acceptable alignment (Little et al., 1981, Little et al., 1988).

1.2 Causes of relapse and post-treatment change

The aetiology of relapse is multi-factorial, including: 1) forces exerted from the elastic recoil of fibres of the periodontal ligament, 2) pressure from the oral and facial soft tissues and, 3) occlusal forces. Post-treatment growth and development of the face, which continues throughout life, is responsible for the age related changes seen in the occlusion (Melrose and Millet, 1998).

1.2.1 Periodontal fibres

The principal fibres of the periodontal ligament take approximately two to three months to reorganize following tooth movement whilst the collagen fibres of the gingivae can take four to six months (Reitan, 1967). However, realignment of the supracrestal fibres, containing oxytalan and elastin, located around the cervical region of the tooth, can take much longer (>230 days) (Reitan, 1967). The elastic recoil of these periodontal fibres tends to move the teeth back to their original position. The stretching of the supracrestal fibres is most marked after de-rotating teeth and closure of interdental space. Therefore teeth should be maintained in their new position for a period long enough for these fibres to remodel.

1.2.2 Oral soft tissue pressures

Teeth are subject to a number of forces in the mouth, intrinsically from the periodontal ligament and extrinsically from the tongue, lips and cheek musculature. Teeth do not move under normal circumstances as they lie in a position of equilibrium or balance. To produce a change in the position of the teeth a force must be of sufficient duration i.e. six hours or more per day (Proffit, 1978). Active soft tissue pressure seen during eating, swallowing or chewing is too short in duration to be of significance in causing relapse (Proffit, 1978). The resting pressures of the soft tissues will determine the ultimate stability of the tooth position. Therefore, orthodontic treatment must aim to maintain teeth in a zone of equilibrium to prevent relapse.

1.2.3 Occlusion

Occlusal forces also play a role in the stability of the corrected malocclusion. Achievement of Roth's functional occlusal goals will reduce the possibility that unwanted interferences or displacing occlusal contacts will cause changes in tooth position (Roth, 1976). It has been shown that after reducing an overbite, relapse is reduced if a favourable interincisal angle is achieved and the lower incisor edge lies 0-2 mm anterior to the centre of the upper incisor root known as the centroid (Houston, 1989). After correcting a posterior crossbite it is suggested that achieving good interdigitation of the buccal segment teeth will increase stability while achieving a positive overbite is important for stability following correction of an anterior crossbite (Mitchell, 2001).

1.2.4 Facial growth

As the face continues to grow even during adulthood, stability of treatment will depend on both the tooth movements carried out in treatment, the growth of the facial and oral tissues and also the dentoalveolar adaptation to these growth changes (Behrents el al., 1989). Arch length and intercanine width tend to reduce with time due to normal physiological process (Sinclair and Little, 1983). As a result, crowding, particularly of the lower incisor region, tends to increase with age. This is thought to be due to sagittal and vertical mandibular growth. The decrease in arch length and width continues actively in the 20-30 year age range but although this process continues after the age of 30 the rate of constriction is much less (Little, 1990).

1.3 Risk factors for relapse

A number of features of the occlusion are thought to increase the risk of relapse. Severely rotated teeth and closure of a median diastema or generalised spacing are particularly at risk due to the elastic recoil of the periodontal fibres. Rotations should be corrected early in treatment to allow for the reorganisation of the individual periodontal ligament fibres. Alteration of pre-treatment lower arch form and in particular the intercanine width together with excessive anteroposterior movement of the lower incisors can increase the risk of relapse. It has been suggested that if the lower incisors are proclined by more than 2 mm, permanent fixed retention is required (Proffit, 1993). Closure of space secondary to adult periodontal disease is liable to re-open due to the decrease in force exerted from a reduced periodontal ligament acting on the teeth to resist the forces from the oral soft tissues. Treatment of an anterior open bite is associated with a significant rate of relapse with stability rates reported of only 82% for surgical correction and 75% for non-surgical correction after 12 months (Greenlee et al., 2011).

1.4 Prevention of relapse

Retention involves the use of appliances with or without adjunctive techniques to prevent any changes in tooth position in a sagittal, transverse, vertical or rotational direction. Adjunctive techniques include circumferential supracrestal fibrotomy or pericision, fraenectomy and interproximal dental reduction. Pericision, involves the excision of the supracrestal gingival fibres around the cervical region of the tooth. This has been shown to reduce rotational relapse by 30% (Edwards, 1998). Fraenectomy involves apical repositioning of the fraenum with denudation of the alveolar bone and excision of the transseptal fibers between the central incisors. This procedure was found to reduce relapse of a midline diastema by 77% (Edwards, 1977). Interproximal dental reduction involves the removal of up to 0.25 mm of enamel from each tooth at a contact point. It has been suggested that this broadens the contact points, which then provides a buttressing effect making teeth more resistant to movement caused by soft tissue pressure (Boese, 1980). The combined use of circumferential supracrestal fibrotomy together with interproximal reduction has been reported to alleviate the need for retainers and provide good stability for between four and nine years following the removal of orthodontic appliances (Boese, 1980). Interproximal dental reduction has more recently been shown to be an effective alternative to the use of orthodontic retainers for between three and seven years after the removal of orthodontic appliances (Aasen and Espeland, 2005, Tynelius et al., 2015). Although these techniques are used they are not currently considered reliable enough to provide adequate stability following orthodontic tooth movement (Littlewood et al., 2016). Therefore, the following appliances are most frequently used to provide retention.

1.5 Appliances used in retention

Appliances used in retention are designed to maintain the new position of the teeth following orthodontic treatment and can be classified as removable or fixed. Removable appliances include the Hawley retainer, Begg retainer, Barrer retainer and thermoplastic or vacuum-formed retainers. Removable retainers are advantageous in that they can be removed for oral hygiene procedures but in contrast they can affect the patient’s speech (Mitchell, 2013). Ultimately the effectiveness of the retainer depends on individual patient compliance with the prescribed wear regime (Mitchell, 2013).

1.5.1 The Hawley retainer

The Hawley retainer, one of the most commonly used retainers, was originally fabricated from gold wire and vulcanised rubber (‘vulcanite’) (Hawley, 1919). Modern versions consist of an acrylic baseplate which may include an anterior bite plane to maintain overbite correction with 0.7 mm stainless steel cribs on the upper first permanent molars and a 0.7 mm stainless steel labial bow extending from canine to canine. The labial bow can then be fitted or contoured with acrylic resin to increase the contact around the labial surface of the incisors. This improves retention of the appliance in the mouth and also gives better rotational control of the incisors (Luther and Nelson-Moon, 2013). In cases where first premolars have been extracted the labial bow can be soldered to the cribs on the first permanent molars so as not to cause the extraction space to re-open (Luther and Nelson-Moon, 2013).

1.5.2 The Begg Retainer

The Begg retainer is similar to a Hawley retainer but no cribs are placed onto the first permanent molars (Begg and Kesling, 1971). The labial bow extends around the distal aspect of the terminal molar and is secured in the acrylic base plate. The Begg retainer tends to provide less retention than Hawley retainers and the labial bow, due to its increased length is more prone to distortion (Luther and Nelson-Moon, 2013).

1.5.3 The Barrer retainer

The Barrer appliance also known as the spring retainer appliance originally consisted of acrylated labial and lingual bows extending from canine to canine on both labial and lingual aspects of the teeth (Barrer, 1975). The design was later modified to include cribs on the first permanent molars due to the risk of swallowing or aspiration with an appliance of this size. The Barrer appliance, alongside acting as a retainer, can also be used to correct minor irregularities of incisor alignment.

1.5.4 The fixed or bonded retainer

Fixed retention involves bonding a piece of wire to the palatal or lingual surfaces of the teeth usually in the anterior region from canine to canine to maintain tooth alignment while still allowing physiological movement of these teeth. The wire commonly consists of flexible multi-stranded or co-axial stainless steel wire, round in cross section, bonded passively to the teeth. Single-strand wires can also be used but multi-stranded bonded retainers have been shown to be more effective than single-strand wires (Al-Nimri et al., 2009). The diameter of the multi-stranded wire can range from 0.0175 to 0.032 inches. Bonded retainers can be pre-fabricated chair-side or in the laboratory. As they are fixed they do not rely on patient compliance and do not interfere with speech. Bonded retainers are aesthetic, being hidden on the palatal or lingual surface of the teeth and prolonged use of a bonded retainer has been shown to decrease the likelihood of lower labial segment relapse (Sadowsky et al., 1994). However, fixed retainers are time consuming to place and technique sensitive. They can also lead to increased plaque and calculus accumulation unless excellent oral hygiene is maintained (Storman and Ehmer, 2002). Decalcification is also a risk to the teeth if a partial debond goes unrecognised (Artun, 1984). Fixed retainers should always be supplemented with a removable retainer, which can be worn in the event of debonding or breakage of the fixed retainer.

	Hawley	Begg	Barrer	Bonded
Removable	✓	✓	✓	✕
Robust	✓	✕	✕	✓
Retentive	✓	✕	✓	✓
Facilitates oral hygiene	✓	✓	✓	✕
Technique sensitive	✕	✕	✕	✓
Aesthetic	✕	✕	✕	✓

Table 1.1 Features of retention appliances.

1.6 The thermoplastic retainer

Thermoplastic retainers also known as clear overlay or vacuum-formed retainers are made from thermoplastic material that has been heated, softened and moulded to extend closely around the teeth and their associated gingivae.

1.6.1 History and development of the thermoplastic retainer

Thermoplastic retainers were first introduced by Ponitz in 1971 as an ‘invisible retainer’ (Ponitz, 1971). The process of fabrication was described whereby a sheet of ‘clear plastic 5 inches square’ (the type of plastic was not specifically designated, however the author does refer to the materials cellulose acetate butyrate, polyurethane, polyvinylacetate-polyethylene plymer, polycarbonate-cycolace and latex as being used to fabricate mouthguards and transparent retainers) was heated to 121 °C in an oven for 15 min. The pre-heating step was required to remove any moisture from the plastic that would later cause porosity in the finished retainer. The sheet was then further heated to a temperature between 188 °C – 199 °C. When the plastic began to slump it was placed over a stone model on a vacuum forming unit. The plastic was then pulled down and adapted around the stone model of teeth. The vacuum unit, together with the pressure applied to adapt the plastic, ensured that there were no air inclusions in the final retainer. Following cooling, any flash was then trimmed away using scissors or a bur. The plastic covered all labial or buccal and lingual or palatal surfaces of the teeth and their associated gingivae for approximately 1-2 mm on the buccal aspect and 3-4 mm on the lingual aspect. Originally, in the maxillary arch the plastic extended to cover the entire palate to the post dam region but modern designs prescribe that it only extends to cover 3-4 mm of the palatal gingivae leaving the palate free. The reduction of soft tissue coverage reduces retention and rigidity of the retainer but facilitates better oral hygiene and improves comfort for the patient. Thermoplastic retainers are retained by engagement of the undercut gingival to the interdental contact point. Therefore, if oral hygiene is poor and the gingivae are hyperplastic this will preclude their use as a retainer. The retainer covers all occlusal surfaces and extends to the most distal erupted tooth to prevent any overeruption or dentoalveolar changes during use of the retainer. The advantages of thermoplastic retainers are the ease of fabrication, accuracy of fit and the speed of insertion due to the lack of need for adjustment (Ponitz, 1971).

McNamara et al. (1985) further described the use of the thermoplastic retainer as an inexpensive temporary retainer between different phases of treatment and also as a finishing retainer to allow minor adjustments of final tooth position. He described its fabrication using the Biostar (Scheu Dental Iserlohn, Germany, distributed by Great Lakes Orthodontics Ltd, Tonawanda NY) positive pressure thermal forming machine, which is still used today. Most similar machines generally use positive pressure to adapt the plastic to the stone model and not a vacuum as originally described.

Sheridan et al. (1993) specified the use of the Essix (Raintree Essix Inc., New Orleans, Los Angelus) thermoplastic material, a copolyester, as the desired material for use in the fabrication of thermoplastic retainers and subsequently popularised the term ‘Essix retainers’, which is commonly used today to generically describe thermoplastic retainers. He recommended only extending the retainer from canine to canine and used 0.75 mm thermoplastic copolyester to fabricate the retainer. It was suggested that the copolyester sheet thickness reduced to 0.375 mm during thermoforming. It was reported that 0.5 mm material thickness did not have sufficient rigidity after thermoforming to maintain alignment while material that was 1 mm in thickness lacked flexibility for insertion and removal of the retainer from the mouth (Sheridan et al., 1993). Today, the thickness of the thermoplastic material can vary from 0.5 to 3 mm (Luther and Nelson-Moon, 2013).

The advantages of the ‘Essix retainer’ suggested by Sheridan (1993) were the ‘absolute stability’ of the anterior teeth, durability and ease of cleaning, low cost, ease of fabrication, minimal bulk, the brilliant appearance of the teeth caused by light reflection ability and the ability ‘to supervise retention over the phone’. He also stated that for success to be achieved duplicate retainers should be provided to the patient. As the retainer only extended from canine to canine, this retainer had a tendency to create an open bite in some patients.

Wang (1997), in an attempt to address the excessive flexibility of 0.5 mm copolyester, incorporated a cylindrical curve in the retainer so as to provide maximum stiffness of the plastic while providing a less bulky retainer.   He soldered a piece of wire, adapted to the arch form, around the buccal aspect of the teeth before thermoforming the plastic sheet over the cast. This created a cylindrical channel in the retainer that increased its rigidity. The thinner material was suggested to allow settling of the occlusion while also encouraging excellent patient compliance (Wang, 1997). However this design, possibly due to increased fabrication time and questions over its durability is not widely used in the United Kingdom today.

1.7 Trends in selection of retainer type

Despite the long term use and prevalence of orthodontic retainers there remains a lack of scientific evidence to support clinical decision making with regards to retention of the post-treatment corrected tooth position in orthodontic practice (Littlewood et al., 2006). It is now recognised that all orthodontic treatment requires retention for an indefinite period as even if teeth are retained past the period required for the supracrestal fibres to reorganise, long-term studies have shown that teeth may relapse after this time (Little et al., 1988). However, there is great variation in the retention protocols recommended by orthodontists, which appears to be largely based on personal preference and non-scientific criteria (Littlewood et al., 2006). In the United Kingdom, a study of private practitioners showed a preference for thermoplastic retainers in the upper arch and fixed bonded retainers in the lower arch (Singh et al., 2009). Similarly in Australia and New Zealand thermoplastic retainers were most commonly prescribed for the maxilla while a fixed canine-to canine bonded retainer was used in the mandibular arch (Wong and Freer, 2004). In the Netherlands fixed retainers were preferred for upper and lower arches while in Norway there was a preference for a bonded retainer in the mandible while both a bonded and removable retainer was prescribed for the maxillary arch (Vandevska-Radunovic et al., 2013; Renkema et al., 2009). In the Republic of Ireland thermoplastic retainers were most commonly used in the maxilla and mandible (Meade and Millett, 2013). In the United States, the Hawley retainer is most commonly used in the maxilla followed by the thermoplastic retainer while in the mandible a fixed bonded retainer is most frequently used (Valiathan and Hughes, 2010; Pratt et al., 2011). A trend towards increased use of thermoplastic retainers and decreased use of Hawley retainers was also reported (Pratt et al., 2011). In all of the countries surveyed, the majority of orthodontists recommended the use of orthodontic retainers indefinitely.

1.8 Wear regimes

The recommended wear regimes for removable retainers depend mostly on an individual clinician's personal preference. The majority of orthodontists prescribe a period of full time wear for removable retainers followed by part-time wear. The full time wear prescription is generally longer for Hawley retainers varying from approximately 3-9 months while for the thermoplastic retainers a period of 1 week up to 3 months is typically recommended (Wang, 1997; Singh et al., 2009; Wong and Freer, 2009). It is important, if recommending full time wear of thermoplastic retainers, that patients do not eat or drink with the retainer in place due to the risk of the retainer acting as a reservoir for cariogenic food or drink which could cause significant damage to teeth (Meade and Millett, 2015; Luther and Nelson Moon, 2013). A number of studies have investigated whether any of the various wear regimens recommended is more effective at maintaining the corrected occlusion. A study in Sweden compared a group wearing a thermoplastic retainer full time for 3 months followed by night time only wear with a group wearing the retainer for 1 week full time followed by night time only wear thereafter (Jaderberg et al., 2012). After 6 months there was no clinically significant difference in Little's irregularity index, overjet or overbite for both the maxillary and mandibular arch for both groups. This is interesting as the lower thermoplastic retainer only covered the anterior region from canine to canine and there would have been a risk of introducing an open bite in those patients wearing the retainer full time for 3 months. Similarly, there have been two randomized clinical trials in the UK comparing part time versus full time wear of the thermoplastic retainers (Gill et al., 2007; Thicket and Power, 2010). Wear regimes were either full time for six months or full time for three months gradually reducing to 1-2 nights per week by 12 months. Part-time regimes were part time for six months or part time for the first six months reducing to 1-2 nights per week by 12 months. Gill et al. (2007) recorded changes in the occlusion after 6 months while Thickett and Power (2010) compared changes in the occlusion after 12 months of retention. No significant differences in Little's Irregularity index, intercanine and intermolar width, arch length, and Peer Assessment Rating scores between the two groups were observed. There was a significant difference in the overbite in the study by Thickett and Power (2010), which was greater for those wearing the retainer part-time only compared to those who had an initial period of full time wear. The actual difference was 0.6 mm, which is unlikely to be clinically significant. It would appear that part time only wear of thermoplastic retainers is sufficient to maintain alignment and the occlusion following orthodontic treatment. This was the only recommendation made by a recent Cochrane review on retention procedures for stabilising tooth position after treatment with orthodontic braces (Littlewood et al., 2016).

1.9 Patient acceptability

One of the perceived advantages of thermoplastic retainers relates to an improved cosmetic appearance and higher patient acceptability over Hawley retainers (Sheridan et al., 1992). In a study that looked to quantify a layperson's assessment of acceptability with orthodontic appliances, clear aligners, lingual braces and ceramic systems had the highest rate of acceptability, being rated acceptable by over 90% of participants (Rosvall et al., 2009). A clear aligner has the same appearance as a thermoplastic retainer. This contrasted with stainless steel fixed appliances, which were considered acceptable by only 55% of those surveyed. Higher levels of patient acceptability could lead to better compliance suggested, over a six-month period, wherein significantly more patients who were prescribed thermoplastic retainers wore them as instructed compared to those who were prescribed a Hawley retainer (Hichens et al., 2007). Also patients who were asked to wear a Hawley retainer reported greater embarrassment and speech problems than those who had a clear retainer (Hichens et al., 2007). Overall higher satisfaction levels were reported with thermoplastic retainers than Hawley retainers (Hichens et al., 2007). Pratt et al. (2011) also found that in the short term i.e. the first two years after debonding, there was greater compliance with the use of thermoplastic retainers compared with Hawley retainers. However, after two years no difference in compliance levels between both the Hawley and thermoplastic retainer groups were observed (Pratt et al., 2011). This may be due to deterioration in appearance of the thermoplastic retainer as it covers the occlusal surfaces and would be subject to greater wear than Hawley retainers. Thermoplastic retainers also tend to discolour with time. But Kacer et al. (2010) found no significant association between compliance with retainer wear and type of retainer after 2 years. 24 months after debonding only 45% of patients were reporting daily night-time wear versus 70% at 3 months. These results are similar to that expected in the medical model of compliance which suggests that patient cooperation decreases toward the end of treatment especially for lengthy treatments (Albino et al., 1991). Although it appears evident that patients find a thermoplastic retainer more acceptable than a Hawley retainer the results are equivocal. A study comparing patient satisfaction with the various orthodontic retainers suggested that patients with thermoplastic retainers were more likely to be very satisfied (50%) versus those with a Hawley (35%) or a bonded retainer (36%). Compliance was more likely with a clear or bonded retainer than a Hawley retainer with compliance rates of 65%, 68% and 45% at on average 5.3 years post debonding, respectively (Mollov et al., 2010). In contrast, an alternative study reported significantly more patients, that stated the fixed retainer more acceptable to wear and easier to clean compared with than the thermoplastic retainer (Millet, 2007).

1.10 Effectiveness of thermoplastic retainers

A number of studies have compared the effectiveness of thermoplastic retainers with other retention appliances in maintaining the post-treatment occlusion. Thermoplastic retainers appear to be more effective than Hawley retainers at maintaining the alignment of the anterior teeth. A randomised controlled trial showed that while there was no significant difference between the retainers in maintaining corrected tooth rotations, overbite and overjet, and incisor irregularity of the maxillary arch, there was a difference in the incisor irregularity of the mandibular arch (Rowland et al., 2007). After 6 months the incisor irregularity in the mandibular arch had increased by 0.56 mm more in the Hawley retainer group compared with the thermoplastic retainer group. The increase in irregularity of 0.56 mm would be clinically significant if it was confined to a single tooth. Demir et al. (2012) also reported significant increases in incisor irregularity for those wearing a Hawley retainer in the mandibular arch after 1 year of retention. Those wearing a thermoplastic retainer showed minimal change in incisor irregularity.

Other studies have shown non-significant differences between retainer types when investigating the change in incisor irregularity (Lindauer and Schoff, 1998, Tibbets, 1994, Barlin et al., 2011). However, the study by Lindauer and Schoff (1998) had a recall rate of less than 72% and would have therefore resulted in significant attrition bias. The study by Barlin et al. (2011) used a modified Little's irregularity index to measure anterior segment malalignment and may not be comparable with the other studies for this outcome measure.

It has been suggested that thermoplastic retainers, due to their inherent flexibility, are not able to maintain arch expansion as effectively as the more rigid Hawley retainer. (Gill et al., 2004; Blake and Garvey, 1998). The literature does not appear to support this suggestion with no change in intercanine and intermolar widths of both arches between 6-12 months after debonding which have been reported by several clinical studies (Rowland et al., 2007, Barlin et al., 2011, Tibbets, 1994).

In comparison to a bonded retainer, thermoplastic retainers appear to be less effective at maintaining incisor alignment. Millet (2007) found significantly more relapse (0.6 mm) with a thermoplastic mandibular retainer than with a bonded retainer.

1.10.1 Occlusal settling of thermoplastic retainers

One of the suggested disadvantages of thermoplastic retainers suggested is that they do not allow occlusal settling after orthodontic treatment (Sauget et al., 1997). This is due to the retainers covering the entire occlusal surfaces of the teeth. An increase in the number of contacts, ideally located occlusally, is thought to be important for long-term stability (Nanda and Nanda, 1992). Increasing the number of contacts reduces the stress delivered to the teeth while ideally located contacts ensures near axial loading of the teeth in function. Hawley retainers tend to allow greater settling of the teeth over thermoplastic retainers in both the short (3 months) and long term (12 months) (Sauget et al., 1997, Nanda and Nanda, 1992). It was postulated that the lower incisors occlude on the palatal acrylic of the Hawley and encourage the eruption and interdigitation of the posterior teeth. In contrast, the thermoplastic retainer, as it is fabricated on the impression taken immediately post-debonding of fixed appliances, tends to maintain the same number of contacts present at this stage and no settling occurs despite being worn on a part time basis. Similarly, no increase in the number of posterior contacts was reported when the thermoplastic retainer was being worn full time for 6 months followed by night only wear for 3 months (Dincer et al., 2010). It was only after this time when the retainers were stopped and then followed up at 2.5 years that there was a significant increase in the number of posterior contacts. It has been suggested that settling should be completed during active treatment so as to ensure greater numbers of ideal contacts and not during the retention phase when there is less control over tooth movements (Razdolsky et al., 1975).

1.10.2 Survival of thermoplastic retainers

A traditional clinical viewpoint is that thermoplastic retainers are not as durable as Hawley retainers and may need replacing more frequently. This has not been borne out by the literature. Hichens et al. (2007), in the 6-month period following orthodontic treatment, found that there was a significantly higher incidence of fracture in the Hawley group (26) compared with the thermoplastic retainer group (9). The number of lost appliances was similar for both groups. However, patients were asked to wear their Hawley retainer full time in the first three months compared with only part time wear for the thermoplastic retainer group, which may have placed increased demands on the Hawley appliance. In the longer term, at 12 months after orthodontic treatment, however, no difference was found between the survival time of thermoplastic retainers compared with Hawley retainers (Sun et al., 2011). Both groups were instructed to wear their appliances full-time except during meals. Fracture, followed by loss of the retainer, was the most common reason cited for retainer failure (Sun et al., 2011). There was no significant difference in the survival time of thermoplastic and the Hawley retainers for both maxillary and mandibular arches. There were a greater number of lost appliances in the thermoplastic retainer group, which may have been due to its transparent appearance (Sun et al., 2011). The mandibular retainers had a lower survival time in both groups (Sun et al., 2011). This may be due to the increased buccal root torque in the molar region creating a lingual undercut posteriorly. Each time the retainer is inserted and removed it has to deform to overcome this undercut leading to fatigue failure along the thinnest portion of the retainer.

In comparison to a bonded retainer thermoplastic retainers have been shown to have lower survival rates with significantly more failures reported. A total of 15 failures (42%) were reported for the thermoplastic retainers versus 7 (17%) for the bonded retainer in the first 12 months after debonding (Millet, 2007).

1.10.3 Care of the thermoplastic retainer

One of the advantages often cited for the thermoplastic retainer is its ease of cleaning as it can be removed (Mitchell, 2007). Toothpaste can be used on acrylic retainers but it is not recommended for thermoplastic retainers as it can 'dull' the appearance of the retainer (Meade and Millet, 2015). Instead, the use of soap and water or a proprietary cleaning agent e.g. Retainer Brite is recommended (Sheridan et al., 1993). There is anecdotal evidence that thermoplastic retainers are being used as trays for carrying bleaching agent in teeth whitening. Sheridan (1999) describes a protocol for bleaching teeth during supervised retention but advises the use of a distinct whitening tray plastic instead of the retainer. The use of thermoplastic retainers for tooth whitening would subject the retainer material to 6% hydrogen peroxide gel and this together with the use of cleaning agents may impact on the mechanical properties of the retainer.

Advantages	Disadvantages
Aesthetic	Less robust may fracture
High patient acceptability	Viscoelastic-may undergo creep
Facilitate oral hygiene procedures	Does not allow settling of occlusion
Easy to fabricate	Depends on patient compliance for effectiveness
Highly retentive	Cannot use if gingivae inflamed and hyperplastic after removal of fixed appliances

Table 1.2 Advantages and disadvantages of thermoplastic retainers.

1.11 Polymer chemistry of some thermoplastic retainers

Most commonly, thermoplastic retainers are made from, either polyethylene copolymers or polypropylene polymers (Raja et al., 2013). Polyethylene copolymers include polyethylene terephthalate and polyethylene terephthalate glycol. Essix ACE is composed of polyethylene terephthalate while Essix C+ is composed of a polypropylene polymer.

1.11.1 Polyethylene Terephthalate

Polyethylene terephthalate (PET) is formed when terephthalic acid (benzene 1,4-dicarboxylic acid) and ethylene glycol (ethane-1,2-diol) are combined under high temperature (approximately 260 °C) and low vacuum pressure in the presence of catalysts (antimony compounds) to form the polymer, PET. The ethylene glycol is an alcohol, which contains two hydroxyl (OH) groups in its molecular structure, while the terephthalic acid is a dicarboxylic aromatic acid, which has a large aromatic ring and two carboxyl groups in its structure. When combined the hydroxyl groups from ethylene glycol react with the carboxyl groups from the acid to form ester (CO-O) groups, which join multiple PET mer units together to form the long chain polymer. This is a condensation polymerisation reaction and water is produced as a by-product.

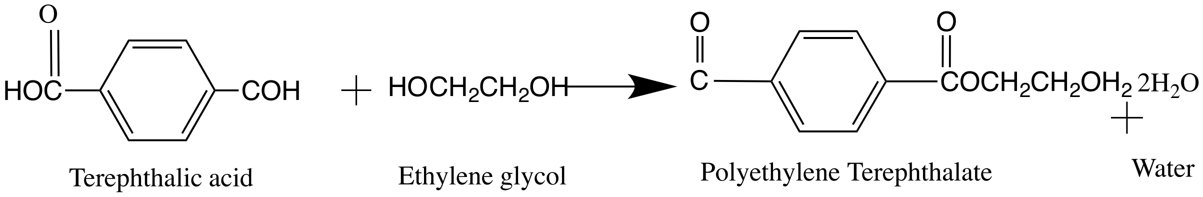

Figure 1.1 Polymerisation reaction to form polyethylene terephthalate

1.11.2 Chemistry of Polypropylene

Polypropylene is a linear hydrocarbon polymer. Its chemical structure is $CH_2=CHCH_3$. The propylene monomer is combined under relatively low heat and pressure in the presence of a catalyst to produce polypropylene. This is an addition polymerisation reaction and so no by-product is produced. There is little or no unsaturation in the polymer (Figure 1.2).

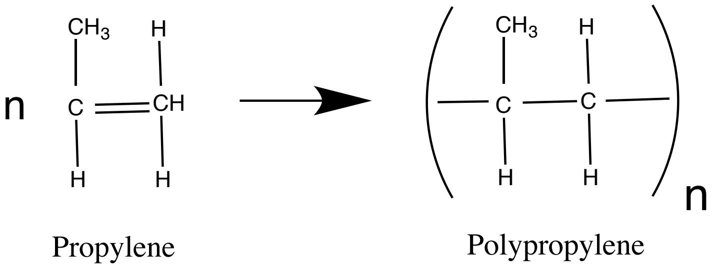

Figure 1.2 Polymerization reaction to form polypropylene

The methyl group can adopt various spatial arrangements or tacticity, in relation to the backbone chain. The methyl side groups can be placed all on one side of the polymer chain, known as isotactic. If they alternate on opposite sides of the chain, this is known as syndiotactic. Irregular, random placement of the side groups along the backbone chain referred to as atactic, gives the least symmetrical structure to the molecules (Shackleford, 1996). The methyl group attached to every alternate carbon atom in the backbone chain can alter the polymers properties. It can cause either stiffening of the chain increasing the crystalline melting point or can interfere with molecular symmetry, which reduces crystallinity and therefore the melting point (Flinn and Trojan, 1995). Chemically the methyl group also makes polypropylene less stable as the tertiary carbon atom provides a site for oxidation (http://www.bpf.co.uk/plastipedia/polymers/pp.aspx, 2016).

1.12 Mechanical and physical polymer properties related to thermoplastic materials

The mechanical properties of thermoplastic polymers are dependent on a number of factors including:

- Interchain forces
- Degree of polymerization
- Crystallinity
- Glass transition temperature.

1.12.1 Interchain non-covalent forces

The interchain bonds or forces between molecules have significant effects on the properties of the polymer due to their ability to limit the motion of the molecules within the polymer. Linear polymers have covalent bonds within the molecules and weaker non-covalent bonds or forces between molecules. For thermoplastics, there is little cross-linking between the molecules (Shackleford, 1996). Intermolecular forces include Van der Waal forces, dipole-

dipole interactions and the stronger hydrogen bonds (Mills, 2005). Dipole-dipole forces exist between the chains of polyethylene terephthalate. Van der Waal forces exist between the chains of polypropylene. The strength of Van der Waal interactions that can form in polypropylene depends on the tacticity of the methyl group in the polypropylene polymer (Flinn and Trojan, 1995). Isotacticity, forms the most and strongest inter-chain forces due to the regularity of its structure, whereas syndiotactic and atactic chains form less weaker Van der Waal forces in polypropylene (Carraher, 2011). The inter-chain forces are important as the load required to fracture the polymer is related to the energy required to separate the molecules rather than break the bonds within the molecules (Flinn and Trojan, 1995). Crystallization of the polymer is favoured by more regular configurations of the polymer chains, which also allows stronger inter-chain forces (Flinn and Trojan 1995).

1.12.2 Degree of polymerization

The number of mer units or the average length of a polymer chain in a polymer molecule is known as the degree of polymerization. The degree of polymerization has a significant effect on mechanical properties of a polymer (Shackelford, 1996). Generally, as the degree of polymerization increases, the tensile strength, melting point, rigidity and hardness increase (Shackleford, 1996; Anderson et al., 2003). Polymers, which have less mer units or shorter chain length, are more likely to crystallize. However they usually show lower strength as the chains can slide past each other due to less entanglement thereby allowing fracture to occur. Longer chain polymers are less likely to crystallise but they generally exhibit higher strength due to greater entanglement of the polymer chains (Flinn and Trojan, 1995).

1.12.3 Crystallinity

The degree of crystallinity is important in linear polymers as it affects the physical and optical properties of the polymer (Flinn and Trojan, 1995). Increasing the degree of crystallinity generally increases the strength, melting point and rigidity of the polymer. Only isotactic and syndiotactic polymers are capable of crystallizing.

The crystalline structure was initially thought to take the form of a fringed micelle with the boundaries of the crystallite poorly defined and chains of molecules scattered throughout amorphous regions (Flinn and Trojan, 1995). However, it has been shown that the polymers form crystals by folding of chains back and forth to build up a regular structure called lamellae (Daniels, 1989). Between the lamellae, amorphous regions can exist or linkages can form between two lamellae, known as tie molecules. Several lamellae combine to form fibrils. Spherulitic crystals are composed of fibrils, which radiate symmetrically from the centre. The amorphous phase exists between the fibrils and lamellae.

Crystallization can be induced by thermal crystallization or by the application of stress/strain to the polymer (Demirel et al., 2011). Thermal crystallization occurs when the polymer is heated above its glass transition temperature and is then slowly cooled from the molten state, which allows the chains to take on an ordered arrangement. Stress-induced crystallization involves the stretching of the un-oriented polymer, which causes the polymer chains to align in a parallel ordered fashion facilitating the formation of crystals.

The more regular the structure of the molecule is, the more likely it will crystallize. However, partial crystallization rather than total crystallization is only ever achieved (Flinn and Trojan, 1995; Demirel et al., 2011, Anderson et al. 2003). The more ordered regions lead to a higher density of the polymer compared to the amorphous poorly packed regions. Branching of the molecular chains by the addition of polymeric molecules to the side of the chain can increase the structural complexity and reduce the degree of crystallinity.

Increased crystallinity and larger crystals may make the material more opaque or translucent as light scatters at grain boundaries (Anderson et al., 2003). Essix C+, a PP polymer is opaque. A polymer containing a lower degree of crystallinity and a greater amorphous content with smaller crystals or a completely amorphous polymer will be more transparent due to less refraction of light as it traverses the material e.g. Essix ACE, a PET polymer.

Due to the regularity of its chemical and geometric structure, PET is able to form crystals. PET generally exists as a semi-crystalline polymer with both amorphous and crystalline regions within the structure. It has been suggested to have a degree of crystallinity of 30-40% (Ehrenstein and Theriault, 2001).

PET also exists as a completely amorphous or non-crystalline material where the polymer chains are disordered. Amorphous polymers have a homogenous structure whereas semi-crystalline polymers have a heterogeneous structure due to interspersed amorphous and crystalline regions (Demirel et al., 2011).

Polypropylene shows crystallinity in both isotactic and syndiotactic states. It is thought to have a degree of crystallinity between 70-80% (Ehrenstein and Theriault, 2001). With increasing isotacticity, crystallinity increases as the spherulites become more densely packed (Van der Vaal et al., 1998).

1.12.4 Glass transition temperature

The glass transition temperature is the temperature at which the amorphous regions of the polymer change from a glassy to rubbery state. The chains in an amorphous polymer are only connected with weak intermolecular forces and when the temperature is raised these forces are weakened and the molecular chains become more mobile. Mechanical properties of polymers including the elastic modulus and tensile strength undergo distinct change in the region of the glass transition temperature (Landel and Nielson, 1993). The glass transition temperature of thermoplastics is affected by the amount of free volume in the polymer, the intermolecular forces between molecules of the polymer, chain mobility and the chain length. Higher amounts of free volume, weaker intermolecular forces, less chain stiffness and shorter chain length contribute to a lower glass transition temperature in the polymer (Flinn and Trojan, 1995). The glass transition temperature for amorphous PET is approximately 70 °C and for polypropylene (isotactic) it is 0 °C. Therefore, at room temperature, PET tends to be glassier in nature while polypropylene has a more rubbery state. Amorphous polymers are characterised by their Tg while semi-crystalline polymers tend to be characterised by their melting temperature.

1.12.5 Viscoelasticity

Both PET and polypropylene demonstrate viscoelastic behaviour. Creep is a measure of the increase in strain of a material, when the stress applied is held constant over a period of time while stress relaxation is the reduction in stress when the strain is held constant over time (Anderson et al., 2003). Tests for viscoelastic behaviour of a material give an indication of its dimensional stability over time.

The occurrence of creep is due to the breaking of intermolecular forces i.e. Van der Waal forces between the macromoelcules rather than stretching of the backbone of the polymer (Lechat et al., 2011). Factors affecting the rate of creep of a polymer include molecular mobility, stress level and time. Increasing temperature generally results in an increase in molecular mobility and therefore reduces the resistance to creep (Shackleford, 1996). The creep behaviour of a polymer is dependent on the load applied but in a non-linear fashion (Daniels, 1989). The resistance to creep tends to increase with increasing crystallinity of the polymer (Ladouce et al., 1994).

Liu et al., (2009) examined the creep behaviour of polypropylene under different environmental conditions including temperature and stress. With increasing temperature the intermolecular forces decreased. This allowed the molecular chain segments to move more easily which accelerated the creep failure of the polypropylene under a given stress. As tensile stress increased, the activation barrier for bond dissociation decreased, so the rate of creep increased.

Creep curves of PP and PET have been described as having three distinct phases 1) primary creep –where strain grows sharply with time, 2) secondary creep where strain increases linearly with time and 3) tertiary creep where strain increases non-linearly with time. (Drozdov, 2010; Lechat et al., 2011). The primary creep is attributed to the elongation and deformation of the crystalline skeleton, which induces the movement of the amorphous phase. During secondary creep, the polymer is subject to viscous flow and this constitutes the majority of creep behaviour. The final stage tertiary creep, where the creep rate increases sharply is due to the decrease in cross sectional area of the polymer due to necking occurring in the material leading eventually to fracture. This tertiary phase has been attributed to re-organisation of the lamellar crystals along the creep direction, with a change from an ellipsoidal crystalline structure to a fibrillar structure and an increase in free volume (Jia et al., 2015). These stages of creep of a polymer are shown in figure 1.3.

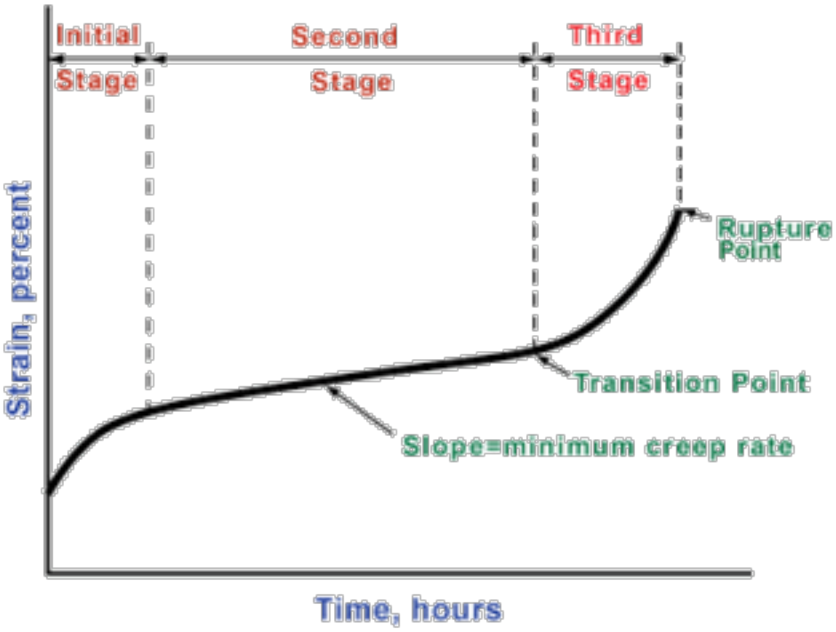

Figure 1.3 Time-strain plot displaying initial or primary, secondary and tertiary stages of creep of a polymer. Source of image: (https://www.nde-ed.org/EducationResources/CommunityCollege/Materials/Mechanical/Creep.htm, 2016)

1.12.6 Tensile strength

Fracture has been cited as the most common reason for failure of thermoplastic retainers (Sun et al., 2011). PET displays three distinct fracture behaviours during tensile testing. These are ductile, semi-ductile and brittle depending on the depth of the notch in the test specimen (Ogazi-Onyemaechi et al., 2010). It was suggested that this behaviour is related to the skin-core structure of the PET specimen. It appears that when the notch is located within the skin region the fracture is ductile or semi-ductile in nature. When the notch penetrates to the core of the PET specimen, the fracture behaviour becomes more brittle.

Similarly, three tensile fracture morphologies were identified for high isotactic polypropylenes: brittle fracture, crazing-tearing and brittle fracture with ductile pulling of fibrils (Dasari et al., 2003). These behaviours appeared dependent on the rate of strain. At lower displacement rates crazing-tearing was seen but with an increase in displacement rate there was an increase in brittle fracture with ductile pulling but at higher displacement rates only the brittle mode of fracture was observed.

The effects of a simulated intra-oral environment on the tensile strength of several dental thermoplastic materials have been investigated (Ryokawa et al., 2006). The study suggested that the tensile yield strength and elastic modulus of Essix C+ (polypropylene) material decreased after thermoforming and immersion in water for 24 hours at 37 °C compared with similar samples stored ‘dry’ at a room temperature of 23 °C (Ryokawa et al., 2006).

The essential work fracture test was developed as an alternative test for fracture toughness of ductile thin plastic sheets (Broberg 1975). The effects of distilled water and various mouthwashes, on the essential work fracture of Essix C+ (polypropylene polymer) and Tru-Tain Splint material (polyethylene terephthalate glycol) was investigated by Pascual et al. (2010). The specimens were stored for 160 hours at 25 °C with the fluids being changed every 24 h. For the Essix C+ material it was reported that the immersion solution did not affect the essential work fracture of the material except when comparing the effect of hydrogen peroxide (3% solution) with distilled water. The hydrogen peroxide solution appeared to increase the energy required to initiate a fracture in the polypropylene polymer, but the other solutions appeared to have no effect. For polyethylene terephthalate glycol the immersion solutions did not affect the energy required to initiate fracture for this material.

1.12.7 Uniaxial tensile cyclic loading

Fatigue failure in thermoplastics can be due to crack propagation or thermal softening (Mai et al., 1981). Thermal softening occurs when the heat that builds up in the specimen during cyclic loading is not dissipated so that the threshold for heat distortion is exceeded and thermal softening failure occurs.

Under cyclic loading conditions of between 450 and 4000 cycles per minute with no air cooling polypropylene does not show brittle-like fatigue failure but undergoes thermal softening whether the specimens are notched or unnotched (Mai et al., 1981).

The failure of PET under cyclic loading is distinct from that observed under tensile stress (Lechat et al., 2006). The tensile failure of PET fibres has two distinct stages:

1. Initiation of the crack on the surface of the fibre followed by growth of the crack with plastic deformation leading to a v-shaped crack developing.
2. Catastrophic failure of the fibre

Under cyclic loading a different morphology of failure known as fatigue failure has been described for PET fibres:

1. Initiation of the crack on the surface
2. Followed by a deviation of the crack so that it propagates at an angle to the fibre axis
3. Propagation of the crack resulting in the creation of a detached portion of material
4. Failure occurring as the portion becomes too small to bear the load of the maximum applied cyclic stress.

Lechat et al. (2006) found that the effect of increasing the maximum cyclic load on PET reduces the time to failure whereas increasing the minimum cyclic load increases the time to failure.

Investigation of fatigue of polymers can be based on two philosophies-total life philosophy and defect tolerant philosophy (Ritchie and Murakami, 2003) The total life philosophy involves defect free specimens being cyclically loaded and failure of the specimen is based on the crack nucleation and subsequent growth of the crack to a critical size. The defect tolerant philosophy is based on the idea that fatigue life is determined by the number of cycles needed to propagate a crack of initial size to a critical dimension. Tests can be based on stress or strain loading. Strain based fatigue testing involves the complete reversal of the loading conditions. This is generally accompanied by cyclic softening (Rabinowitz and Beardmore, 1974).

1.13 Aims of this study

With the increasing and widespread use of thermoplastic retainers in providing retention post orthodontic treatment, the aims of this study are to examine the effect of cleaning agents and a whitening gel on the mechanical and physical properties of both polyethylene terephthalate and polypropylene materials (Essix ACE and Essix C+ , respectively). In particular, assessing the effects of immersion following cyclic loading on the tensile strength, creep and thermal properties of these materials.

1.13.1 Null hypotheses

The null hypotheses for this study were:

1. Twice per day immersion of the materials in different cleaning agents and whitening gel for 14 days has no effect on the tensile strength of the materials tested.
2. Twice per day immersion of the materials in distilled water and Retainer Brite for 14 days has no effect on the level of creep shown by the materials tested.
3. Twice per day immersion of the materials in distilled water and Retainer Brite for 14 days followed by uniaxial tensile cyclic loading of the materials has no effect on both of the materials tensile strength.
4. Twice per day immersion of the materials in distilled water and Retainer Brite for 14 days has no effect on the glass transition temperature of PET or the melting temperature of PP.

Chapter 2: Materials and Methods

2.1

The effect of cleaning agents and whitening gel on the tensile strength of thermoplastic orthodontic retainer materials.

A pilot study was initially carried out to identify a consistent test specimen fabrication technique. Mechanical testing was performed using a universal testing apparatus (MTS, Model 42, Universal Testing Machine, Chicago, USA). Twenty-five specimens of PP and PET were fabricated, which then underwent a varied immersion protocol before testing. For the pilot study 5 specimens were used per immersion group.

2.1.1 Specimen preparation

A dumb-bell shaped acrylic block was fabricated to act as a template to make each PP or PET test specimen with the dimensions illustrated in figure 2.1.

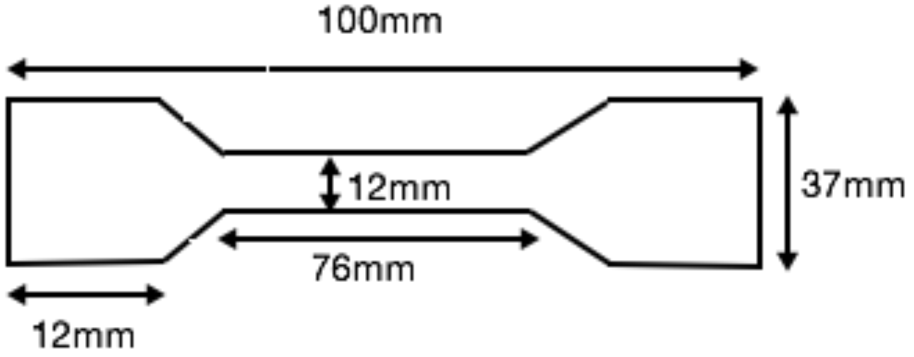

Figure 2.1. Schematic of acrylic block used as template (not drawn to scale).

Each test specimen was thermo-formed over the acrylic block from a circular blank of thermoplastic material, which was 125 mm in diameter and 1 mm thick. The circular blank of material was either Essix ACE (PET) or Essix C+ (PP) (Dentsply-Raintree Essix) supplied by Ortho-Care (UK) Limited, West Yorkshire, United Kingdom.

A blank was heated as per the manufacturer's instructions using a Biostar V positive pressure thermal-forming machine (Scheu Dental Iserlohn, Germany, distributed by Great Lakes Orthodontics Ltd, Tonawanda NY). Each proprietary material was thermoformed according to the manufacturers recommendations.

The Essix ACE (PET) was heated for 35 s at 220 °C. The Essix C+ (PP) material was heated for 50 s at 220 °C. When the blank had been adequately heated, it was pulled down over the acrylic block and the positive pressure generated by the Biostar machine adapted it around the acrylic block. The thermoformed specimen was then allowed to cool before being removed from the machine. Both the Essix ACE and Essix C+ specimens were cooled for 120 seconds as per the manufacturer's instructions.

The thermoformed circular blank was removed from the Biostar machine and it was then peeled away from the acrylic block. The excess material was removed with scissors and the edges of the test specimens were polished with a coral bur at low speed (8000 rpm). The resulting retainer specimen was 98 mm in length, 37 mm wide at both ends and 76 mm long and 12 mm wide in the central portion.

A notch was then cut at the centre of each long edge of the specimen 2 mm deep using a blade 0.433 mm thick to produce a double-edge-notched-tension specimen. Both the blade and the specimen were marked to provide a 2 mm depth notch. A new blade was used to make the notches after every 5th specimen i.e. 10 cuts.

The specimens were then wrapped in foil and stored for 24 h in a room at a temperature of 22 ± 1 °C and a relative humidity of 46 ± 1 % .

10 specimens were fabricated for each immersion group for both the Essix ACE (PET) and Essix C+ (PP) materials giving a total of 50 for Essix ACE and 50 for Essix C+.

The immersion regimen groups were as follows:

1. Dry non-immersed
2. Distilled water
3. Retainer Brite (1 tablet/200 mL distilled water)
4. Sodium Hypochlorite (2% w/w)
5. Whitening gel (16% carbamide peroxide)

Retainer Brite tablets were sourced from Ortho-Care (UK) Limited, West Yorkshire, UK. The constituents of Retainer Brite include potassium persulfate compound, sodium perborate, sodium bicarbonate, sodium sulphate, sodium carbonate and pentasodium triphosphate. The sodium hypochlorite used was undiluted Milton (2% sodium hypochlorite), produced by Procter and Gamble, UK. The whitening gel was also sourced from Ortho-Care (UK) Limited, West Yorkshire, UK. The whitening gel contained 16% carbamide peroxide and was stored in a fridge at 5 °C when not in use.

For the ‘dry’ group for both Essix ACE and Essix C+ samples were tested following 24 h without immersion. The remaining specimens underwent the following immersion protocol.

2.1.2 Specimen immersion

Following 24 h of conditioning, the ten specimens in each group were firstly immersed in distilled water for 30 min. The water was drained and the specimens were dried with paper towels prior to immersion in their respective solutions: distilled water, Retainer Brite solution (1 tablet/200 mL of distilled water), sodium hypochlorite (2% w/w), and whitening gel (16% carbamide peroxide) for 30 min. The time 30 min was chosen as this was the duration recommended by manufacturers for use of the whitening gel. In order to allow comparison between groups and standardisation of the immersion protocol all groups were immersed for 30 min.

After 30 min, the specimens were removed from the immersion solutions and dried with paper towels. They were then wrapped in foil and stored in a room at 22 ± 1 °C at 46 ± 1 % relative humidity until the next immersion period.

The immersion protocol was repeated 12 h later on the same day and then twice per day for 14 days. After the final immersion all samples were dried with paper towel and wrapped in foil prior to tensile testing in a controlled environment at 22 ± 1 °C at 46 ± 1% relative humidity.

The cross sectional area of each specimen was calculated before the specimen underwent uni-axial tensile testing. The width was measured between the two notches. The average of the thickness of 6 points close to the notch (3 on either side) was taken as the thickness of the specimen. These measurements were carried out using a digital calliper (Whitworth electronic digital calliper) correct to 0.01mm.

The specimens were gripped at one end to a fixed clamp and at the other end to a mobile crosshead to apply a tensile force to the material. A 5 kN load cell was used to measure the tensile strength. The crosshead speed was set at 1 mm/minute. The specimens were loaded in tension to fracture. The load at specimen failure was recorded using the MTS software connected to the MTS Universal Testing Machine. The data was then exported to Microsoft Excel for analysis.

From the load-extension curves obtained the tensile strength was calculated using Equation 2.1:

Equation 2.1: $$\text{Tensile strength (MPa)} = \frac{\text{Load (N)}}{\text{Cross sectional area (mm}^2\text{)}}$$

2.2

The effect of cyclic loading on the tensile strength of thermoplastic orthodontic retainer materials.

Using an identical specimen fabrication method to section 2.1.1, 10 specimens for each of the three groups (dry, distilled water, Retainer Brite) for both Essix ACE and Essix C+ were thermoformed using the Biostar positive pressure thermal forming machine. The two immersion groups chosen for cyclic load testing, creep testing and thermal testing were based on the results of the pilot study which showed distilled water and Retainer Brite to cause the least and greatest change inn both materials' tensile strength, respectively.

Double-edged notched specimens were produced using a 0.433mm blade (Stanley, Stanley Black and Decker, Inc.) as outlined in Section 2.1.1. A fresh blade was used after every 5th specimen i.e. 10 cuts.

All specimens underwent conditioning, by wrapping them in foil and storing for 24 h at 22 ± 1 °C, 46 ± 1 % relative humidity.

Following conditioning, the dry specimens were brought to the laboratory for cyclic loading and tensile testing.

The remaining specimens, including the distilled water and Retainer Brite groups, underwent the same immersion protocol as described in section 2.1.2.

The ten specimens of each group were firstly immersed in distilled water for 30 min. The water was drained from the specimens in all groups. The specimens were then each dried with paper towels. They were then immersed in their respective solutions: distilled water, Retainer Brite solution (1 tablet/200 mL of distilled water) for 30 min.

After 30 min, the specimens were removed from the immersion solutions, dried with paper towels and then stored in foil until the next immersion period. The immersion protocol was repeated 12 h later on the same day and then twice per day for 14 days.

After the final immersion all samples were dried with paper towel and stored in foil.

After 24 h the specimens were brought to the laboratory where uniaxial tensile cyclic loading was performed on each specimen using the MTS Universal Testing Machine in a controlled environment of 22 ± 1 °C and relative humidity of 46 ± 1 %.

For the Essix ACE (PET) material cyclic loading was performed between 0 and 100 N using a sinusoidal wave path at a frequency of 0.5 Hertz. 100 N was identified to give 0.5mm deflection of the specimen while staying within the elastic portion of its load-extension curve, identified from previous experiments. 0.5mm of deflection was chosen as it was estimated that a retainer on insertion or removal over and under undercuts around the teeth undergoes a maximum of approximately 0.5mm deflection. 1000 cycles were performed as this equated to approximately 1 year of insertion and removal of an orthodontic retainer.

For the Essix C+ (PP) material cyclic loading was preformed between 0 and 50 N using a sinusoidal wave path at a frequency of 0.5 Hertz as this similarly gave approximately 0.5mm of deflection of the specimen while also remaining within the elastic portion of its load-extension curve. 1000 cycles were also carried out.

When each specimen had completed 1000 cycles of uniaxial tensile loading its tensile strength was tested using the MTS Universal Testing Machine.

The data was captured using the MTS software and exported to Microsoft Excel for collation.

2.3

The effect of distilled water and Retainer Brite on the creep of thermoplastic orthodontic retainer materials.

Using the same specimen mould from section 2.1, 10 specimens for each of the three groups (dry, distilled water and Retainer Brite) were thermoformed using the Biostar V positive pressure thermal forming machine in accordance with the manufacturers instructions as detailed above. Therefore, a total of 30 specimens were thermoformed for Essix ACE and 30 for Essix C+.

The thermoformed circular blank was removed from the Biostar machine, the excess was trimmed with scissors and polished with a coral bur at low speed (8000 rpm).

Three groups with different environmental exposures were studied for each material; dry non-immersed, distilled water and Retainer Brite. The distilled water and Retainer Brite solutions were chosen as these immersion solutions showed the least and greatest effects on the materials' tensile strength in section 2.1 of the study. No notch was cut in these specimens. The specimens were wrapped in foil and conditioned for 24 h in a room at a temperature of 22 ± 1 °C and 46 ± 1 % relative humidity.

The dry specimens were then tested for creep at two-thirds of the mean value of their tensile strength using the MTS Universal Testing Machine so as to avoid forces that may lead to failure of the specimen. The Essix ACE specimens were tested for creep at 200 N for 6000 s. The Essix C+ specimens were tested for creep at 130 N for 6000 s. The universal testing apparatus was programmed to apply a constant force to the material specimen for the duration of the test.

The immersion protocol as detailed in section 2.1.2 of the study was repeated for the distilled water and Retainer Brite groups. The ten specimens in each group were firstly immersed in distilled water for 30 min. The water was drained from the specimens in all groups. The specimens were then each dried with paper towels. They were then immersed in their respective solutions: distilled water, Retainer Brite solution (1 tablet/200 mL of distilled water) for 30 min. After 30 min, the specimens were removed from the immersion solutions, dried with paper towels and then stored in foil until the next immersion period. The immersion protocol was repeated 12 h later on the same day and then twice per day for 14 days.

After the final immersion, all samples were dried with paper towel and stored in foil. After 24 h, creep tests were performed in a controlled environment using the MTS Universal Testing Machine. Data was captured using the MTS software and exported to Microsoft Excel.

2.4 The effect of distilled water and Retainer Brite on the thermal properties of thermoplastic orthodontic retainer materials.

Differential scanning calorimetry was used to investigate the effect of the immersion regimen on the glass transition temperature of PET and the degree of crystallization of PP. Three specimens of each material for each sample group were prepared as outlined in Section 2.1.1. Three sample groups were subjected to different immersion regimes, dry, distilled water and Retainer Brite, respectively. No notches were placed in the test specimens. The specimens were wrapped in foil and conditioned for 24 h at 22 ± 1 °C at 46 ± 1 % relative humidity before undergoing the immersion protocol as described above. The specimens were tested using a Perkin Elmer TAC-7DX calorimeter. The calorimeter was first calibrated using an indium sample. For the PET material a punch was used to cut out a sample (3 mm in diameter) from each specimen. The sample was then weighed using a Perkin Elmer microbalance correct to 0.01 mg. The sample was sealed and then transferred to the sample aluminium pan in the Perkin Elmer calorimeter. The mass was entered into the programme, which was set for heat to flow into the sample pot at a rate of 10 °C per minute from 25 °C up to 100 °C. Using the proprietary software the glass transition temperature for each PET sample was determined from the thermograms obtained. An average glass transition temperature was calculated for each immersion group.

For the PP specimens a sample was cut from each specimen with scissors to fit in the test pan. The sample was weighed using the Elkin Palmer microbalance. The sample was then sealed and placed in the sample aluminium pan in the Perkin Elmer calorimeter. The mass was entered into the programme software and the calorimeter was set to heat the sample at a rate of 10 °C per minute from a starting temperature of 30 °C to a maximum temperature of 180 °C.

The amount of heat given off (Joules/gram) when the PP specimen melted (the melting peak area) was calculated using the Perkin Elmer software and the thermograms obtained. This figure was then used to calculate the degree of crystallization of the PP samples using the following equation, Equation 2.2:

Equation 2.2:

$$\mathbf{Xc = \frac{\Delta Hm}{\Delta Hm0} \times 100}$$

where Xc=degree of crystallization, ΔHm=melting enthalpy for the sample, ΔHm0=melting enthalpy for a 100% crystalline sample. The melting enthalpy for a 100% crystalline PP is 209 J/g.

The average degree of crystallinity for each immersion group was then determined.

2.5 Statistical Analysis

Statistical analysis of the results obtained was carried out using SPSS Statistics version 21.0 (IBM, UK).

The mean tensile stress, and creep of each immersion group together with their respective standard deviations were calculated.

Comparisons of the materials under each immersion condition with regard to tensile stress and creep were performed using two-way ANOVA with tukey post-hoc tests and one-way ANOVA tests at $\alpha = 0.05$.

Chapter Three: Results

3.1 The effect of immersion on the tensile strength of Essix ACE (PET) and Essix C+ (PP)

Tensile testing of PET and PP was carried out following immersion in their respective solutions twice daily for 14 days. The mean tensile strengths of PET and PP were calculated for each immersion group and are displayed in the following graphs (figures 3.1 and 3.2, respectively).

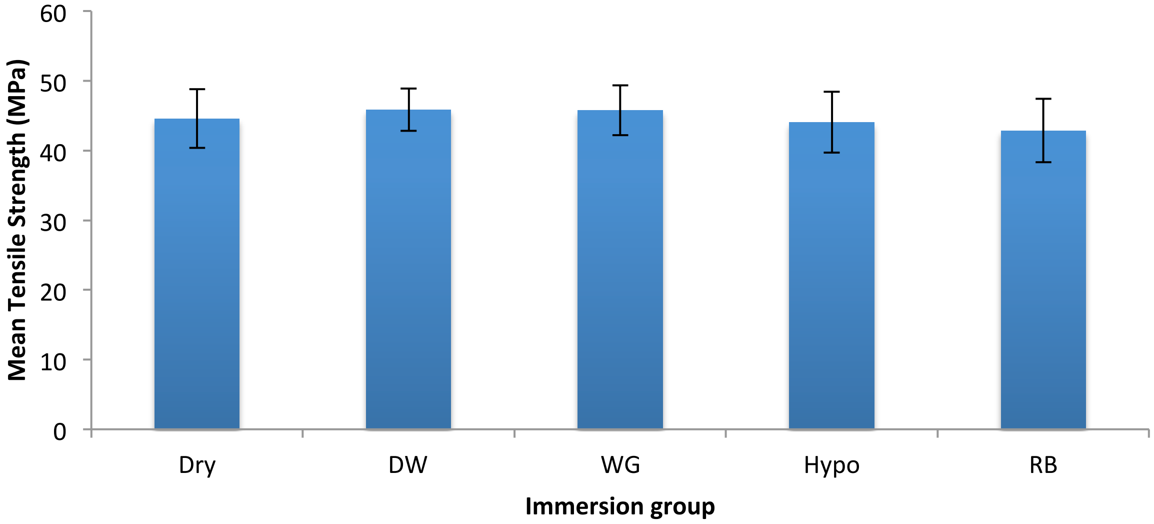

Figure 3.1 Mean tensile strength with SD of PET specimens: Dry, DW= distilled water, WG= whitening gel, Hypo=sodium hypochlorite, RB=Retainer Brite. (n=10) (Error bars show one standard deviation).

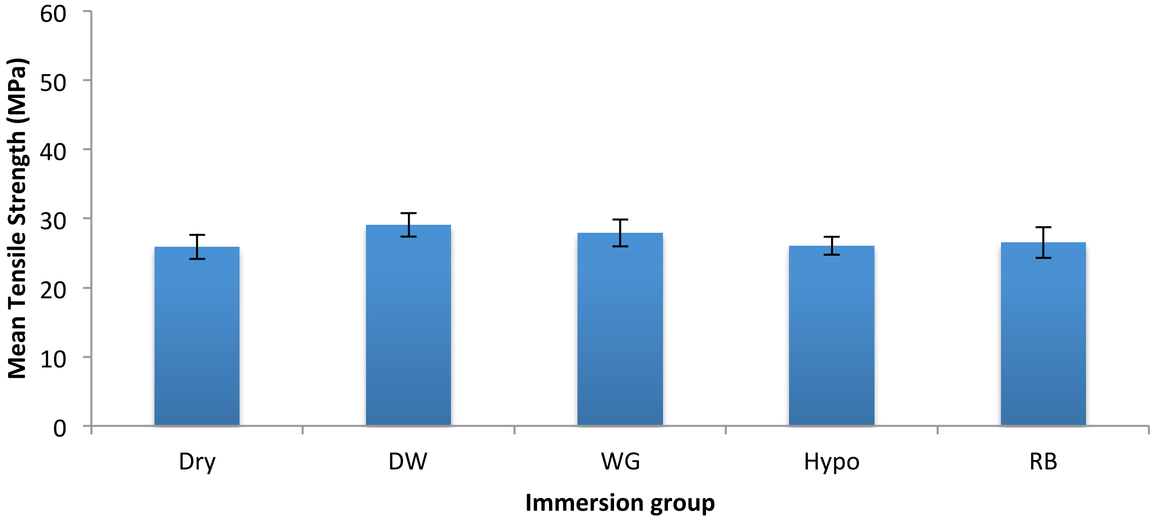

Figure 3.2 Mean tensile strength with SD of PP: Dry, DW=distilled water, WG=whitening gel, Hypo= sodium hypochlorite, RB= Retainer Brite. (n=10). (Error bars show one standard deviation).

The following figures show a typical load-extension plot on a common scale generated from tensile testing of PET and PP, figure 3.3 and 3.4, respectively.

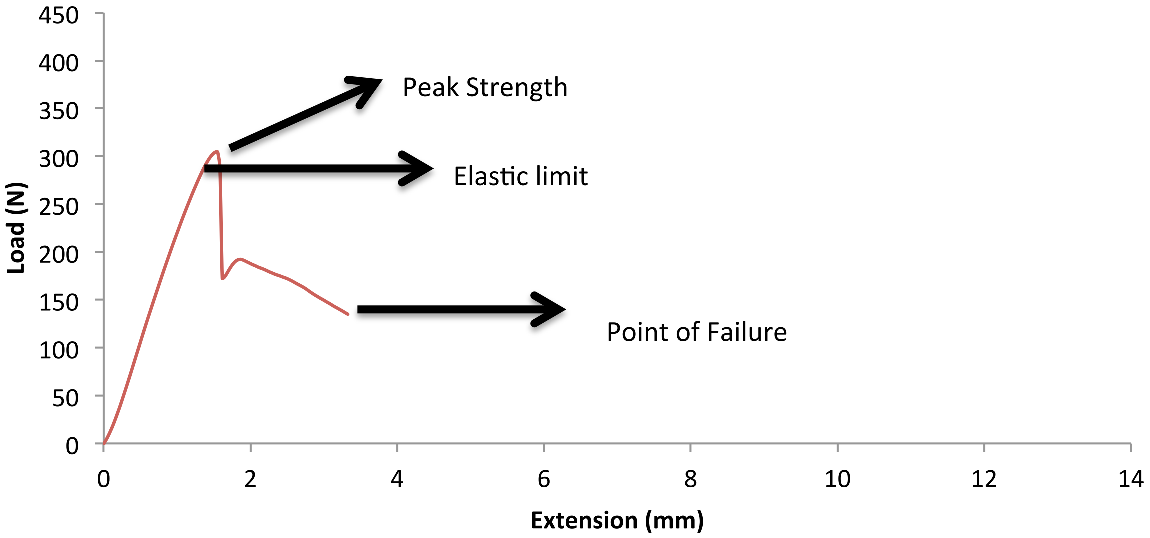

Figure 3.3 Load-extension plot generated from uni-axial tensile testing of dry non-immersed PET sample.

The load extension plot of PET samples showed a steep linear rise initially up to the elastic limit of the material. The load continued to rise non-linearly to the point of maximum strength. The strength of the samples then decreased sharply due to strain softening. A further small rise in load to a second peak was then observed and can be accounted for by stress induced crystallization before gradually reducing to the point of failure.

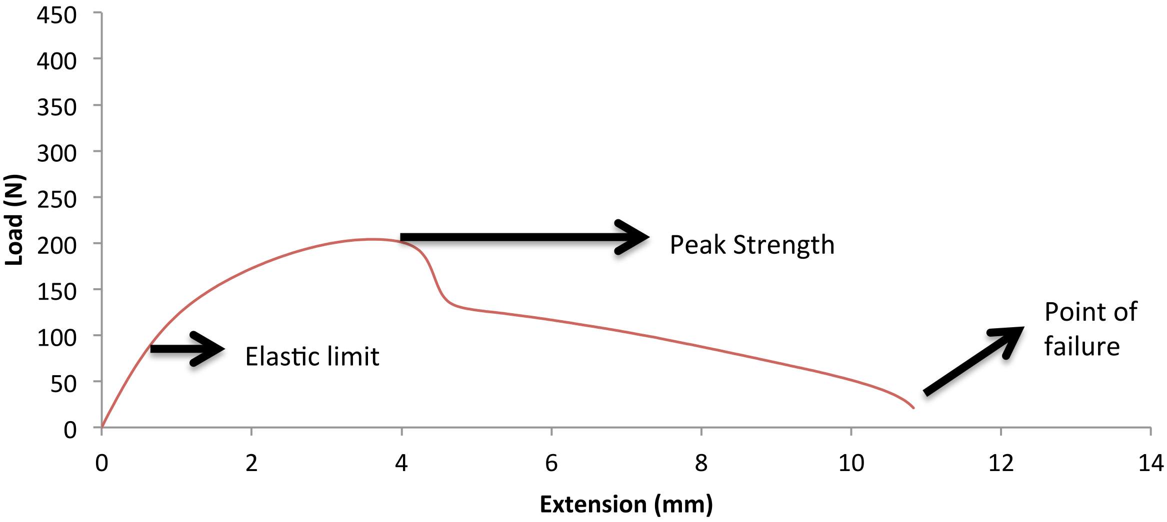

Figure 3.4 Load-extension plot generated from uni-axial tensile testing of dry non-immersed PP sample.

The load-extension plot of PP samples demonstrated a small linear increase initially. The load then continued to increase in a non-linear fashion to its point of maximum strength. The graph then showed the load decreased continuously initially at a faster rate compared with the gradual decrease that followed until reaching the point of failure. Unlike the PET load-extension graph there is no second peak in the PP graph.

The mean elastic limit, peak strength and extension at peak strength for both polyethylene terephthalate (PET) and polypropylene (PP) are tabulated in Table 3.1.

Material	Extension at mean elastic limit mm (SD)	Mean peak strength MPa (SD)	Mean extension at peak strength mm (SD)
PET			
Dry	1.5(0.2)	44.6 (4.2)	1.5 (0.2)
Distilled water	1.7(0.1)	45.8 (3.1)	2.0 (0.2)
Whitening gel	1.8 (0.2)	45.8 (3.6)	2.0 (0.2)
Sodium Hypochlorite	1.7 (0.2)	44.0 (4.4)	1.7 (0.2)
Retainer Brite	1.7 (0.3)	42.9 (4.5)	1.7 (0.3)
PP			
Dry	0.7 (0.1)	25.9 (1.7)	3.6 (0.4)
Distilled water	1.2 (0.2)	29.1 (1.7)	4.0 (0.6)
Whitening gel	0.9 (0.3)	26.5 (2.2)	4.1 (0.9)
Sodium Hypochlorite	0.8 (0.2)	26.0 (1.3)	3.8 (0.5)
Retainer Brite	0.6 (0.2)	29.1 (1.7)	3.6 (0.6)

Table 3.1 Mean elastic limit, mean peak strength and mean extension at peak strength for both materials under different immersion conditions.

The mean tensile strength of dry non-immersed PET was 44.5 (4.1) MPa whilst that for dry non-immersed PP was 25.9 (1.7) MPa. A two-way ANOVA identified that the type of retainer material (PET or PP) significantly influenced the mean tensile strength ($p<0.01$) whereas the immersion regimen had no significant impact on strength ($p=0.111$). A significant interaction between the two factors was observed ($p=0.049$) indicating that, the magnitude of the effect of material choice on mean tensile strength, was influenced by the type of immersion medium. Post hoc tests on the tensile strength of both materials after undergoing immersion showed no significant effect of the immersion on the materials' tensile strength.

The amount of extension the material underwent before it experienced a significant decrease in its tensile strength was also compared between the materials and between immersion groups. The mean extension of non-immersed PET was 1.5 (0.2) mm while that for PP was 3.6 (0.4) mm. A two-way ANOVA identified that the type of retainer material (PET or PP) significantly influenced mean extension ($p<0.01$). Furthermore, a significant impact of immersion regimen on mean extension was identified ($p=0.014$).

The immersion of PET in Retainer Brite and sodium hypochlorite did not significantly affect the amount of extension before reaching its yield point with mean extension of 1.8 mm and 1.7 mm respectively. However the immersion of PET in distilled water and whitening gel increased the amount of extension to 2 (0.2) mm, which was significant ($p<0.001$).

The PP material showed greater extension before undergoing a significant decrease in its tensile strength. The effects of immersion of PP in distilled water, Retainer Brite, sodium hypochlorite and whitening gel tended to increase the amount of this extension with mean extension of 4.0 mm 4.1 mm 3.8 mm and 3.6 mm, respectively. But post-hoc tukey tests showed no significant differences between the immersion groups of PP (p values >0.05).

The elastic limits of PET and PP were also determined from the load-extension plots obtained. A two-way ANOVA showed that the type of retainer material significantly influenced the mean elastic limit ($p<0.01$) and that the immersion regimen also significantly affected the mean elastic limit ($p<0.01$). A significant interaction between the two factors was also seen ($p=0.006$) indicating that, the magnitude of the effect of material choice on the elastic limit, was affected by the type of immersion medium. Post-hoc tests showed that compared to the dry materials, the immersion of both materials in distilled water and whitening gel significantly affected the elastic limit of the material ($p<0.01$) with a tendency to increase it for both PET and PP. The other immersion regimen did not appear to affect the materials in a similar way with no significant differences observed ($p>0.05$).

The plots of load versus extension generated from uniaxial tensile testing of PET and PP following immersion are shown in Appendix 1.

3.2 The effect of uniaxial tensile cyclic loading and immersion on Essix ACE (PET) and Essix C+ (PP)

Following immersion of the PET and PP test specimens in their respective immersion solutions, the specimens then underwent 1000 cycles of uniaxial tensile cyclic loading. Tensile strength testing of the PET and PP specimens was then carried out. From the load-extension plots generated, the mean elastic limit, mean peak strength and mean extension at peak strength were calculated and are displayed in Table 3.2.

Material	Extension at mean elastic limit mm (SD)	Mean peak strength MPa (SD)	Mean extension at peak strength mm (SD)
PET			
Dry + Cyclic Loading	1.8 (0.2)	45.7 (3.6)	1.8 (0.2)
Distilled water + Cyclic Loading	1.6 (0.2)	40.0 (3.5)	1.7 (0.3)
Retainer Brite + Cyclic Loading	1.6 (0.1)	41.7 (2.8)	1.6 (0.1)
PP			
Dry + Cyclic loading	1.2 (0.2)	28.1 (1.0)	3.6 (0.3)
Distilled water + Cyclic loading	1.2 (0.2)	27.7 (1.5)	3.1 (0.3)
Retainer Brite + Cyclic loading	1.3 (0.2)	28.3 (1.5)	3.1 (0.2)

Table 3.2 Mean extension at elastic limit, mean peak strength and mean elongation at peak strength for specimens that have undergone immersion followed by uniaxial tensile cyclic loading.

The mean tensile strength of dry PET and PP following cyclic loading was 45.1 (3.7) MPa and 28.1 (1.0) MPa, respectively. A two-way ANOVA showed that both the choice of material ($p<0.001$) and the cyclic loading following immersion of the materials ($p=0.002$) had a significant effect on the tensile strength of the materials. There was also a significant interaction between both factors ($p=0.005$) suggesting that the magnitude of the effect of material choice on the tensile strength of the material was affected by the uniaxial cyclic loading following immersion regime. For PET, cyclic loading together with immersion in distilled water and Retainer Brite solution significantly reduced its mean tensile strength compared with dry PET specimens ($p=0.002$ and $p=0.032$, respectively).

For specimens that had been cyclically loaded, a two-way ANOVA demonstrated a significant impact of material ($p<0.01$) and immersion regimen ($p<0.01$) on mean extension. A significant interaction between the two factors ($p=0.037$) was observed indicating that the nature of the effect of material type on mean extension is dependent on the immersion regimen.

There was no significant interaction between the choice of material and the effect of cyclic loading and immersion on the elastic limit of the materials ($p=0.132$). The choice of material significantly affected the elastic limit of the material ($p<0.05$) but cyclic loading followed by immersion did not have a significant effect on the elastic limit of the material ($p=0.279$).

The load-extension plots of PET and PP generated following immersion and uniaxial tensile cyclic loading are shown in Appendix 2.

3.3 The effect of immersion on the creep of Essix ACE (PET) and Essix C+ (PP)

Un-notched PET and PP test specimens were prepared for creep testing. After undergoing the immersion regimens for 14 days creep testing of the PET and PP specimens was carried out. The amount of creep observed after 10 minutes for each PET and PP specimen was calculated from the extension-time plots generated. The mean creep of the PET and PP specimens for each immersion group was calculated and is shown in table 3.3 and figure 3.7 and 3.8.

Material	Mean creep mm (SD)
PET	
Dry	0.07 (0.02)
Distilled water	0.07 (0.02)
Retainer Brite	0.07 (0.02)
PP	
Dry	0.85 (0.17)
Distilled water	0.62 (0.08)
Retainer Brite	0.56 (0.1)

Table 3.3 Mean creep shown by PET and PP following immersion in distilled water and Retainer Brite.

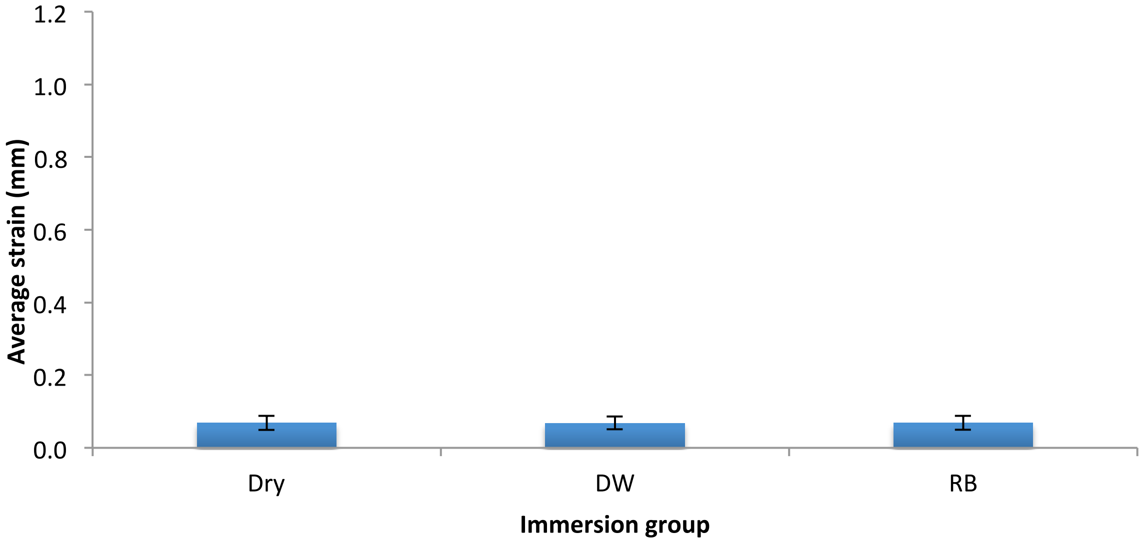

Figure 3.5 Mean creep shown by PET. Dry, DW=distilled water, RB= Retainer Brite. (Error bars show one standard deviation).

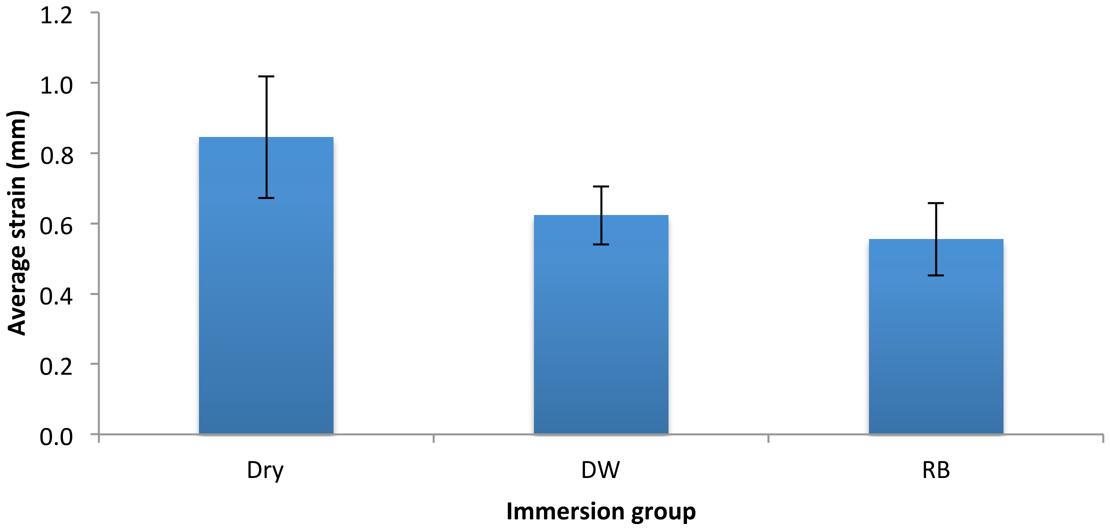

Figure 3.6 Mean creep shown by PP. Dry, DW= distilled water, RB= Retainer Brite. (Error bars show one standard deviation).

Both PET and PP showed evidence of creep. The mean creep of dry non-immersed PET specimens was 0.07 (0.02) mm while that for PP was 0.9 (0.2) mm. A two-way ANOVA showed that the choice of material had a significant effect on the amount of creep of the material ($p<0.05$), as did the immersion regimen ($p<0.05$). There was also a significant interaction between the two variables indicating that the magnitude of the effect of choice of material on the creep of the material is influenced by the immersion regimen, to which, that material is subjected to ($p <0.05$). Additional one-way ANOVA tests ran for each individual material showed that the immersion of PET in distilled water or Retainer Brite had no significant effect on the amount of creep shown by PET. The creep of PP was however more susceptible to the effects of the immersion regimen. The immersion of PP in distilled water and Retainer Brite both significantly reduced the amount of creep shown by the material during creep testing ($p =0.001$ and $p<0.01$ respectively). The plots of extension versus time generated from creep tests of the dry PET and PP are shown in figure 3.7 and 3.8, respectively. These plots both display the primary and secondary stages of a creep curve. The initial or primary creep shows a sharp initial increase in strain, which is quickly followed by the secondary creep stage. The secondary creep stage constitutes the majority of the creep. In this stage the strain is seen to increase linearly with time. The tertiary stage of creep leading to failure has not been reached after 10 minutes for either PET or PP. The plots for the creep of PET and PP following immersion are shown in Appendix III.

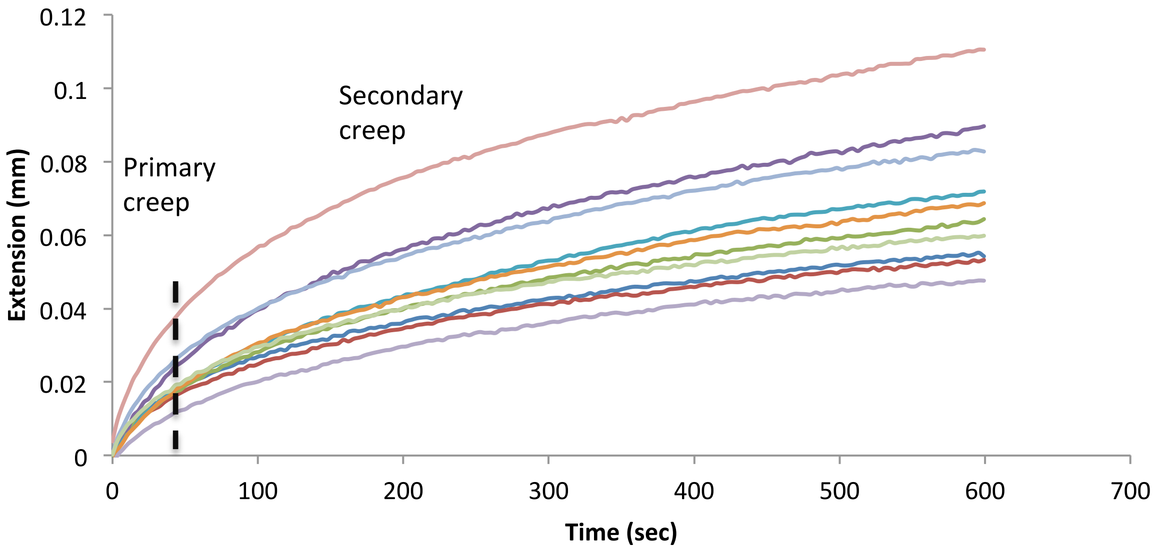

Figure 3.7 Extension-time plots generated from creep testing of dry non-immersed PET samples (n=10)

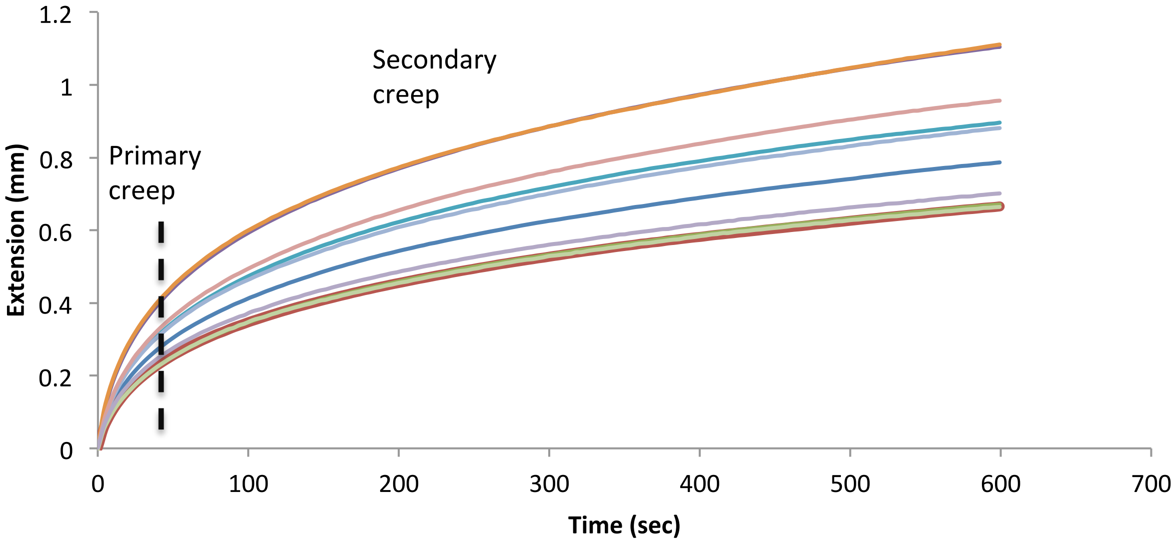

Figure 3.8 Extension-time plots generated from creep testing of dry non-immersed PP samples (n=10)

3.4 The effect of immersion on the glass transition temperature of Essix ACE (PET) and the degree of crystallization of Essix C+ (PP)

Differential scanning calorimetry was carried out on both PET and PP specimens that had undergone the immersion regimen as previously described. From the thermograms generated the glass transition temperature of the PET specimens and the degree of crystallization of the PP specimens were determined. The thermograms generated from a dry PET and dry PP are shown in figure 3.9 and 3.10 respectively.

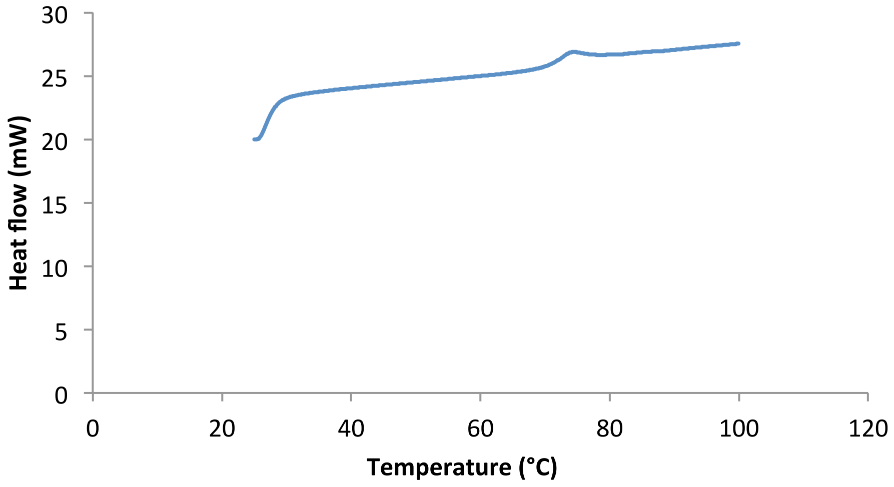

Figure 3.9 Thermogram generated from differential scanning calorimetry testing of dry non-immersed PET sample.

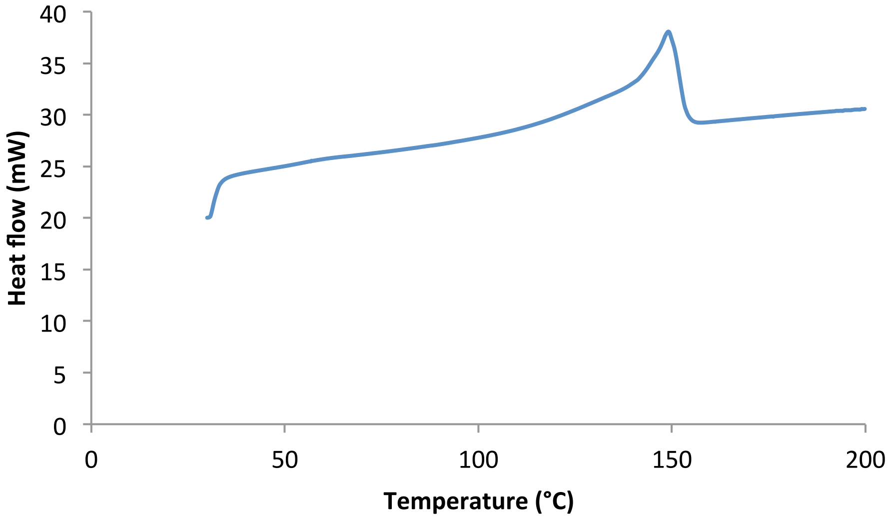

Figure 3.10 Thermogram generated from differential scanning calorimetry testing of dry non-immersed PP sample.

From these, the mean glass transition temperature for each immersion group of the PET specimens and the mean degree of crystallization for each immersion group of the PP specimens were calculated and are displayed in tables 3.4 and 3.5. A sample of a thermogram from each immersion group generated is shown in Appendix IV.

Material	Mass (mg)	Glass Transition Temperature (Degrees Celsius)	Mean (SD)
PET			
Dry 1	16.57	70.7	
Dry 2	16.11	71.3	
Dry 3	16.05	71.2	**71.1 (0.3)**
Distilled H_2O 1	15.64	69.8	
Distilled H_2O 2	15.49	68.9	
Distilled H_2O 3	15.9	68.4	**69.0 (0.7) ***
Retainer Brite 1	16.5	69.5	
Retainer Brite 2	16.16	70	
Retainer Brite 3	16.28	70.7	**70.1 (0.6)**

Table 3.4 Glass transition temperatures of samples of PET with averages for each immersion group calculated from DSC thermograms generated. *=Statistically significant in comparison to dry PET ($p<0.05$).

Material	Mass (mg)	ΔHm (J/g)	ΔHm0 (J/g)	Degree of crystallinity (%)	Average (SD)
PP					
Dry 1	12.8	80.3	209	38.4	
Dry 2	13.21	80.9	209	38.7	
Dry 3	9.53	80.2	209	38.4	**38.5 (0.2)**
Distilled H_2O 1	12.15	77.9	209	37.3	
Distilled H_2O 2	11.31	80.6	209	38.6	
Distilled H_2O 3	11.51	79.2	209	37.9	**37.9 (0.7)**
Retainer Brite 1	6.88	79.9	209	38.2	
Retainer Brite 2	8.74	77.2	209	37	
Retainer Brite 3	9.04	77.9	209	37	**37.4 (0.7)**

Table 3.5 Degree of crystallinity of samples of PP with averages for each immersion group calculated from DSC thermograms generated.

The PET material did not show a melting point on the thermograms generated. This indicated that the PET was non-crystalline or amorphous in nature. However when heated above its glass transition temperature the PET material did not undergo crystallization either. It was felt that the PET material is amorphous but has been inhibited from crystallising.

A one-way ANOVA test of the effect of immersion on the glass transition temperature of PET showed that the immersion of PET in distilled water significantly affected the glass transition temperature of PET reducing it from 71 to 69 °C ($p=0.014$). The immersion of PET in Retainer Brite had no significant effect on the glass transition temperature of PET.

The degree of crystallinity of PP was approximately 38%. A one-way ANOVA test of the effect of immersion of PP in distilled water and Retainer Brite on the degree of crystallinity of PP showed no significant effect ($p=0.13$).

Chapter Four: Discussion

4.1 The effect of immersion on the tensile strength of Essix ACE (PET) and Essix C+ (PP)

Mechanical testing identified significant differences in the mean tensile strength of the PET and PP substrates used in this investigation. The mean tensile strength of dry PET was 44.5 (4.1) MPa while that for dry PP was significantly lower at 25.9 (1.7) MPa ($p<0.01$). The difference in tensile strength seen may be explained by differences in the molecular structure, the degree of crystallization and the glass transition temperature of the PET and PP materials. PP consists of linear hydrocarbon chains with a methyl side group attached. The PET material however, has an aromatic benzene ring and short aliphatic chain in the backbone, which gives greater rigidity and strength to the PET material as the benzene ring prevents rotation of the polymer molecules (steric hindrance). The ester group in the PET molecules also gives polarity to the molecules. This facilitates the formation of stronger dipole-dipole interactions between the PET molecules than the non-polar Van der Waal interactions seen in PP. An increase in the degree of crystallization is associated with increased strength due to a greater number of secondary intermolecular bonds, which exist when the polymer chains are closely packed (Flinn and Trojan, 1995). Differential scanning calorimetry of the PET and PP materials in this investigation showed the PET specimens to be amorphous while the PP showed a degree of crystallization of 38%. It could be expected that an amorphous PET would have a lower strength than a semi-crystalline PP. However, PP at room temperature of 22 ±1 °C is above its Tg of 0 °C while PET is below its Tg of 71°C. Above the Tg, the polymer chains of PP show greater mobility with reduced numbers of secondary intermolecular forces thereby leading to reduced strength while the chains of PET tend to resist movement.

The PET and PP materials also demonstrated differences in the nature of their stress-strain behaviour as seen on the load-extension curves generated. The PP substrates showed greater elasticity and flow with a more gradual increase in stress to peak strength compared with the PET specimens. This can be explained due to the fact that PP at the temperature at which the tensile tests were carried out was above its Tg while PET was below its Tg. PET showed a more brittle or glass-like nature to its fracture while the PP material behaved in a more ductile manner.

A two-way ANOVA showed that the immersion regimen had no significant effect on the tensile strength of either PET or PP. This is dissimilar to a study by Ryokawa (2006) who found a significant decrease in tensile strength of PP after immersion in water for 24 h at 37°C. This may be explained in part due to the immersion regime used in this investigation. The immersion of the material twice daily for 30 minutes in distilled water followed by the cleaning agent or whitening gel may not have been of sufficient duration to affect the tensile strength of PET or PP. Similar results to this study were found in an investigation of the effect of immersion of Essix C+ (PP) and Tru-Tain Splint material (Polyethylene terephthalate glycol, PETG) in various mouthwashes (Pascual et al., 2010). In this study the retainer materials were immersed in Crest Pro Health, Polident, Listerene and 3% hydrogen peroxide for 160 hours at 25 °C. The energy required to initiate a fracture known as the essential work of fracture and energy required to propagate the fracture, known as the plastic work of fracture were measured. This longer immersion regime did not affect the essential work of fracture of PP or PETG. Ahn et al. (2015) investigated the effect of intra-oral exposure on the tensile strength of a PETG copolymer thermoplastic retainer. The mean tensile strength of this retainer material at 21 ± 0.49 MPa was similar to the PP specimens used in this study. Similarly to this investigation, a short-term (2 weeks) immersion of the PETG material in saliva did not significantly affect its tensile strength. Six months intra-oral exposure however, significantly increased the tensile strength of PETG. Future work may wish to evaluate the effect of the immersion regimen in the longer term.

There was a significant difference in the amount of extension shown by PP and PET before reaching their peak strength ($p < 0.01$). The mean extension of PET was 1.5 (0.2) mm compared to 3.6 (0.4) mm for PP. This may be explained by the difference in chemical structure of PET and PP with PET having a more rigid backbone structure due to the benzene ring group, which would resist movement of the polymer chains. PP, being above its Tg at room temperature has greater mobility of the polymer chains, making it more ductile. The immersion of PET in distilled water significantly increased the mean extension to 2 (0.2) mm ($p<0.001$). This may be explained in part due to the plasticizing effect of water on PET (Chen et al., 1998). Exposure of polymers to water can result in water absorption and swelling of the material (Jabarin and Lofgren, 1986, Ryokawa et al., 2006). This occurs due to the formation of intermolecular bonds between the water and the polymer. Water can enter the polymer by two ways: sorption and diffusion (Woishnis and Ebnesajjad, 2012). Sorption is the entrance of water into polymer by interaction with the polymer molecule, while diffusion is the distribution of the water molecules by random molecular order throughout the material. Jabarin and Lofgren (1986) reported that water sorption by PET reaches equilibrium after approximately 25 h exposure at 23 °C. The glass transition temperature has also been shown to decrease in proportion to the amount of water uptake (Jabarin and Lofgren, 1986, Chen et al., 1998). This was also shown in this study where the Tg of PET showed a significant decrease after immersion in distilled water ($p=0.014$). Jabarin and Lofgren (1986) also reported a decrease in ultimate tensile strength with increasing moisture content of the PET material. In this study no significant effect on the tensile strength of PET was seen after immersion in distilled water. This may be due to the immersion period being significantly shorter (to reflect a clinically relevant immersion protocol) than that required to reach saturation point of the material. The duration of 30 minutes was based on maufacturers' recommendations for use of the whitening gel. This was slightly longer than that recommended for the use of the Retainer Brite (until the colour changes from blue to a clear colour or approximately 20 min) and would be significantly shorter than the duration that a retainer would be worn clinically for 10-12 hours per day. However it was necessary to choose a standard duration of immersion to facilitate comparison between the immersion groups.

Two-way ANOVA post-hoc tests in this study showed no significant effect of immersion in distilled water on the tensile strength of PP. A similar result was also reported in an investigation of the effect of water absorption on all-polypropylene composites (Deng et al., 2010). Polypropylene acted as a hydrophobic polymer, demonstrating only a negligible amount of water absorption (0.03% w/w) following immersion in water for one month. There was also no significant effect on the tensile strength of the all-polypropylene composite due to water absorption.

In light of the study by Ahn et al., (2015) where two weeks full time intra-oral exposure of the retainer had no effect on the tensile strength of the retainer, it may be deduced that it is unlikely that 10-12 hours of retainer wear would affect the tensile strength of a similar orthodontic retainer. Clinically, patients can be advised that the use of agents such as water, Retainer Brite or Milton to clean their orthodontic retainer is safe and does not increase the risk of fracture. However, the combined effects of immersion in saliva for 10-12 hours followed by the use of a cleaning agent have not been tested and this may be considered for investigation in future studies. Also, it is possible to conclude that patients may use their orthodontic retainer as a carrier for whitening gel (6% hydrogen peroxide) without affecting its resistance to fracture. However the accurate fit required of an orthodontic retainer together with its rigidity may preclude its use for this purpose due to the lack of a recess for the whitening gel.

4.2 The effect of immersion and uniaxial tensile cyclic loading on the tensile strength of Essix ACE (PET) and Essix C+ (PP)

Uniaxial tensile cyclic load testing of the PET and PP materials was carried out in order to determine the effects of repeated insertion and removal of an orthodontic retainer on its strength. It was estimated that an orthodontic retainer would flex up to a maximum of 0.5 mm when seating or removing it over the gingival undercuts in the mouth. The cyclic load tests were set up so that the stress applied to the PET and PP material generated a 0.5 mm deflection of the material while remaining within the elastic portion of the stress-strain curve of that material. 1000 cycles were carried out to demonstrate the effects of insertion and removal over 1 year. Following cyclic loading the tensile strength of the material was tested.

Cyclic loading of the dry non-immersed PET and PP specimens had no significant effect on either material's tensile strength (Table 3.1 and Table 3.2). Ductile polymers have been reported to undergo cyclic softening when subject to cyclic stress-strain deformation (Rabinowitz and Beardmore, 1974). This softening is a mechanical phenomenon with molecular rearrangements occurring at a microscopic level to accommodate the changes in strain. During cyclic loading an initial incubation period occurs where the material remains unchanged following an initial stress-strain cycle. This represents a period where the number of mobile defects in the material is too low to contribute to significant strain. Following this a steady state is reached and maintained over a number of cycles. The strain recovery balances the applied strain and the defect population and molecular rearrangement produced by the softening are maintained. Finally a region of crack propagation resulting in fatigue failure is seen. The peak tensile stress achieved with each cycle reduces due to the decrease in cross sectional area of the specimen with each successive cycle as the crack growth increases. A second phenomenon, thermal softening of the polymer may also occur as the local temperature rises due to the cyclic loading (Suresh, 1998). The temperature increase in the polymer is due to hysteretic energy dissipated as heat by each cycle. This results in plastic flow of the material (Suresh, 1998). In this investigation, the PET and PP materials were not loaded until fatigue failure occurred. The number of cycles of loading (1000) in this study may not have been sufficient to bring about significant cyclic or thermal softening of the dry material specimens to significantly affect the PET and PP materials' tensile strength. It is also possible that the stress required to cause 0.5mm strain of the material was not sufficient to cause the materials to reach a steady state of cyclic softening and therefore not having a significant effect on the tensile strength of the dry materials.

Two-way ANOVA post hoc tests showed that for PET, cyclic loading together with immersion in distilled water and Retainer Brite solution significantly reduced its mean tensile strength compared with dry PET specimens (p=0.002 and p=0.032, respectively).

The combined effects of immersion followed by cyclic loading may have allowed greater mobility between the polymer chains, which resulted in the reduced tensile strength seen. The increased mobility and weakening of the intermolecular bonds may be explained by cyclic softening resulting in the generation of mobile defects within the material. The Tg of PET was shown by DSC in this investigation to be significantly lowered following immersion in distilled water. The production of heat during the cyclic loading would also have lead to the PET specimens coming closer to this lower Tg. Therefore after the cyclic loading the PET material would have been in a softened state with accumulated defects. When the specimens were then tested in tension these factors may have contributed to the decrease in tensile strength seen. It is interesting that both the immersion and cyclic loading combine together to affect PET’s tensile strength while neither immersion nor cyclic loading individually, affected the tensile strength of PET significantly.

For the PP specimens, immersion in distilled water and cyclic loading did not affect the tensile strength of PP which may have been due to the resistance of PP to water sorption (Deng et al., 2010). The organised and closely packed structure of the semi-crystalline PP would allow stronger secondary forces between the polymer chains which then may not have been susceptible to the softening effects of 1000 cycles of uniaxial tensile cyclic loading. It is possible that evidence of softening may be seen with a longer duration of cyclic loading.

Cyclic load testing together with immersion of the retainer in cleaning agents or distilled water would simulate in part daily use of an orthodontic retainer by the patient. The implication that the combined effects of immersion and cyclic loading reduces tensile strength of PET material would suggest that in the long term, daily insertion and removal together with the use of water or Retainer Brite as a cleaning agent may be expected to affect the tensile strength of the PET orthodontic retainer. For orthodontic retainers fabricated from PP daily cleaning and insertion and removal of the retainer from the mouth would not be expected to significantly affect its tensile strength.

4.3 The effect of cleaning agents on the amount of creep of Essix ACE (PET) and Essix C+ (PP)

All plastics demonstrate creep behaviour. The ability of an orthodontic retainer to resist creep would greatly benefit the patient. This would mean that the retainer would be less likely to undergo changes in its dimension, which could affect the fit of the retainer and its ability to maintain the corrected tooth position.

The principle mechanism in polymer creep is the uncoiling of the polymer chains and the movement of the polymer chains past each other (Murray, 1993). The process of creep in polymers was detailed as three stages (Jia et al, 2015). The primary creep is attributed to an initial elastic deformation together with a fast initial rate of plastic flow, which quickly decreases. This is attributed to movement of the amorphous region. During secondary creep, strain increases linearly with time and constitutes the majority of creep behaviour. The final stage tertiary creep, where the creep increases non-linearly, has been attributed to the re-organisation of the lamellar crystals along the creep direction, with a change from an ellipsoidal crystalline structure to a fibrillar structure and an increase in free volume (Jia et al., 2015). There were significant differences in the amount of creep shown by PET and PP ($p<0.05$). Dry PET showed 0.1mm of creep after 10 minutes while dry PP showed 0.9 mm. Immersion in distilled water had no effect on the creep of PET but immersion of PP in distilled water significantly reduced the amount of creep shown by PP. Lechat (2011) proposed that what occurs at a microstructural level when PET undergoes creep involves the breaking of secondary van der Waal bonds rather than an interaction with the backbone structure of the polymer. Similarly Liu et al., (2009) when describing the creep behaviour of PP found that creep failure occurred more quickly under conditions that enhanced bond dissociation between the molecules rather than within the molecules such as increasing temperature and increasing stress. The creep of glassy rigid polymers is dependent on the elastic modulus and the difference between the Tg and the ambient temperature of testing (Nielsen and Landel, 1994).

The greater amount of creep seen in the dry PP material may be explained in part due to PP having a lower elastic modulus than PET as seen in the stress-strain curves obtained. The PP specimens were also above their Tg at the temperature the creep tests were carried out unlike the dry PET material, which was well below its Tg. This would lead to greater mobility of the PP chains when subjected to a constant load. The PET chains although amorphous would be more resistant to mobility being in a more glassy rigid state below its Tg (Nielsen and Landel, 1994).

The immersion of PET in distilled water and Retainer Brite did not affect the amount of creep shown by the PET material. Ryokawa et al. (2006) found that water sorption by amorphous plastics was higher than that of semi-crystalline plastics. The mechanism of this water absorption is dependent on the free volume with amorphous polymers having a greater free volume. However, Jabarin and Lofgren (1986) reported that PET only reaches saturation after 25 h of exposure to water at 23 °C. The lack of effect of immersion in distilled water and Retainer Brite on the creep of the PET material may be due the immersion regimen not being of sufficient duration to cause an effect. Although differential scanning calorimetry showed the immersion of PET in water did significantly reduce its Tg this was not sufficient enough to cause a significant change in the amount of creep shown by the PET specimens.

The reduction in the amount of creep shown by PP following immersion in distilled water and Retainer Brite cannot be explained by a similar mechanism. PP has been shown to be relatively resistant to water absorption (Deng et al., 2010). Above the Tg, increasing the degree of crystallisation was reported to reduce the amount of creep seen (Nielsen and Landel, 1994). However differential scanning calorimetry carried out in this study showed that the immersion in water and Retainer Brite had no effect on the percentage crystallization of PP. Water if it was absorbed by the PP would be expected to increase the mobility of the polymer chains by interfering with the secondary intermolecular forces between the molecules. This effect was not seen in this study with a reduction in creep following immersion in water and Retainer Brite rather than an increase as would be expected.

Clinically the use of PET material for the fabrication of an orthodontic retainer would appear to infer an advantage of a reduced amount of creep which appears to be unaffected by the use of a cleaning agent or the short term immersion in distilled water. This would ensure that the retainer remains closely adapted to the aligned teeth. The PP material showed greater amount of creep than PET and although this did reduce with immersion in water and Retainer Brite to 0.6mm approximately this is still significantly more than 0.1mm of observed with the PET material.

4.4 Conclusions of the null hypotheses

The null hypotheses proposed for this study were therefore:

1. True for twice per day immersion of the materials in different cleaning agents and whitening gel for 14 days had no effect on the tensile strength of the materials tested.
2. False for twice per day immersion of the materials in distilled water and Retainer Brite for 14 days had no effect on the level of creep shown by the materials tested as immersion of PP in water and Retainer Brite had a significant effect on the amount of creep seen.
3. False for twice per day immersion of the materials in distilled water and Retainer Brite for 14 days followed by uniaxial tensile cyclic loading of the materials had no effect on both of the materials tensile strength as immersion of the PET material in water and Retainer Brite followed by 1000 cycles of cyclic loading had a significant effect on the tensile strength of PET.
4. False for twice per day immersion of the materials in distilled water and Retainer Brite for 14 days had no effect on the glass transition temperature of PET or the melting temperature of PP as immersion of PET in distilled water had a significant effect on the glass transition temperature of PET.

Chapter Five: Conclusions

- This study has shown that PET and PP orthodontic retainer materials differ significantly in their mechanical and thermal properties. This is manifested in the significant differences seen in the tensile strength and the amount of creep shown by PET and PP. This investigation has also shown the effects of an immersion regimen and uniaxial cyclic loading on the tensile strength and thermal properties of PET and PP.
- PET had a significantly higher tensile strength than PP. PET also showed a more brittle nature to its fracture than PP. PP was more ductile.
- The immersion of PET and PP in distilled water, sodium hypochlorite (2% w/w), Retainer Brite and whitening gel (16 % carbamide peroxide) had no effect on the tensile strength of either material.
- Uniaxial tensile cyclic loading had no effect on the tensile strength of dry non-immersed PET or PP. The immersion of PET in distilled water and Retainer Brite followed by cyclic loading significantly reduced its tensile strength. The immersion of PP in distilled water or Retainer Brite followed by cyclic loading did not significantly affect the tensile strength of PP.
- The PET material showed significantly less creep than the PP material. PET showed 0.1mm of creep whereas PP showed 0.9mm of creep over 10 minutes at a force two-thirds of their respective tensile strengths. The immersion of PET in distilled water or Retainer Brite had no effect on the amount of creep shown by the PET material. The immersion of PP in distilled water and Retainer Brite significantly reduced the amount of creep shown by the PP material.
- Differential scanning calorimetry of the PET specimens revealed it to be an amorphous non-crystallizing version of PET. The glass transition temperature of the dry non-immersed PET specimens was shown to be 71 °C. The immersion of PET in

distilled water significantly reduced the glass transition temperature of PET. Differential scanning calorimetry of the PP specimens showed the PP material to have a degree of crystallization of 38%. The immersion of PP in distilled water or Retainer Brite had no significant effect on the degree of crystallization of PP.

- Clinically the use of Essix ACE (PET) material for the fabrication of orthodontic retainers in preference to Essix C+ (PP) infers the advantages of higher tensile strength and less creep. This indicates that retainers made from Essix ACE may be less likely to fracture and more likely to maintain good dimensional stability than those made from Essix C+. The use of the cleaning agents and whitening gel tested can be considered safe at least in the short term for both of the materials tested.
- The first null hypothesis (Section 1.13.1) of this study was accepted that the short-term immersion of two orthodontic retainer materials in distilled water, cleaning agents and whitening gel had no effect on the tensile strength of these materials. The remaining three null hypotheses were rejected by this study: short term immersion of the two orthodontic retainer materials in distilled water or Retainer Brite had significant effects on the amount of creep seen, the tensile strength following cyclic loading and the thermal properties of these materials.

Chapter Six: Future work

This study has investigated the effect of short-term immersion, on the mechanical properties of two types of orthodontic retainer materials (PET and PP), in distilled water, sodium hypochlorite, Retainer Brite and whitening gel. The effect of, short-term immersion in distilled water and Retainer Brite, on the thermal properties of the same two orthodontic retainer materials was also studied. The immersion regimen consisted of twice daily immersion of the materials in distilled water for 30 minutes followed by their respective solutions for 30 minutes for 14 days. This equated to approximately one month use of cleaning agents on the retainer materials. Although this has given us an insight into the effects of the use of these agents in the short term, it would be interesting to consider the effects of these agents over a longer period e.g. six to twelve months. In particular, as the PET material only becomes saturated with water after immersion for 25 h at 23 °C, an area for exploration would be the effects of the cleaning agents on an already saturated PET specimen as the retainer is immersed in saliva for at least 12 hours per day and in some cases 24 h. Similar polymer materials are used to align teeth, which are worn on a full time basis so the effects of cleaning agents on a saturated polymer would be relevant to this area of orthodontics also.

The closeness of fit of an orthodontic retainer is paramount for it to act effectively in maintaining the corrected tooth position. It may be interesting to investigate how this close fit changes over time. This study investigated the effect of an immersion regime on the creep of the polymer materials. Another method of investigating this would be to measure the volume of new and used retainers to determine any changes that occur over a period of time.

A future study investigating the effects on retainer materials of intra-oral exposure for 10-12 hours per day together with the immersion regimen used in this study would closely simulate daily clinical use of the retainer and would help draw definitive conclusions regarding care of a thermoplastic retainer. Designing an appropriate test specimen for this study however, may prove challenging.

Chapter Seven: References

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Chapter Eight: Appendices

8.1 Appendix I- Load-extension plots generated of dry non-immersed and following immersion of PET and PP.

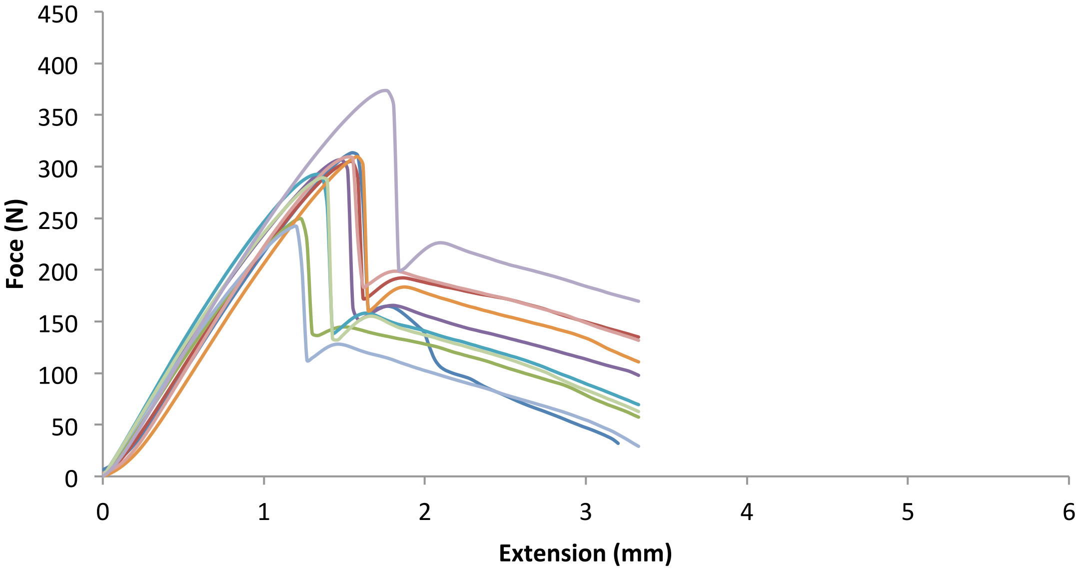

Figure 8.1 Load-extension plots generated from uni-axial tensile testing of dry non-immersed PET samples (n=10)

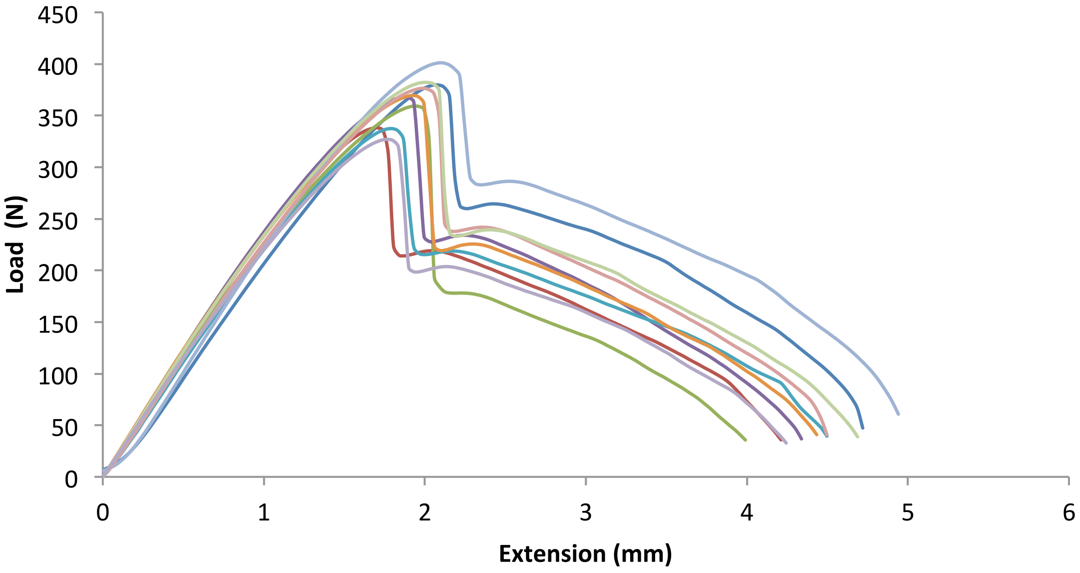

Figure 8.2. Load-extension plots generated from uni-axial tensile testing of PET samples following 2 weeks immersion in distilled water (n=10)

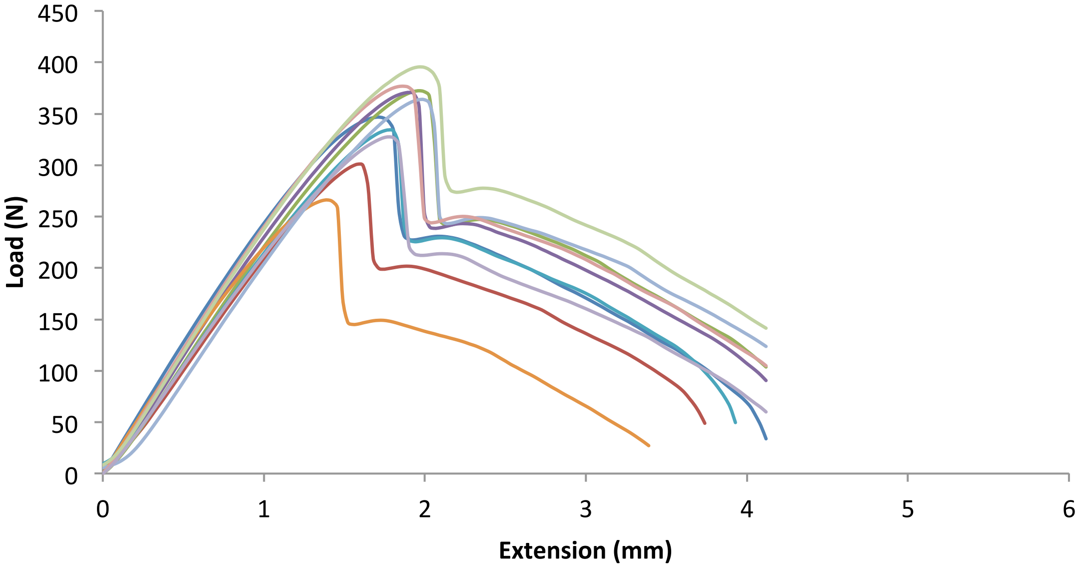

Figure 8.3. Load-extension plots generated from uni-axial tensile testing of PET samples following 2 weeks immersion in whitening gel (16% carbamide peroxide) (n=10)

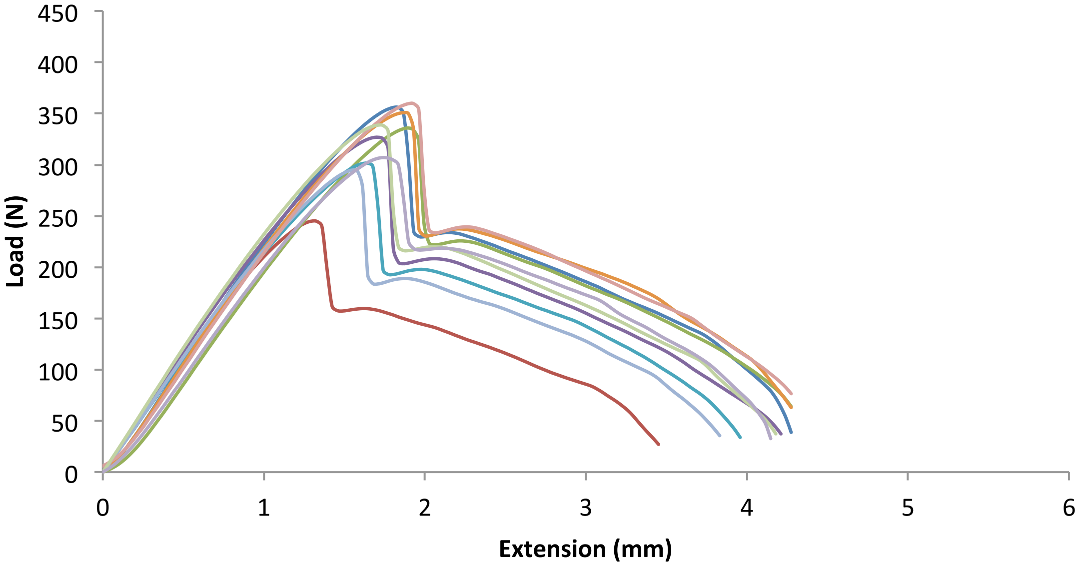

Figure 8.4. Load-extension plots generated from uni-axial tensile testing of PET samples following 2 weeks immersion in sodium hypochlorite (n=10)

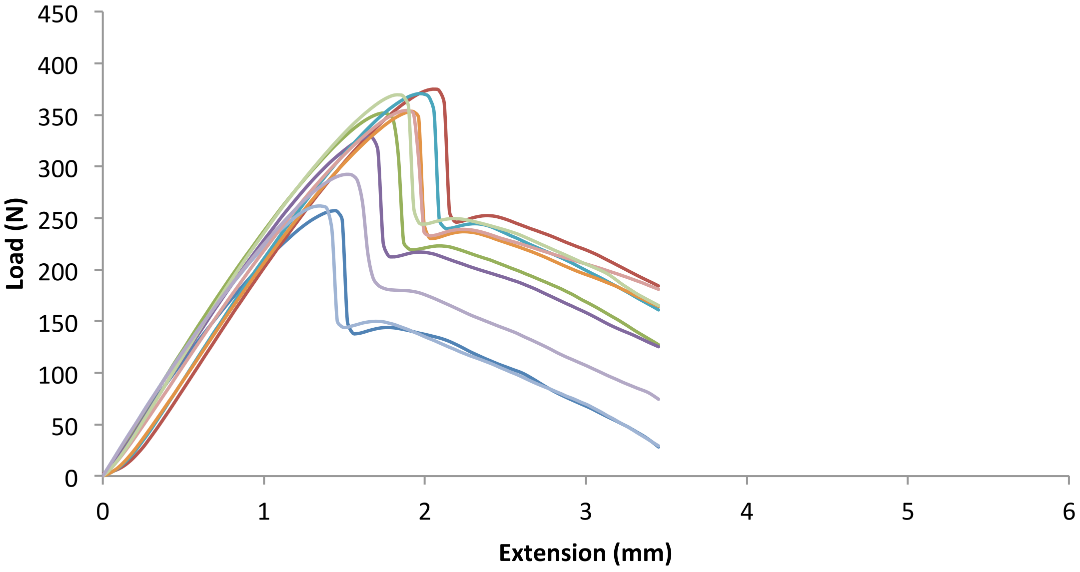

Figure 8.5. Load-extension plots generated from uni-axial tensile testing of PET samples following 2 weeks immersion in Retainer Brite (n=10)

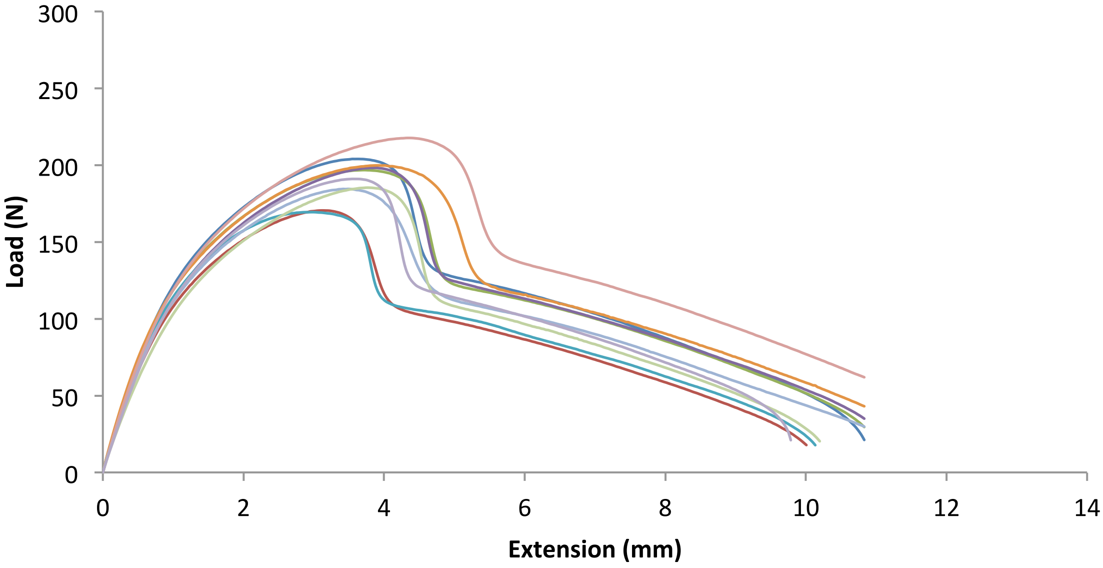

Figure 8.6. Load-extension plots generated from uni-axial tensile testing of dry non-immersed PP samples (n=10)

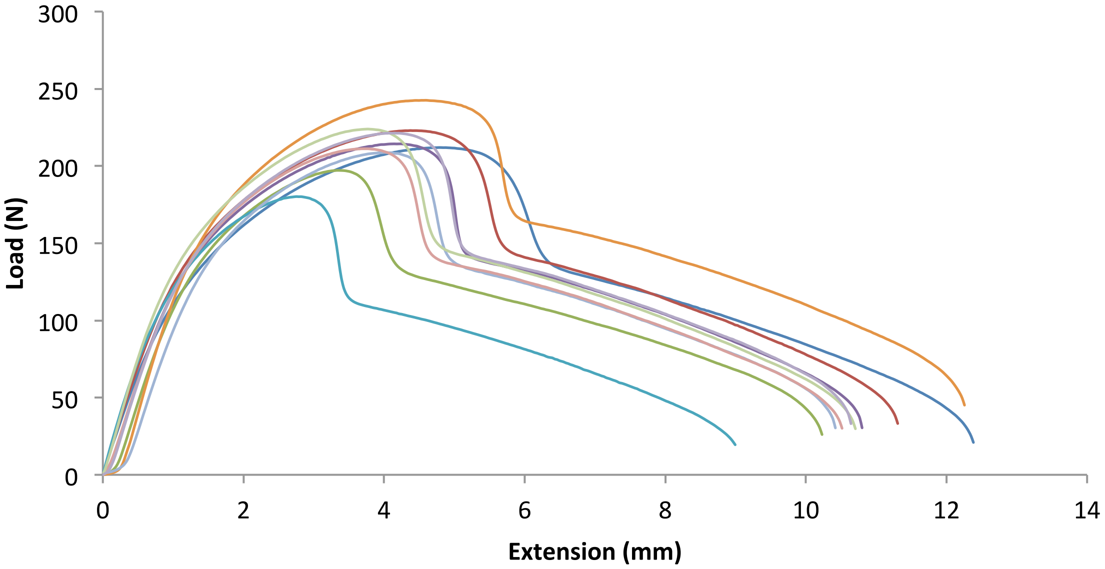

Figure 8.7. Load-extension plots generated from uni-axial tensile testing of PP samples following 2 weeks immersion in distilled water (n=10)

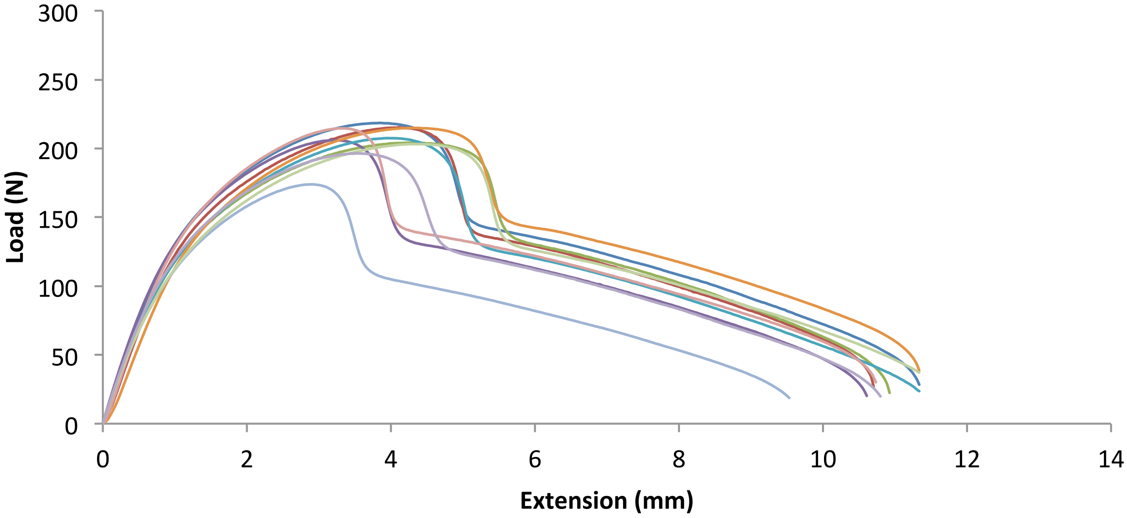

Figure 8.8. Load-extension plots generated from uni-axial tensile testing of PP samples following 2 weeks immersion in whitening gel (16% carbamide peroxide) (n=10)

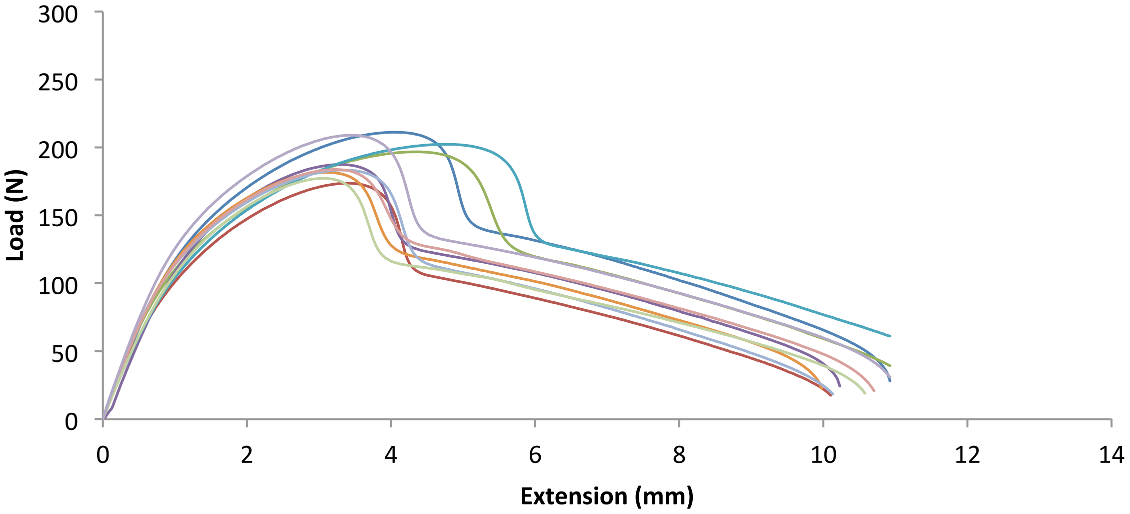

Figure 8.9 Load-extension plots generated from uni-axial tensile testing of PP samples following 2 weeks immersion in sodium hypochlorite (n=10)

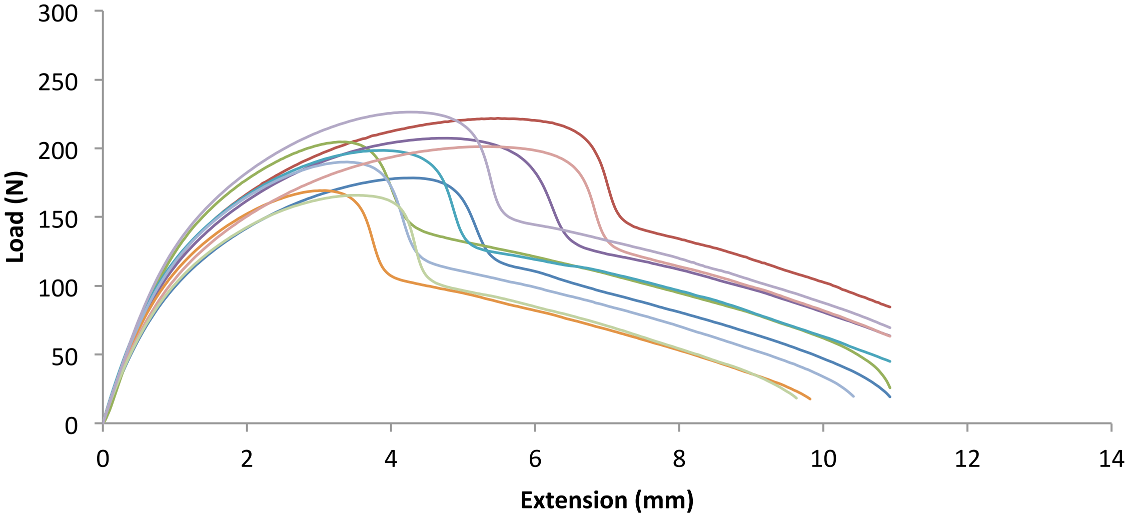

Figure 8.10 Load-extension plots generated from uni-axial tensile testing of PP samples following 2 weeks immersion in Retainer Brite (n=10)

8.2 Appendix II - Load-extension plots generated from tensile testing following immersion and uni-axial tensile cyclic loading of PET and PP.

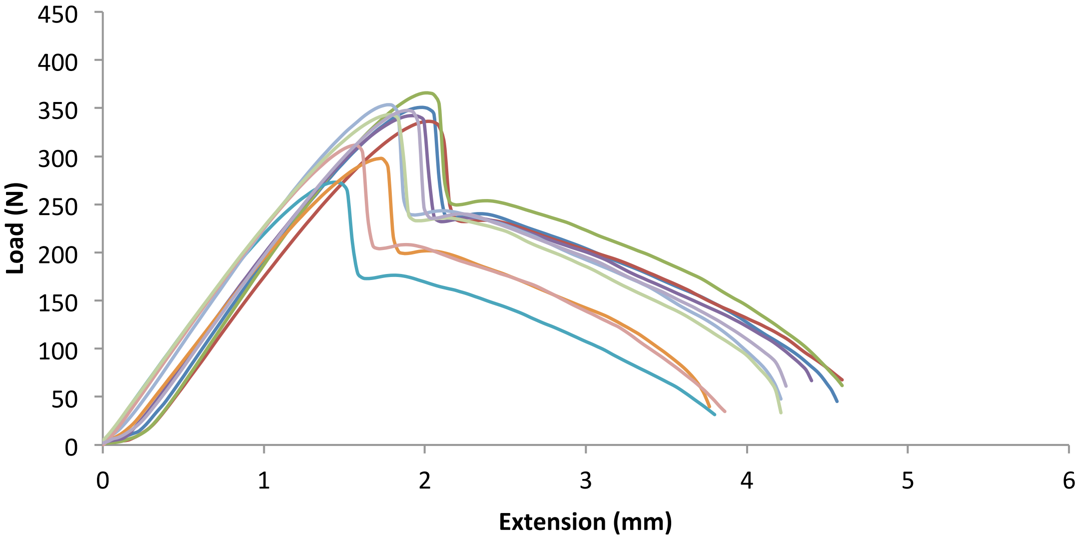

Figure 8.11 Load-extension plots generated from uni-axial tensile testing of dry non-immersed PET samples following cyclic loading at 100N (1000 cycles) (n=10)

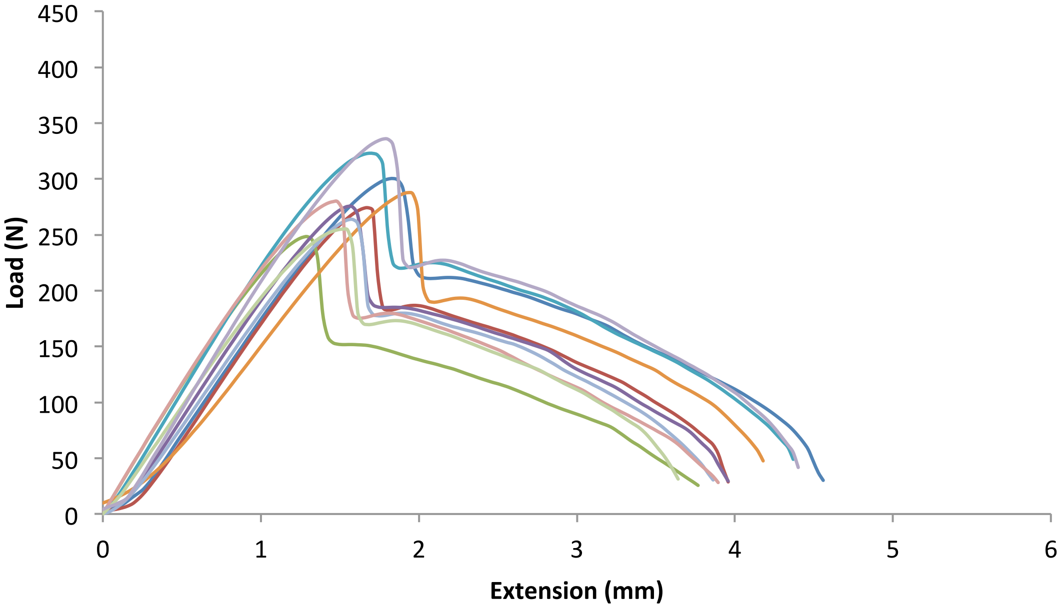

Figure 8.12 Load-extension plots generated from uni-axial tensile testing of PET samples after immersion in distilled water for two weeks followed by cyclic loading at 100N (1000 cycles) (n=10)

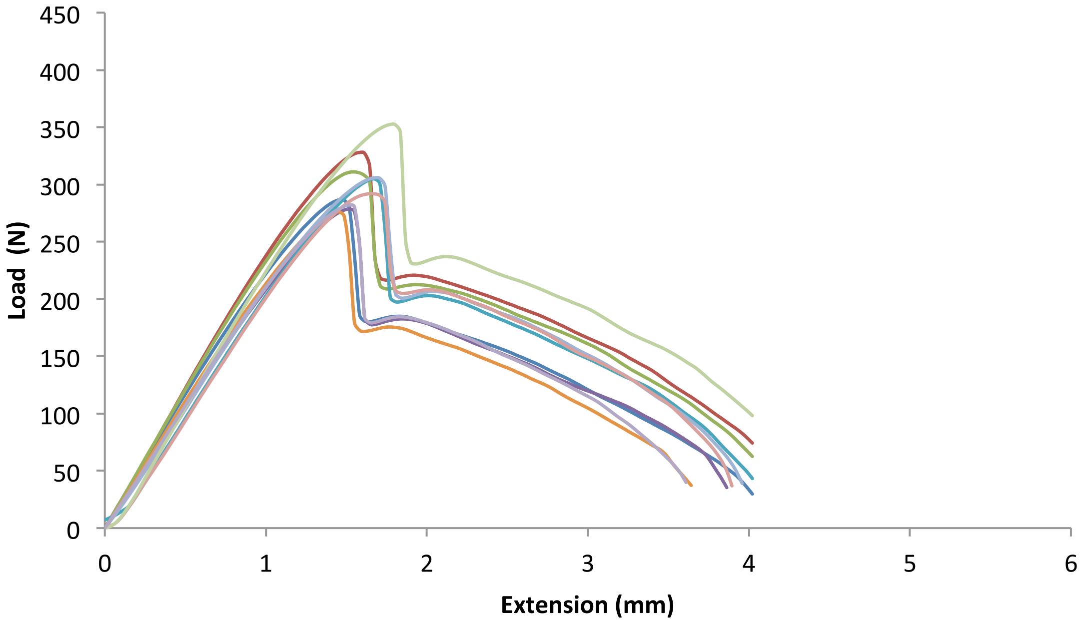

Figure 8.13 Load-extension plots generated from uni-axial tensile testing of PET samples after immersion in Retainer Brite for two weeks followed by cyclic loading at 100N (1000 cycles) (n=10)

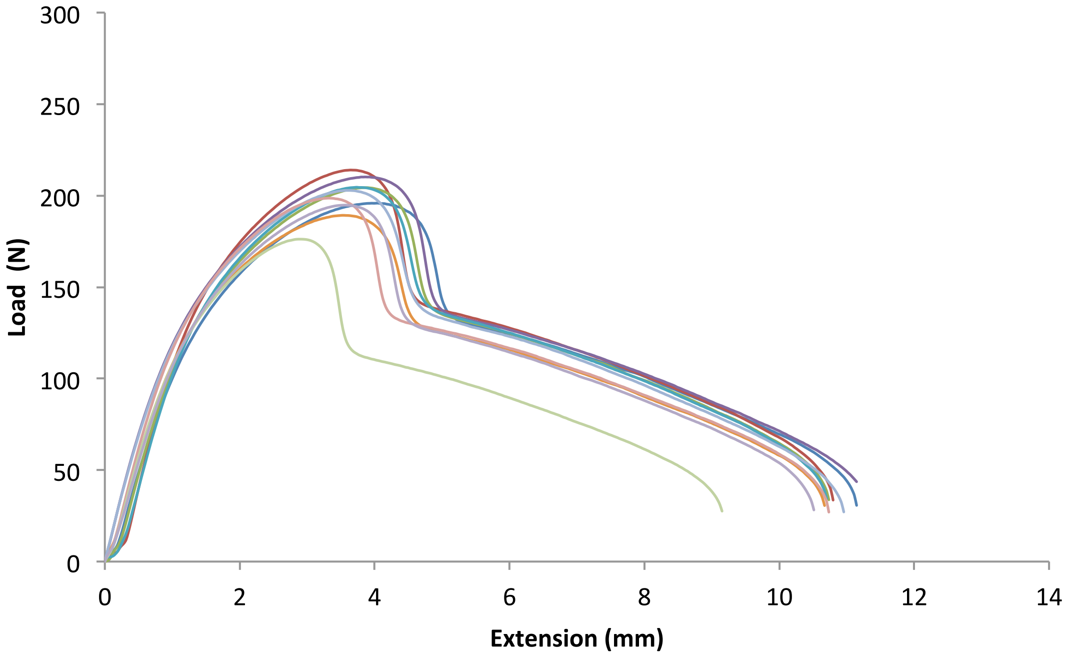

Figure 8.14 Load-extension plots generated from uni-axial tensile testing of dry non immersed PP samples after cyclic loading (1000 cycles) at 50N (n=10)

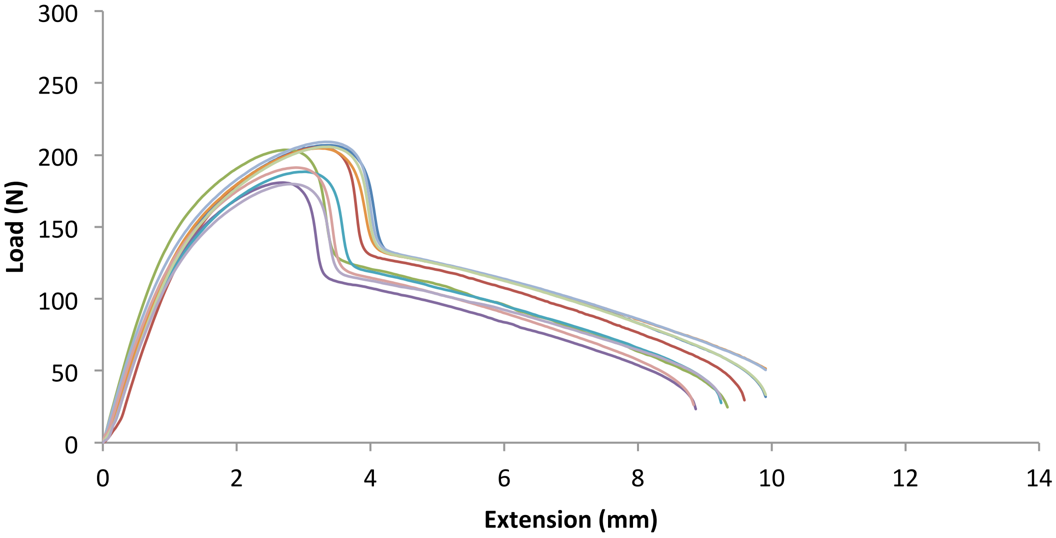

Figure 8.15 Load-extension plots generated from uni-axial tensile testing of PP samples after immersion in distilled water for 2 weeks followed by cyclic loading at 50N (1000 cycles) (n=10)

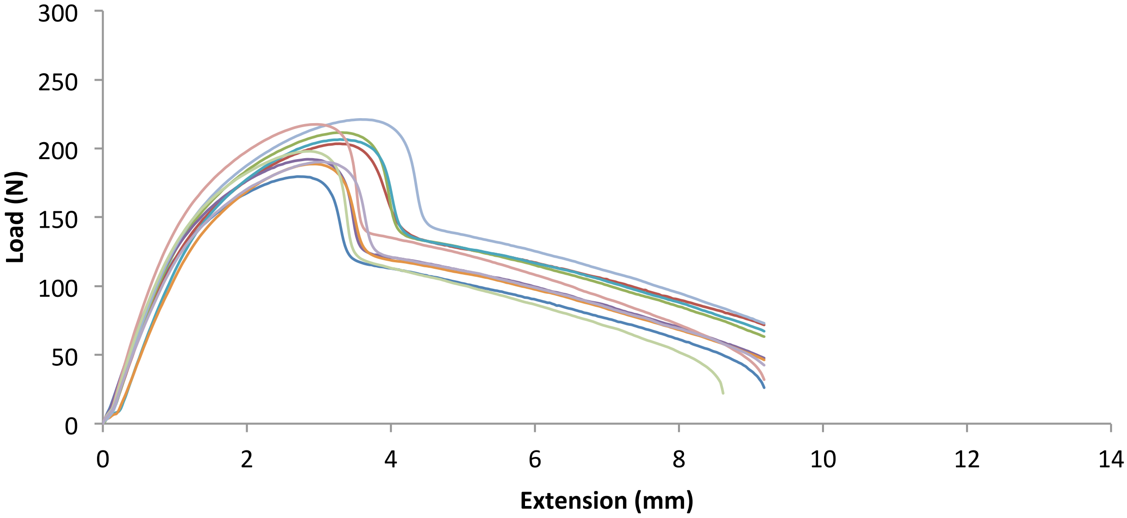

Figure 8.16 Load-extension plots generated from uni-axial tensile testing of PP samples after immersion in Retainer Brite for 2 weeks followed by cyclic loading at 50N (1000 cycles) (n=10)

8.3 Appendix III- Extension-time plots generated from creep testing of PET and PP.

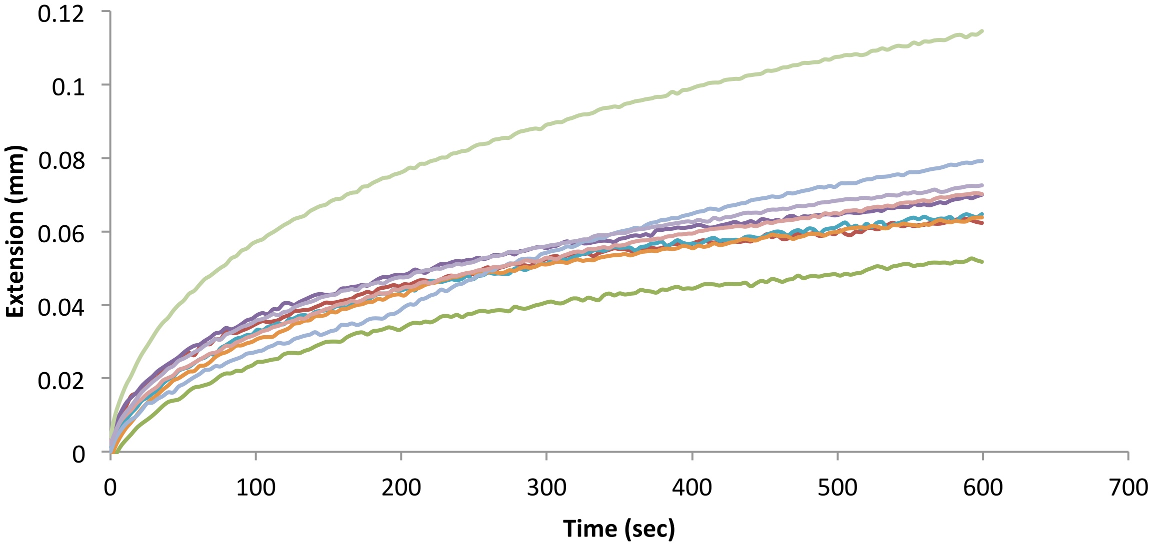

Figure 8.17 Extension-time plots generated from creep testing of PET samples following immersion in distilled water for two weeks (n=9)

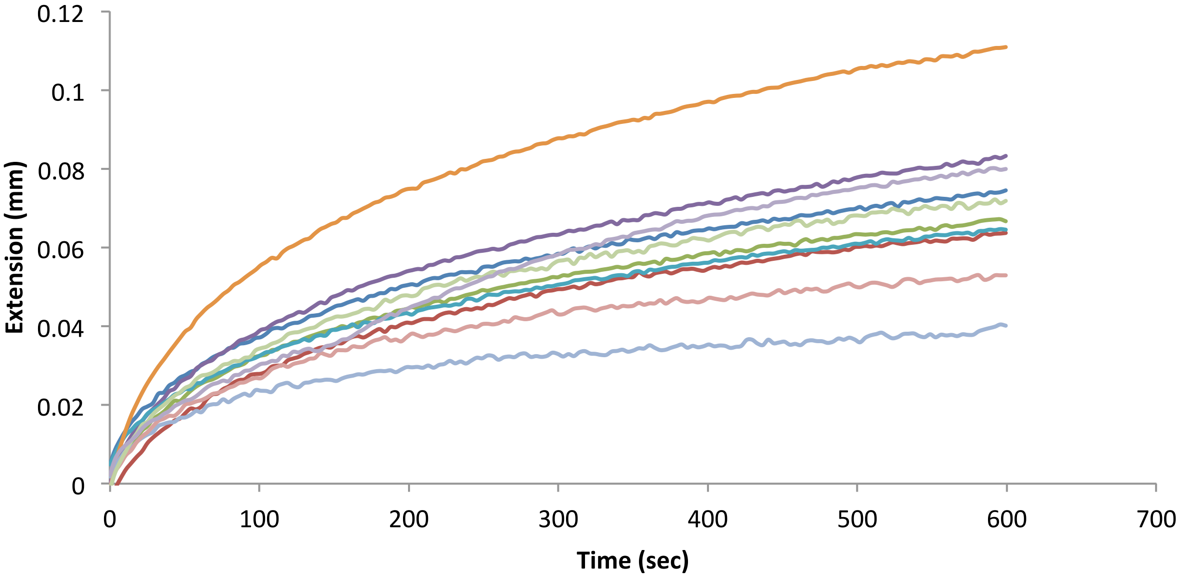

Figure 8.18 Extension-time plots generated from creep testing of PET samples following immersion in Retainer Brite for two weeks (n=10)

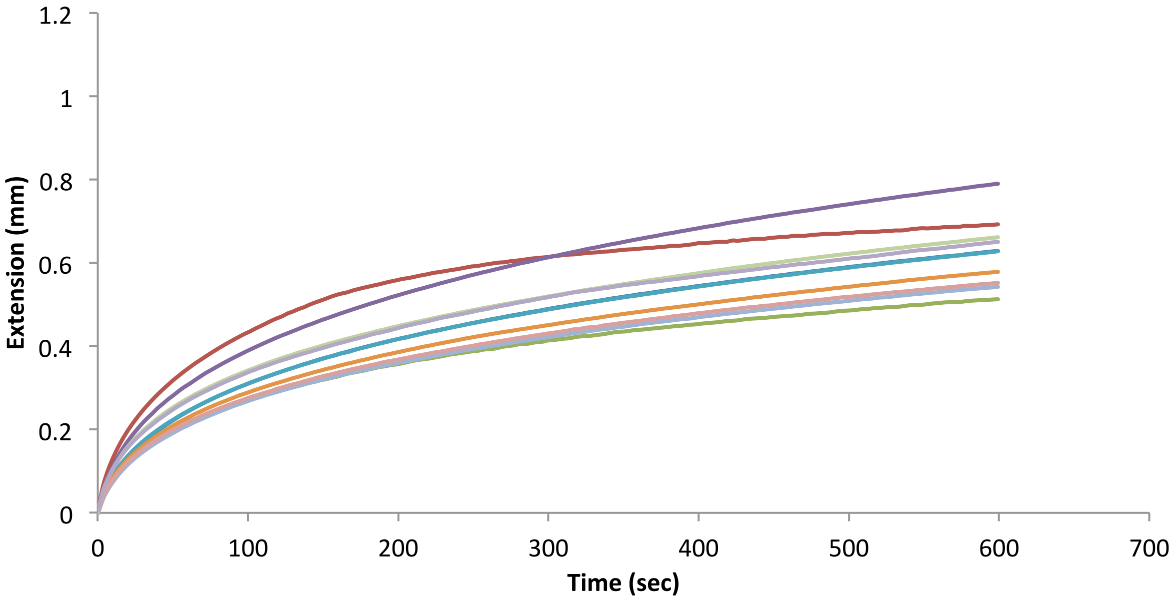

Figure 8.19 Extension-time plots generated from creep testing of PP samples following immersion in distilled water for two weeks (n=10)

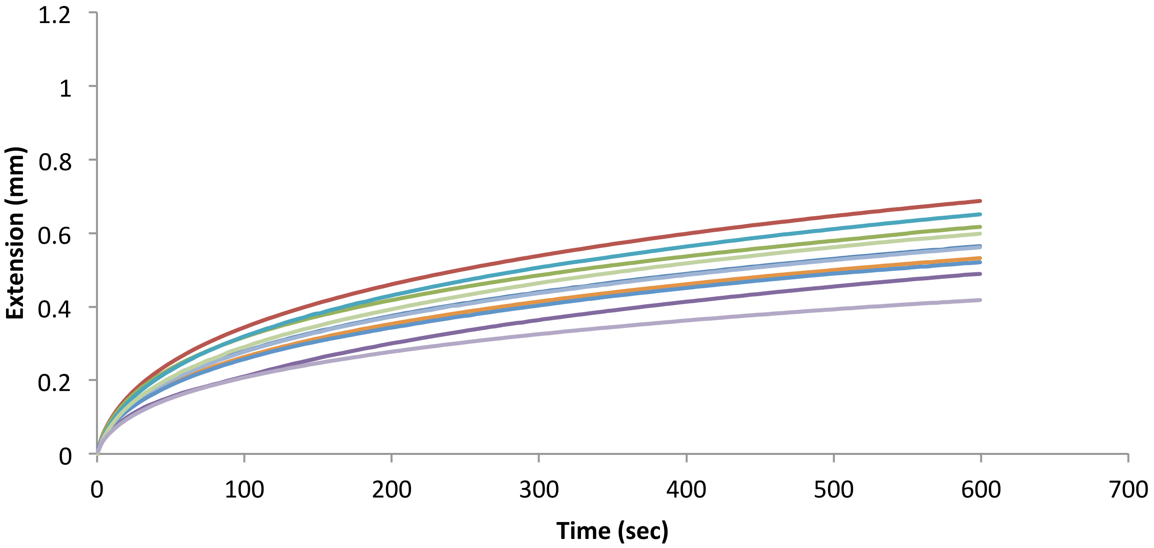

Figure 8.20 Extension-time plots generated from creep testing of PP samples following immersion in Retainer Brite for two weeks (n=10)

8.4 Appendix IV

Thermograms generated from differential scanning calorimetry of PET and PP.

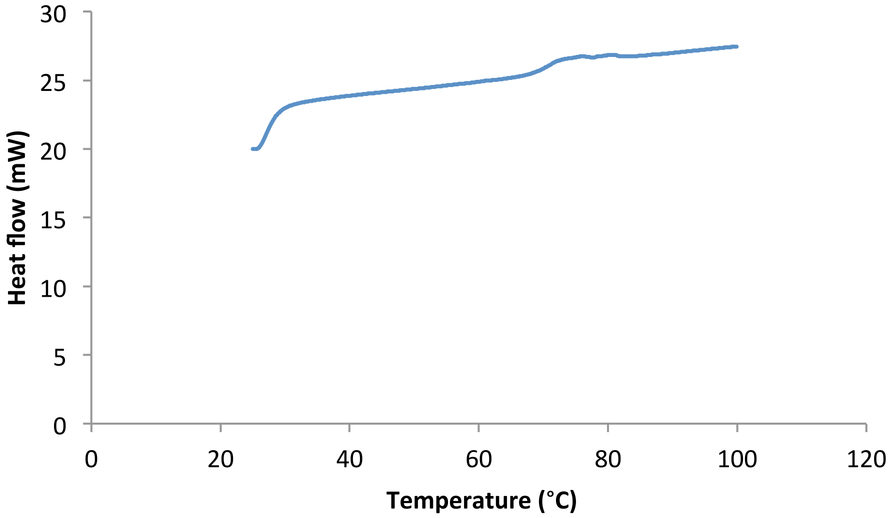

Figure 8.21 Thermogram generated from differential scanning calorimetry testing of PET sample after immersion in distilled water

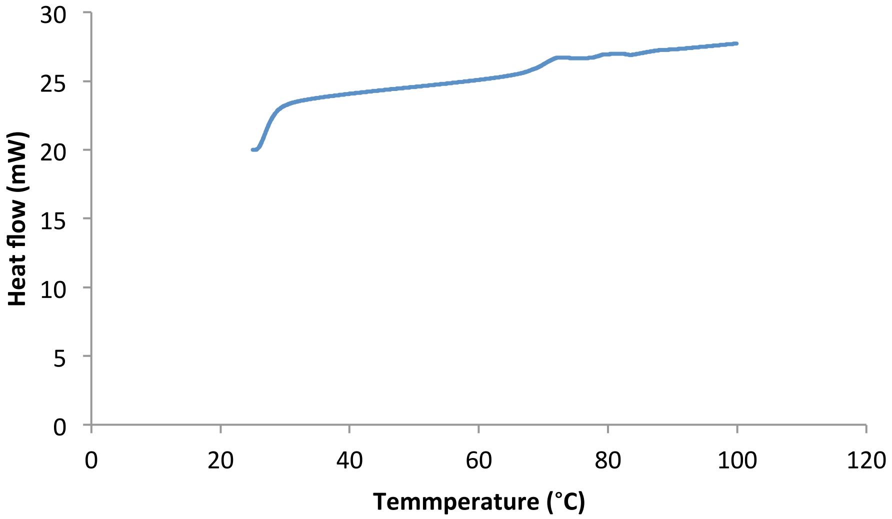

Figure 8.22 Thermogram generated from differential scanning calorimetry testing of PET sample after immersion in Retainer Brite.

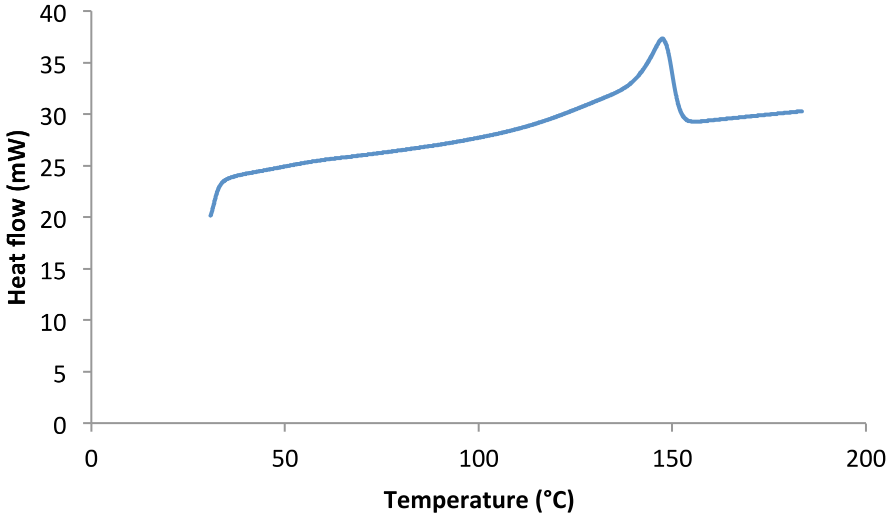

Figure 8.23 Thermogram generated from differential scanning calorimetry testing of PP sample after immersion in distilled water.

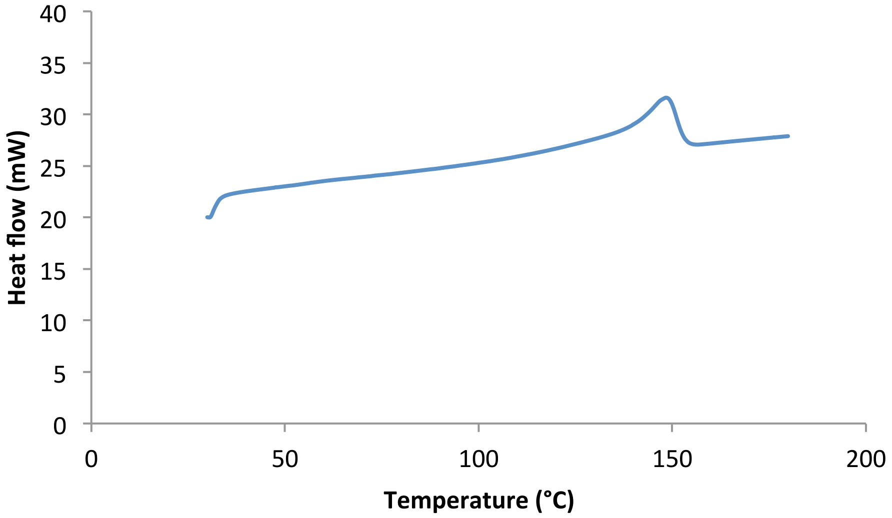

Figure 8.24 Thermogram generated from differential scanning calorimetry testing of PP sample after immersion in Retainer Brite.