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Synthesis and Characterisation of Styrene Butadiene Styrene Based Grafted Copolymers for Use in Potential Biomedical Applications

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1. Introduction

In the annals of history the evolution of the synthetic rubber industry can be traced to the early 1930s where the first emulsion polymerised styrene butadiene rubber known as Buna S was prepared by I. G. Farbenindustrie in Germany. But it was not until the US Government in 1940 established the Rubber Reserve Company, a stockpile of natural rubber and the development of a synthetic rubber program came into full fruition. However, when the United States entered World War II, the synthetic rubber plants owned by the US Government were either closed or sold to private industry between the years 1946 and 1955, and from this the development of this formidable technology began. In the early 1960's one primary objective prevailed and that was the economical polymerisation of polyisoprene with a high cis-1,4 structure, which is the synthetic version of natural rubber (Holden & Hansen, 2004). Around this time, workers at Shell investigated lithium metal initiators for isoprene polymerisation and found that alkyllithiums yielded some interesting results. In particular, there was no chain termination or chain transfer steps present. Thus, when all of the original monomer was consumed, the polymer chain still remained active and could initiate further polymerisation if more monomer, either of the same or different species, were added (Holden & Hansen, 2004). Parallel with these developments, tri-block copolymers using difunctional initiators were also reported in the literature (Szwarc et al., 1956; Szwarc, 1956). These block copolymers were produced under conditions that gave polydiene segments a relatively low 1,4 content (Holden & Hansen, 2002). However, poor elastomeric properties were acknowledged whereby the rheological properties of both polybutadiene (PB) (Gruver, 1964) and isoprene (Holden, 1965) resulted in the materials exhibiting Newtonian behaviour and the viscosities of the pure polymers approach constant values as the shear rate approaches zero. This behaviour resulted in bales of these elastomers appearing to be solid but in fact behaved as viscous liquids which hindered both their storage and commercial attractiveness. In light of this, Shell chemical research polymerised polydiene elastomers with various molecular weights to combat this problem (Holden & Hansen, 2004). Later studies included work on block copolymers resulting in the formation of a material which contained short blocks of polystyrene on either end of the elastomeric chain to form a styrene butadiene styrene (SBS), as illustrated in Figure 1. In contrast to the diene homopolymer, these block copolymers demonstrated, non-Newtonian

behaviour, high tensile strength, high elongation and rapid and almost complete recovery after elongation (Holden & Hansen, 2004; Holden, 1962)

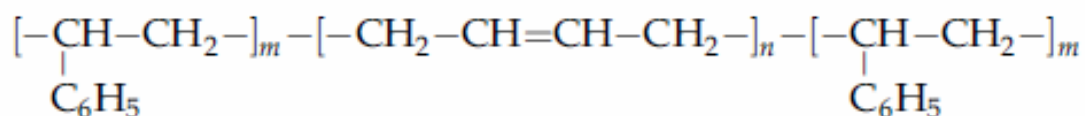


Fig. 1. Structure of a styrene-butadiene-styrene block copolymer.

Depending on the overall butadiene content, SBS block copolymers can either be used as thermoplastic elastomers (Holden & Kricheldorf, 2004) or as blend components enhancing the mechanical performance of transparent polystyrene (PS)-based plastics (Knoll & Niessner, 1998) and (Wagner, 2004). A very similar behaviour is also found for styrene-isoprene (SI) block copolymers. Due to their compatibility with PS and the wide range of possible mechanical properties, these two materials dominate the market for block copolymers in plastics even over 40 years after their discovery (Nestle et al., 2007).

2. Phase separation of SBR and SBS copolymers

One of the most important properties of a SBS structure is the phase separated system, where the two phases (polystyrene and polybutadiene) retain many of the properties of their respective homopolymers. For example, tri-block copolymers have two glass transition temperatures (T_g) which are characteristic of the respective homopolymer (Polystyrene $\sim 100^\circ\text{C}$ and Polybutadiene $\sim 90^\circ\text{C}$) whereas styrene butadiene rubber copolymers have a single intermediate T_g . Regarding the aforementioned material, experimentally a single glass transition can be found at about -65°C which is in accordance with a material with a styrene content of 23% (Van der Vegt, 2005). A graphic illustrating the glass rubbery transition of the two aforementioned copolymers is presented in Figure 2. Thus, at room temperature the polystyrene phase is strong and rigid where as the polybutadiene phase is soft and elastomeric.

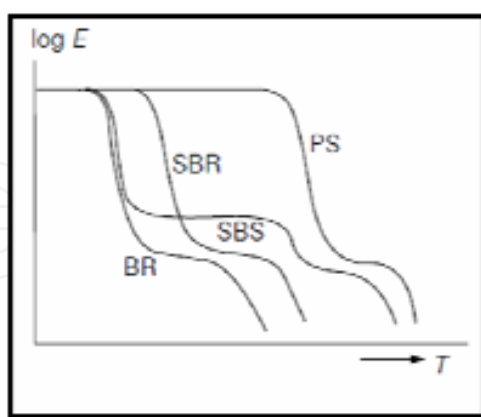


Fig. 2. The glass-rubber transitions for styrene and butadiene copolymer systems (Van der Vegt, 2005).

If the polystyrene phase is only a minor part of the total volume, it is then reasonable to postulate a phase structure as illustrated in Figure 3. From this structure, the polystyrene phase consists of separate spherical regions known as domains. Since both ends of each polybutadiene chain are terminated by polystyrene segments, these rigid domains act as

multifunctional junction points to give a crosslinked elastomer network similar in many respects to that of a conventional vulcanised rubber (Brydson, 1978). Thus, when SBS is heated, the domains soften and the network loses its strength resulting in the ability of the block copolymer to flow which is one of the main characteristics associated with these types of thermoplastic elastomers. When the heated block copolymer is cooled, the domains become hard and the original properties are regained.

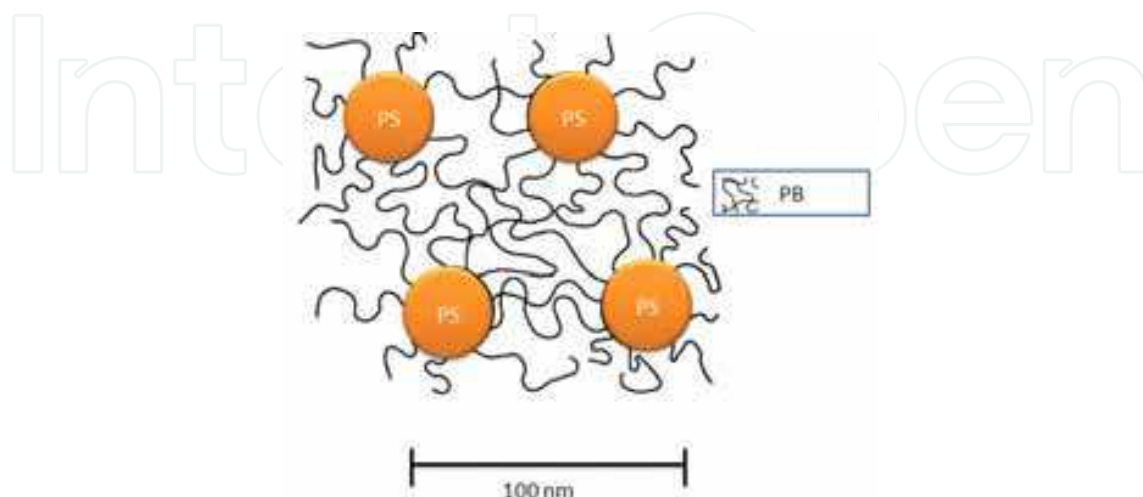


Fig. 3. Phase structure of SBS.

Therefore, when one or more blocks are capable of crystallising, additional transitions (corresponding to the T_m s of the blocks) will be observed whilst both the morphology and solution properties will be more complicated (Brydson, 1978).

3. Morphology evaluation of SBS

Three types of microphase segregation can occur within SBS systems in which one or another of the components are either in spheres, rods (cylinders) or lamellae where the morphology depends on the concentrations of styrene or butadiene used. In an ideal situation the greatest interest is in a system by which the polystyrene segments are concentrated into spherical domains. If, however, a system was produced in which one of the components exists in cylindrical or rod like domains uniformly oriented in a single direction, or the two components were arranged in lamellae, then it should be possible to obtain rubbers which demonstrate anisotropic mechanical properties (Brydson, 1978). According to Adhikari et al., (2003), when investigating the deformation behaviour of styrene butadiene star block copolymer/hPS blends, the microphase separated blends with PS particles in lamellar matrix exhibited debonding at the particle-matrix interface. Therefore, the morphology formation in block copolymers is influenced by a number of factors: these include monomer types, chemical composition and even the processing history. Burford et al., (2003) found that interpenetrating networks (IPNs) made by the polymerisation/crosslinking of styrene in the dispersed styrene rich phase of a block copolymer within a crosslinked elastomeric matrix formed networks which combined stiffness and toughness. This formation of IPNs can allow the production of materials with controlled morphologies and the greater probability of synergistic property enhancement. But the morphologies of these IPNs are generally complex because they show varying degree of phase separation, with phases varying in size, shape and definition at interfaces. Adhikari and co-workers (2004) have researched into the deformation behaviour of

styrene/butadiene block copolymers with a polystyrene content of $\sim 70\%$. They noted that the phase separation behaviour of the copolymers was found to be strongly affected by asymmetric molecular architecture. It has been demonstrated that the phase behaviour of a binary block copolymer/homopolymer mixture is primarily governed by the length of the homopolymer chains relative to the corresponding block of the block copolymer (i.e. the ratio $N_{\text{homo-A}}/N_{\text{block-A}}$, where $N_{\text{homo-A}}$ and $N_{\text{block-A}}$ represent the degree of polymerisation of added homopolymer A and corresponding block A in the block copolymer AB respectively). Thus, there is competition between microphase and macrophase separation in a binary block copolymer/homopolymer blend composition. In such blends, according to Adhikari et al.,(2004) low molecular weight homopolymer is solubilised within the corresponding block of the copolymer at low concentration. As the molecular weight of homopolymer approaches that of the corresponding molecular weight of PS or PB in the copolymer, it tends to segregate to the middle of the microdomains. However, if the molecular weight of the homopolymer is larger than that of the corresponding block of the block copolymer, macrophase separation tends to predominate.

4. Microphase separation of SBS copolymer

Microstructures occur when SBS copolymers undergo microphase separation due to the thermodynamic incompatibility of PS and PB blocks. This separation is a result of the miscibility gap of polybutadiene and polystyrene in the solid-state and is crucial for the properties of the material. Since both the chain architecture of the block copolymer and the microphase separation affect the mobility of the butadiene-rich phase (Nestle et al., 2007). These elements, rich in one block, take the form of either spherical, cylindrical or lamellar domains (as previously discussed) dispersed in a continuous matrix of the other component. The phase-separated structure for SBS contains two homogeneous, nearly pure phases and a third diffuse interphase (Spaans et al., 1999). A schematic of these phases is illustrated in Figure 4.

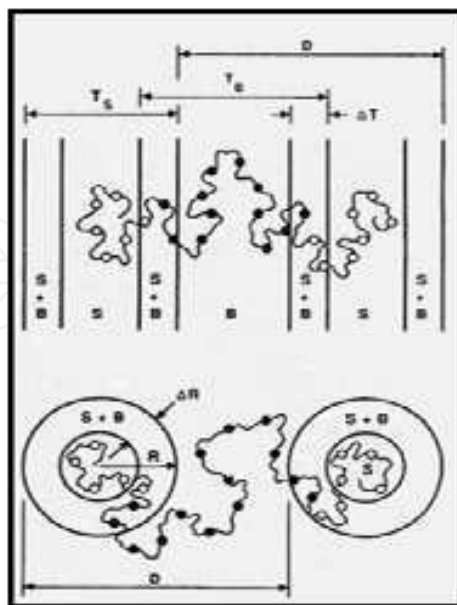


Fig. 4. Schematic representation of SBS molecule embedded in a phase separated microstructure consisting of matrix B, core S and a broad interphase of mixed S and B. S represents styrene and B represents butadiene (Spaans et al., 1999).

Spaans et al., (1999) has correlated this information with a typical DSC thermograph of SBS to represent the locations of these microphase domains. A graphical representation illustrating Spaans concept is shown in Figure 5.

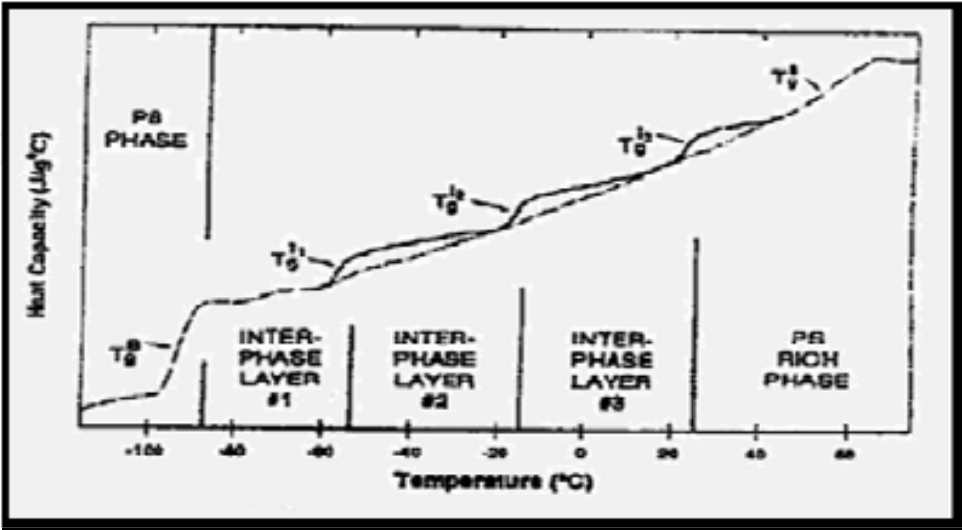


Fig. 5. A graphical representation of a DSC thermograph illustrating the Tg changes in the local heat capacity at a sequence of positions through the interfacial region, as the sample experiences a broad temperature range (Spaans et al., 1999).

5. Thermal properties of a SBS copolymer

Based on experimental data carried out by the authors, a linear tri-block SBS with 69% butadiene content under the trade name Kraton D1101 (see Table 1) was investigated. As presented in Figure 6, a Tg value at -92°C was located in the butadiene rich microphase domain which coincides with the Tg (-90°C) of pure PB and this result is in agreement with the findings of Spaans et al.,(1999) and Kennedy et al., (2009). The glass transition of the PS domain in SBS copolymer can be detected at around 67°C which corresponds with the findings of Spaans et al.,(1999) , Kennedy et al., (2009) and Mohammady et al.,(2005). This value was significantly lower than the Tg at 100°C for a PS homopolymer of comparable molecular weight.

Butadiene/styrene ratio (wt%)		69/31
Total molecular weight		102,000g/ mol
Microstructure of PB		
1,4-trans (%)		42
1,4-cis (%)		49
1,2 (%)		9

Table 1. Physical properties of Kraton D1101

The glass transition for the PS phase in thermoplastic elastomer block copolymer tends to be lower than that of pure homopolymer of the same chemical structure which is due to the

entrapment of some centre block rubbery segments, a kinetic effect which is not thermodynamically favoured (Spaans & Williams, 1995; Escobar et al., 2003). This lowering effect is a consequence of premature molecular motions in the PS domain induced by PB segmental mobility. Munteanu and Vasile (2005) have stated that copolymers with microphase separated morphology can be considered as finite confined systems. This confinement applied by the PB matrix to the PS discrete phase may decrease the T_g of PS in SBS. According to Muhammady *et al.*, (2001) the interfacial interaction and miscible fraction at the domain boundaries also lowers the value of the glass transition. Between T_g values of PB and PS a broad continuous curvature is evident on the DSC thermograph shown in Figure 6. This curvature should be found in all block copolymers which have homogeneous microphases present, as stated by Spaans *et al.*, (1999). At 241°C a thermal transition occurs for SBS block copolymer which is believed to be a first order phase transition and corresponds to findings in literature (Spaans et al., 1999; Kennedy et al., 2009). At this transition the polymer merges into segmental homogeneity resulting in a disorganised/homogeneous state. It has been well established that when block copolymers such as SBS are heated above the upper glass transition temperature, the microstructure of the polymer will be eventually destroyed and the block copolymer will form a homogenous phase. The critical temperature at which this occurs is called an order-disorder transition (ODT) temperature (Spaans et al., 1999; Kennedy et al., 2009; Spaans & Williams, 1995).

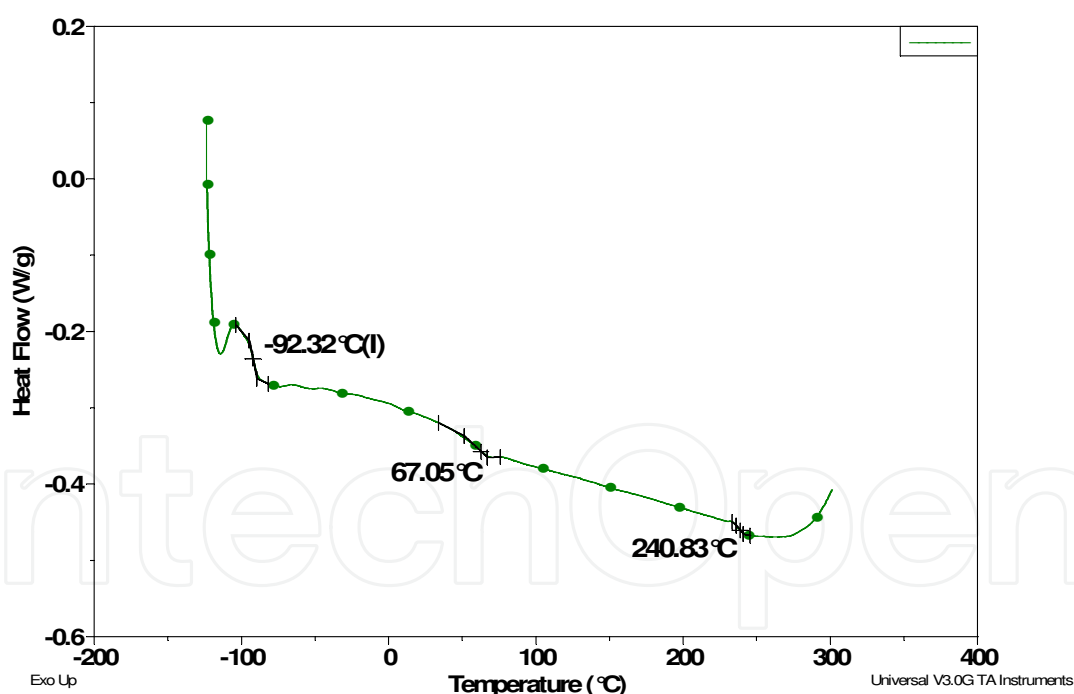


Fig. 6. A DSC thermograph of a SBS copolymer (Kraton D1101), where the T_g values for PB and PS are -92°C and 67°C respectively. The separation temperature, T_s is 241°C.

6. A review of Styrenic graft copolymerisation

Huang and Sundberg (1995a, 1995b, 1995c, 1995d), have published a number of studies on the graft copolymerisation of styrene, benzyl acrylate and benzyl methacrylate onto a cis-

polybutadiene. In their kinetic study, they have shown by the use of different initiators two possible mechanisms occurred where initiators such as benzoyl peroxide (BPO) can abstract allylic hydrogen atoms from polybutadiene while azobisisobutyronitrile (AIBN) cannot extract the allylic hydrogen atom. According to Jiang and Wilkie (1998) neither initiator appears to have significant reactivity towards addition of primary radicals to the double bond of the polybutadiene and the allylic radicals which are generated by hydrogen abstraction can initiate polymerisation of reactive monomers such as styrene and methacrylates leading to the formation of graft copolymers. Graft copolymerisation will still occur for monomers which are initiated by the allylic backbone radicals. This process occurs by addition of the growing polymeric radical to the polybutadiene double bond, producing a saturated alkyl radical which is capable of further initiation of low reactivity monomers. De Sarkar et al.,(1999) found that 1,2 -vinyl double bonds of butadiene occur in a pendant position along the polymer chain making bonds more accessible for grafting. They also postulated that the order of reactivity for vinyl groups are, (i) saturation of 1,2-vinyl bonds is easier than 1,4-trans and (ii) PB is directly proportional to the amount of 1,2-vinyl bonds (De Sarkar et al., 1999). The various structural sequences associated with butadiene are illustrated in Figure 7.

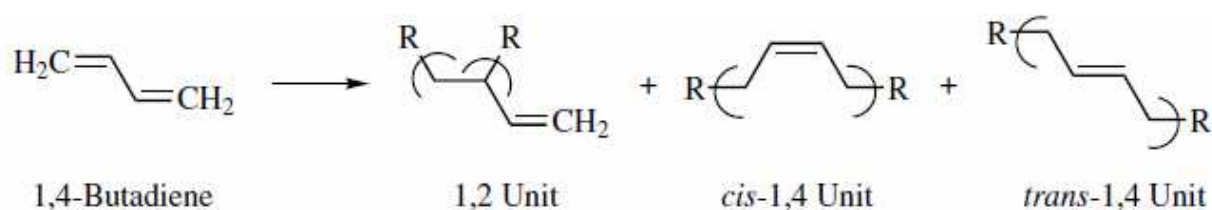


Fig. 7. Various structural formations associated with butadiene.

In the research performed by Madhusudhan and Raghunath (1999), maleic anhydride (MAH) was grafted onto ABS by the addition to the double bond initiated by BPO. Sheng and co-workers (1990) found that BPO initiated the removal of an allylic hydrogen atom while AIBN acted upon the addition of the double bond of SBR which is in agreement with the findings of Huang and Sundberg(1995a, 1995b, 1995c, 1995d). Mrrov and Velichksva (1993) described how MAH was grafted onto SIS only by the removal of an allylic hydrogen atom, whereas Zhang and Li (2003) have investigated the grafting mechanism of SBS with MAH using BPO and AIBN. They found that the variation of C=C content in SBS-g-MAH was used to verify the different graft mechanisms of BPO and AIBN. They concluded that the grafting reaction occurs by the addition onto C=C bond when AIBN was used, while the removal of an allylic hydrogen atom was evident when BPO was used to initiate the reaction.

7. Grafted copolymers with potential medical application

The latest wave of biomedical materials can strengthen the capabilities of many of today's medical products. Some polymeric materials demonstrate properties such as lubricity, biocompatibility and antimicrobial action on device surfaces while others may crack, tear, slip and flake off medical devices due to inherent design flaws. There has been considerable

interest and activity in the application of synthetic polymers in medicine, particularly for surgical and dental implants. The most critical property of a polymeric material is that it has acceptable tissue compatibility. If this criterion is not met, local tissue irritation may result. In general, the chemical structure, electric charge, hydrophilicity and hydrophobicity, surface roughness, micro-heterogeneity, and flexibility of the materials affect the performance of cells and tissues on the materials (Minoura, 1993; Yang & Tsai, 2010). Biocompatibility can be characterised by a whole series of negatives, for example that the material was non-toxic, non-irritant, non-thrombogenic, non-carcinogenic and so on. Such a state of compatibility was most likely to be achieved by a material being inert and unrecognisable by the tissue. A desirable property of a synthetic polymeric material used in biomedical applications is that it has acceptable tissue compatibility. If this criterion is not met, local tissue irritation may result. One particular method used to obtain these desired properties is grafting hydrophilic compounds namely a hydrogel onto hydrophobic backbones. Hydrogels have physical properties similar to those of human tissue and possess excellent tissue compatibility and are used as biomedical materials. The main disadvantages of hydrogels are their poor mechanical properties after swelling. To overcome this problem, Yang & Hsiue (1996) grafted hydroxyethyl methacrylate (HEMA) onto SBS via UV radiation. The mechanical properties of SBS-g-HEMA were found to be superior to those of poly(HEMA) and were identical to those of SBS. From their measurements, the contact angle and blood clotting time, the wetting and non-thrombogenic properties of SBS-g-HEMA were better than those of SBS. Yang *et al.*, (1997) have also researched into the graft copolymerisation of dimethyl amino ethyl methacrylate (DMAEMA) with SBS and it was found that the degree of grafting was related to the irradiation time, DMAEMA concentration and temperature, but the adsorption of albumin and fibrinogen decreased with an increase in the amount of grafting. They continued on their work by the substitution of amino groups on the SBS-g-DMAEMA graft copolymer membrane which was treated with heparin to prepare the heparin containing SBS-g-DMAEMA (SBS-g-DMAEMA-HEP). It was found that, with increased grafting and heparin content, the surface tension and the water content of the SBS-g-DMAEMA membrane increased whereas the contact angle decreased (Yang *et al.*, 1998). Over the past few years, N-isopropylacrylamide (NIPAAm) has appeared in the literature with increasing frequency (Durne *et al.*, 2005; Zhang *et al.*, 2005; Geever *et al.*, 2008; Geever *et al.*, 2007; Geever *et al.*, 2006; Kennedy *et al.*, 2009). Lee and Chen (2001) have grafted N-isopropylacrylamide (NIPAAm) onto SBS via solution polymerisation using benzoyl peroxide as the initiator. This was carried out to improve the water absorption and thermo sensitivity of SBS. Thus, a biomedical material often needs to function dependably without significantly altering the physical or mechanical properties of the substrate. Kennedy *et al.*, (2009, 2010) have successfully grafted SBS with acrylic acid (AA) and SBS with N-isopropylacrylamide (NIPAAm) respectively via UV polymerisation techniques for use as a potential biomedical material and in doing so; they proved that the glass transition values for each of the grafted copolymers increased in the butadiene domain, thus proving that grafting had occurred.

8. Synthesis of graft copolymers of SBS via UV polymerisation

UV polymerisation has become a well established technology which has found a large number of industrial applications due to the relative ease in which the reaction occurs. In

general, a liquid resin containing a photoinitiator (Benzophenone (BP)), is transformed into a solid polymer simply by exposure to UV light (Xiang et al., 2001; Murata et al., 2004; Rohr et al., 2003; Kim et al., 2002). In order to ascertain a possible reaction site of the base polymer, Mateo et al.,(2000) investigated the photoreactions of model compounds of SBS structures 1-heptene, 3-heptenes and cumene. They concluded that the main photoreaction induced by BP in heptene derivatives, models of the cis, trans and vinyl-double bonds of the polybutadiene sequences, is the abstraction of an allylic hydrogen atom by the BP, and that, in minor extension of other hydrogen atoms of the heptene aliphatic chain. In developing grafted systems it was considered by the authors that the allylic hydrogen associated with butadiene in SBS copolymers reacted with the hydrogel monomers using benzophenone via UV polymerisation, as illustrated in Figures 7 and 8 respectively.

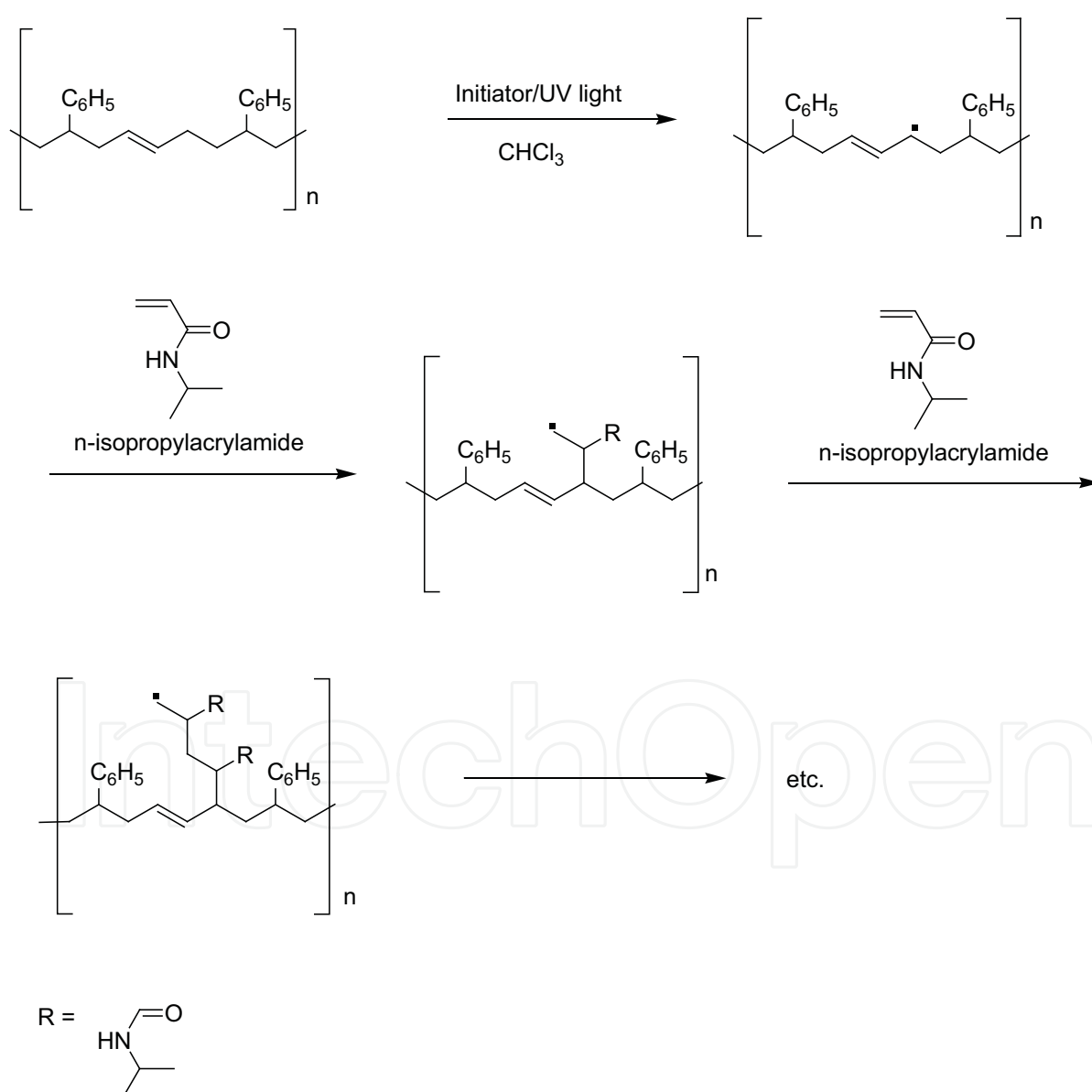


Fig. 7. A scheme showing the reaction of SBS and NIPAAm to yield SBS-g-NIPAAm copolymers (Kennedy et al.,2010).

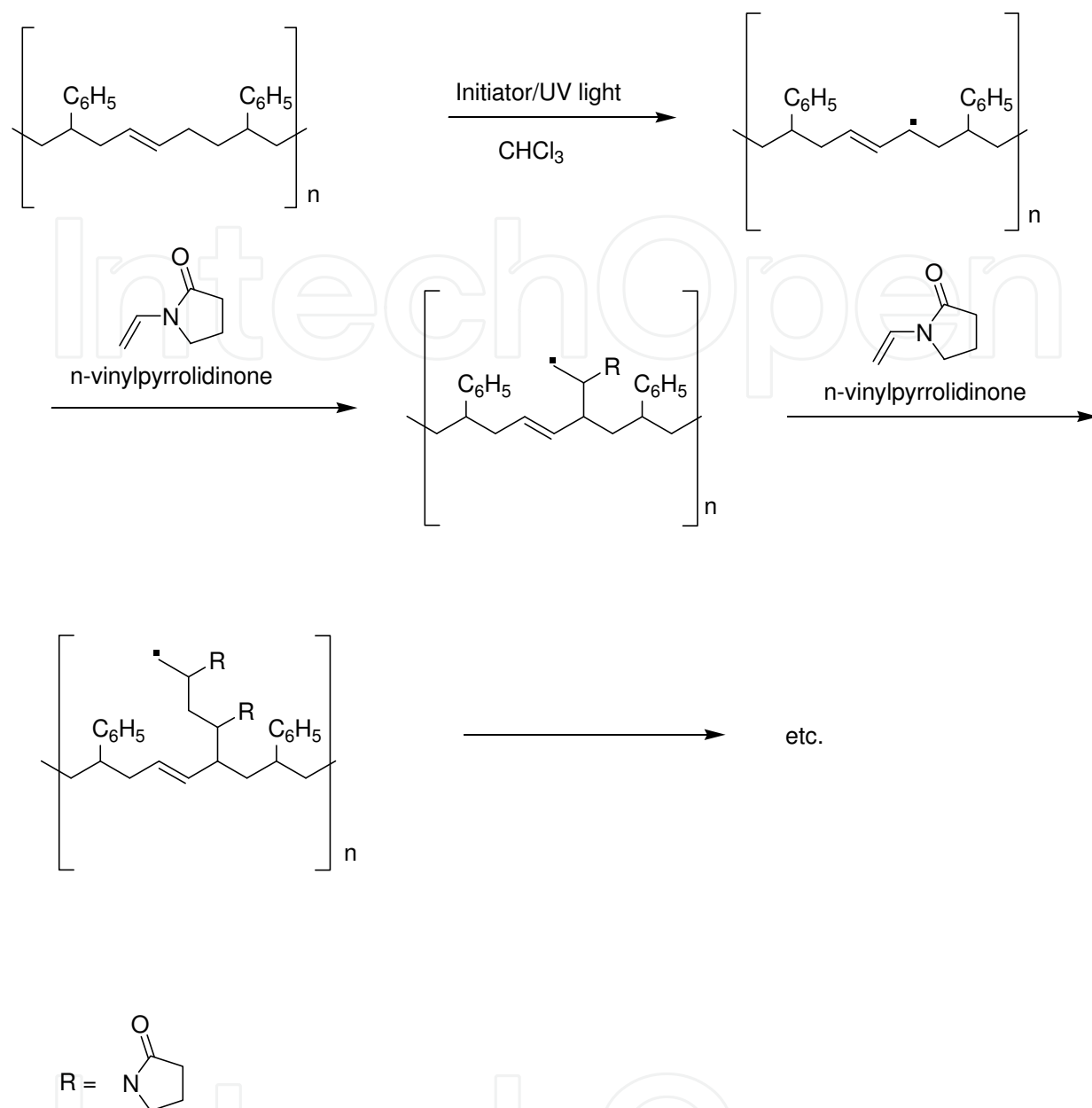


Fig. 8. A proposed scheme illustrating the reaction of SBS and NVP to yield SBS-g-NVP copolymers using Benzophenone as the initiator (Kennedy & Higginbotham, 2010)

9. Thermal-mechanical analysis of the grafted SBS copolymers

To appreciate the importance of these materials for biomedical use, one needs to understand the thermal properties associated with the grafted copolymers. From experimental data (Kennedy et al., 2010) the authors present DSC thermographs showing several concentrations of SBS-g-NIPAAm copolymers (Figure 9). As depicted by the DSC thermographs, exothermic variability existed in the temperature region between 50 and 200°C for each of the grafted copolymers. This variability was the result of both the breakdown of crosslink's which were formed within the SBS copolymer during UV polymerisation and the polymerisation of the monomers to form homopolymers. It was

found, by exposing SBS to concentrated UV light, crosslinking takes place which has an effect on the flexibility of the material. When analysing the butadiene domain, all of the grafted samples have a broad thermal transition when compared to the PB domain of SBS. According to Rohr et al.,(2003) graft copolymerisation can also occur between the homopolymers, thus creating branched or crosslinked architectures. However, within the PB domains, the grafted copolymers that contained higher concentrations (3, 3.5 and 4 mL) of monomer followed the same thermal profile as that of SBS. This behaviour suggests that the pure monomer reacted more readily with itself forming a homopolymer, thus reducing the amount of grafting taking place, thus, increasing the variability within the system. The grafted copolymers which contain monomer concentrations below 2.5mL have broader DSC thermographs within the butadiene rich domain resulting in T_g values of the grafted samples being shifted up wards in the sub ambient domain, suggesting that grafting had occurred within this region, which coincides with the reaction sequences as presented in Figure 7. Similar observations were also found when SBS was grafted onto NVP via DSC analysis.

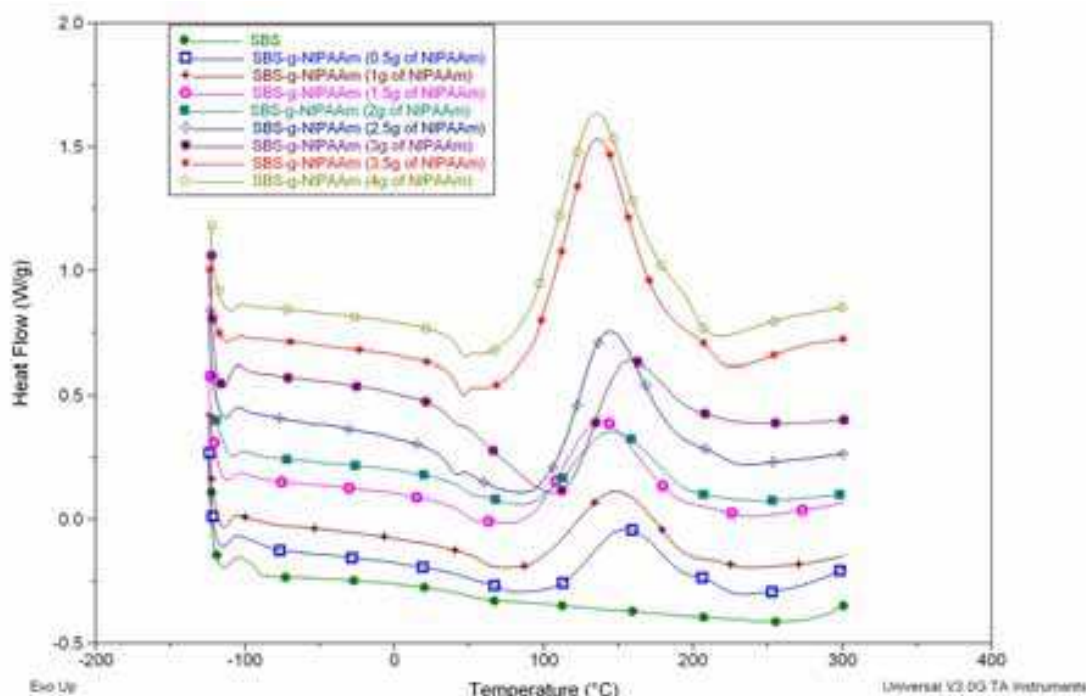


Fig. 9. DSC thermographs of SBS-g-NIPAAm resulting from the reaction of SBS and various concentrations (0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0 g) of NIPAAm.

From DSC analysis it can be speculated that grafting took place for each of the samples tested. However, to further verify the presence of grafting, Dynamic Mechanical Thermal Analysis (DMTA) studies can be utilised (Kennedy et al., 2010). In each of the loss tangent thermograms, illustrated in Figure 10, the peak height of the $\tan \delta$ value corresponds to the glass transition (T_g) of the samples being tested. From thermogram shown in Figure 10, a $\tan \delta$ value for SBS can be detected at -92°C which is associated with the polybutadiene segment. However, there was an increase in $\tan \delta$ from -92°C to -79°C for non-washed SBS-g-NIPAAm copolymer, indicated that grafting had occurred. This reduction in the $\tan \delta$ is an indication that the backbone of the SBS copolymer has lost some of its flexibility, due to

the grafting of a hydrogel to its backbone. To back up this claim, the samples were washed in chloroform under soxhlet extraction for eight days and the $\tan \delta$ value shifted to -74°C . Therefore, it is evident that the $\tan \delta$ values for each of the samples tested increased, establishing that grafting had occurred onto various butadiene segments along the SBS backbone. Thus, suggesting that grafting will increase the T_g of the PB phase by increasing the thermal energy required to free polymer molecules from additional constraints.

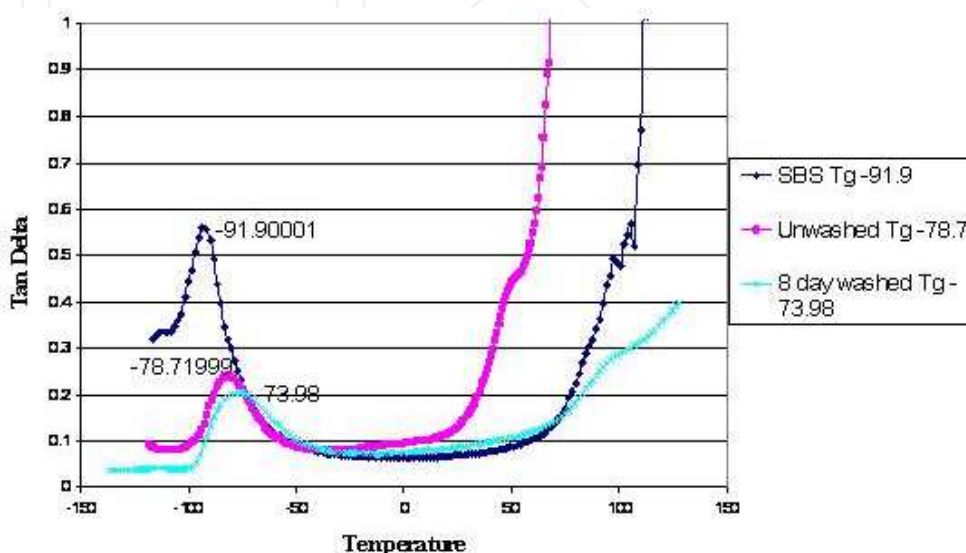


Fig. 10. DMTA spectra representing SBS, non-washed SBS-g-NIPAAm and washed SBS-g-NIPAAm samples after 8 days.

10. Spectral analysis of the grafted SBS copolymers

Infrared spectroscopy has been a valuable technique for materials analysis in the laboratory for over seventy years. An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. With modern software algorithms, infrared is an excellent tool for quantitative analysis. The technique of Attenuated Total Reflectance (ATR) has in recent years revolutionised solid and liquid sample analyses because it combats the most challenging aspects of infrared analyses, namely sample preparation and spectral reproducibility. Within the context of this work Fourier transform infrared spectroscopy was carried out using the Attenuated Total Reflectance (ATR-FTIR) technique as this generated the best results for the study. ATR-FTIR spectroscopy was carried out on SBS, NIPAAm and SBS-g-NIPAAm copolymers as shown in Figure 11. The main bands for characterising the butadiene segment within SBS (Figure 11 (a)) are CH_2 scissoring at 1449 cm^{-1} , trans-1,4 $\text{C}=\text{C}$ out of phase deformation at 964 cm^{-1} , $=\text{CH}$ stretching at 3005 cm^{-1} and C-H stretching at 2916 and 2844 cm^{-1} . Regarding the PS segments, styrene absorption occurs at 697 cm^{-1} , C-H out of plane deformation occurs at 3060 cm^{-1} and at 1601 cm^{-1} aromatic C-C stretching occurs (Munteanu & Vasile, 2005; Romero-Sanchez et al., 2005a; Romero-Sanchez

et al., 2005b). The ATR-FTIR spectrum for NIPAAm shown in Figure 11(b) illustrates bands corresponding to C=O stretching and NH bending for secondary amides at 1655cm^{-1} and 1544cm^{-1} . These bands are present as small shoulders in SBS-g-NIPAAm copolymer shown in Figure 11 (c). The peak at 1545 cm^{-1} for NIPAAm and SBS-g-NIPAAm copolymer was assigned as a symmetric deformation of NH_3^+ . These results correspond to the finding of Erbil et al., (2004) and Ju et al.,(2002). However, the peaks present at 1617 cm^{-1} (C=C) and 1407 cm^{-1} (CH₂=) in the NIPAAm spectrum disappeared for SBS-g-NIPAAm copolymer as illustrated in Figure 11(b). This suggests that NIPAAm had grafted to SBS resulting in the loss of the double bond associated with the monomer.

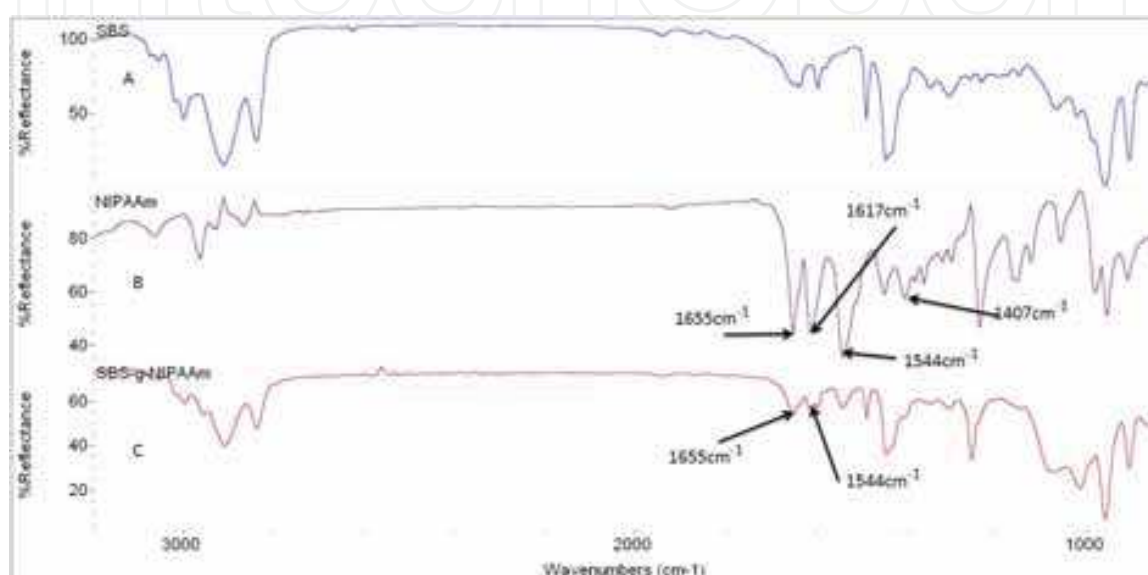


Fig. 11. Comparisons between the different ATR-FTIR spectrums where (a) is SBS (b) is NIPAAm and (c) is SBS-g-NIPAAm.

ATR-FTIR spectral analysis was used in conjunction with the DSC thermographs to analyse SBS-g-NVP copolymers. For illustrative purposes spectra containing non grafted NVP which polymerised to poly *N*-vinyl-2-pyrrolidinone (PVP), SBS-g-NVP using 2.5 g of NVP and SBS are shown in Figure 12. In the case of the PVP spectrum, Figure 12 (a), a broad C=O stretching band was found at 1650 cm^{-1} which corresponds to results obtained by Devine & Higginbotham (2003). Certain authors have found an absorption band for PVP at 1660cm^{-1} and this is called amide I. This band is a combined mode with contributions of C=O and C-N stretching (Muta et al., 2002; Cheryl & Youngli, 2002). ATR-FTIR spectrum for the grafted sample depicted in Figure 12 (c) exhibited a peak at approximately 1664 cm^{-1} , corresponding to the carbonyl group of PVP, which indicates monomeric growth of the grafted side chain. Szaraz et al.,(2000) has found that for pure liquid NVP two very strong bands occur in the IR spectrum. The band at 1629 cm^{-1} , is a carbon-carbon double bond, corresponding to olefinic C=C stretching which is usually found in the region of $1680\text{-}1630\text{ cm}^{-1}$. The band at 1706 cm^{-1} is due to carbonyl stretching between $1750\text{-}1700\text{ cm}^{-1}$. However, as shown in the ATR-FTIR spectrum for grafted SBS-g-NVP copolymer, a small shoulder formed at 1714 cm^{-1} indicating that carbonyl stretching had occurred. This band is associated with un-reacted NVP as outlined by Szaraz et al., (2000) suggesting that NVP is still present within the grafted matrix, and so there is need to wash the samples after they have been fully synthesised.

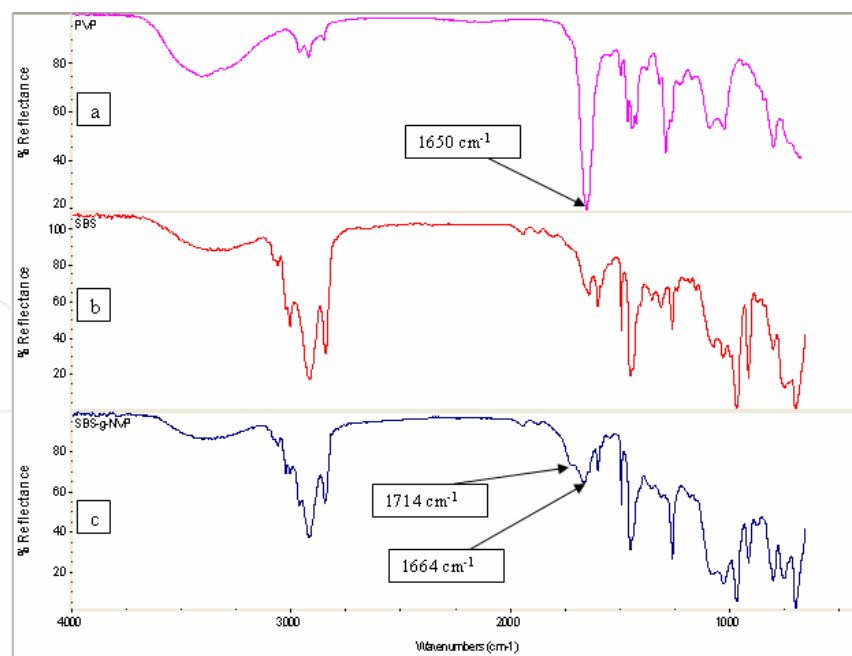


Fig. 12. Comparisons between the different ATR-FTIR spectra where (a) is PVP, (b) is SBS and (c) is SBS-g-NVP. (Kennedy & Higginbotham, 2010)

11. Topography of SBS and the grafted SBS coatings

Improved compatibility is a desired feature for biomedical product such as a coating which comes in contact with blood during clinical use. The response of blood to a foreign material can be aggressive, resulting in surface-induced thrombus (clot) formation, which can impair or disable the function of the coating and most importantly threaten a patient's health. In light of the biomedical potential of SBS based copolymers it is important to have a firm understanding of the materials surface properties. In order to minimise interfacial problems between the host tissues and the fluids, a biomedical material must exhibit a specific surface chemical behaviour (Yang & Tsai, 2010; Adamson, 1990; Andrade, 1985). All synthetic materials used in blood-contacting medical coatings promote surface-induced thrombotic phenomena to various extents. These events are initiated by non-specific protein adsorption followed by platelet adhesion, activation and aggregation on the biomaterial surface. The resulting thrombus can impair the function of the implanted devices, while thromboembolic events can occlude blood vessels leading to serious cardiovascular complications. Hence, non-thrombogenicity is a highly desired surface property for blood-contacting biomaterials. Thus, surface roughness is of significant interest in biomedical coatings because it is an important property which influences friction as well as wettability when in contact with a biological environment.

11.1 White light profilometry

One method of determining surface values of a material is to employ a technique known as White light profilometry which scans a surface using white light, thus providing surface structural analysis without using physical contact. The surfaces are characterised using amplitude parameters such as average surface roughness (R_a) or root mean square (RMS) roughness which can be summarised by a single "average roughness" value which is a close approximation of the arithmetic average roughness-height, calculated from the profile chart

of the surface. The Ra value is the average deviation of all points, calculated using equation 1, from a plane fit of the test surface. A graphic representation showing how Ra is conceived is illustrated in Figure 13.

$$R_a = \frac{1}{L} \int_0^L z(x) dx \quad (1)$$

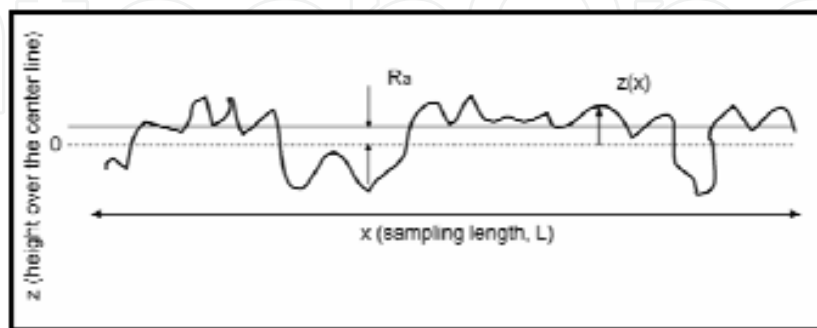


Fig. 13. Illustration of the average roughness, Ra, where $z(x)$ is the surface height in point x relative to a mean line and L is the overall length of the profile under examination.

The standard deviation of the profile heights, RMS, is a parameter calculated by the average of the square roots of all of the Ra values. This parameter is the most widely used and its numerical value is about 11% higher than the Ra value. This parameter is calculated using equation 2.

$$RMS = \sqrt{\frac{1}{L} \int_0^L z(x)^2 dx} \quad (2)$$

The height of a selected material can be evaluated using Peak to Valley (PV) value which is the distance between the highest and lowest points within the sample. A graphical representation of how a PV value is determined is illustrated in Figure 14.

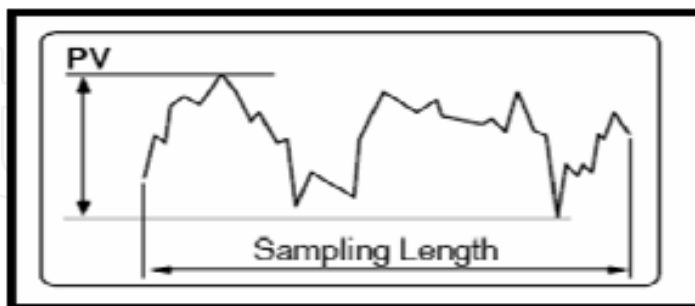


Fig. 14. Illustration of the peak to valley height (PV).

Kennedy et al.,(2010) used this technique to evaluate the roughness and height of SBS-g-NIPAAm grafted copolymers. As illustrated in Figure 15, the root mean square (RMS), as well as Peak to Valley (PV) values were $0.128\mu\text{m}$ and $1.651\mu\text{m}$ respectively for the SBS copolymer. However, when these values were compared to a SBS-g-NIPAAm and SBS-g-NVP copolymers as shown in Figures 16 and 17 respectively, the RMS parameter ($1.125\mu\text{m}$ for SBS-g-NIPAAm and $0.859\mu\text{m}$ for SBS-g-NVP) and the PV value ($13.878\mu\text{m}$ for SBS-g-

NIPAAm and 6.896 μm for SBS-g-NVP) were greater than that of SBS. It was found that the PV of each of the grafted copolymers tested was influenced by monomeric concentrations and the amount of chloroform (used to dissolve SBS) still present in the sample after UV polymerisation. This is an important property characteristic which directly affects the non-thrombogenic properties of the material within a specific biological environment i.e. the smoother the surface, the less likely that thrombosis will occur. However, this roughness may aid in the muco-adhesion properties of the material which is advantageous in biological environments such as arteries.

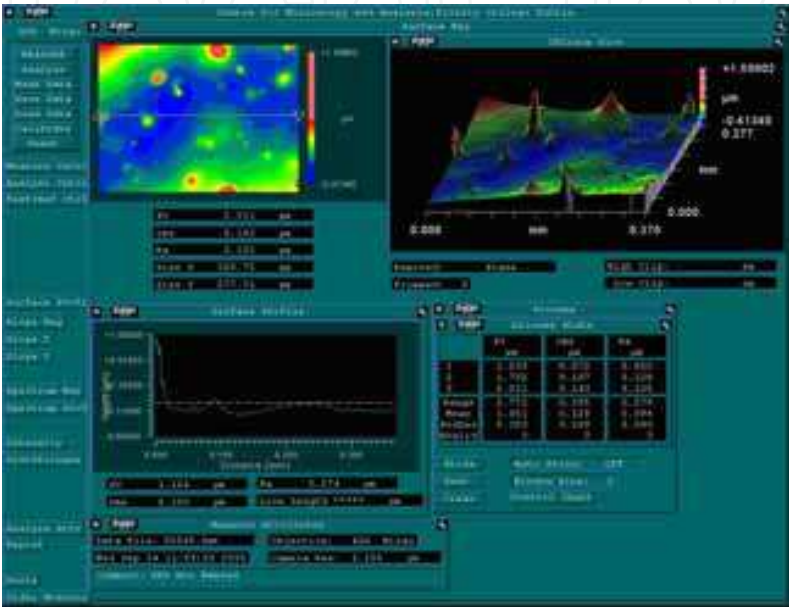


Fig. 15. A white light profilometry scan for a SBS copolymer illustrating 2D and 3D surface profiles as well as the PV value, 1.651 μm and the RMS parameter, 0.128 μm .

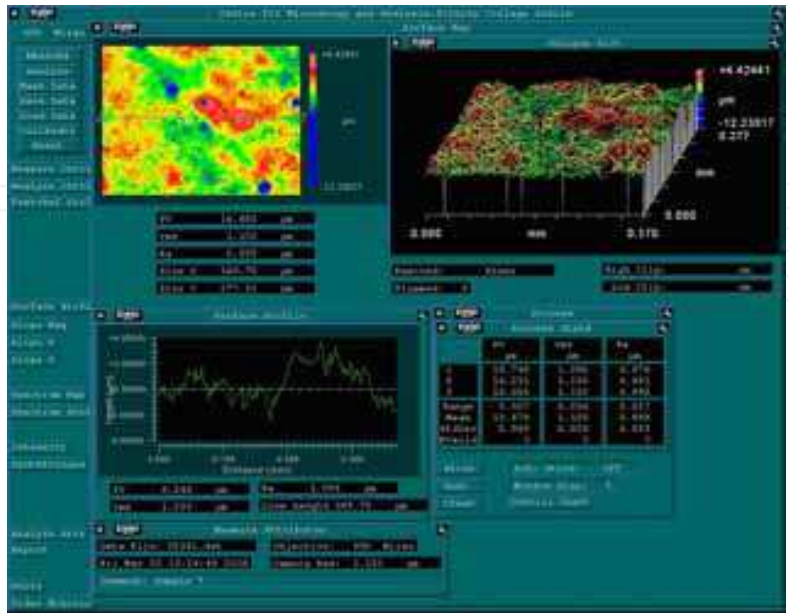


Fig. 16. A white light profilometry scan for a SBS-g-NIPAAm copolymer illustrating 2D and 3D surface profiles as well as the PV value, 13.878 μm and the RMS parameter, 1.125 μm .

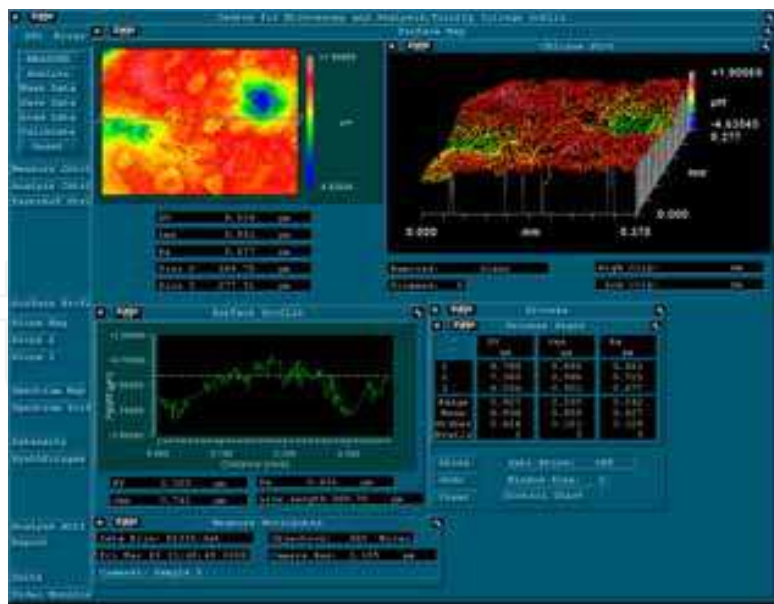
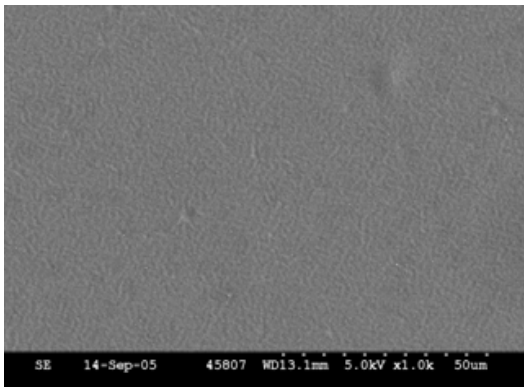


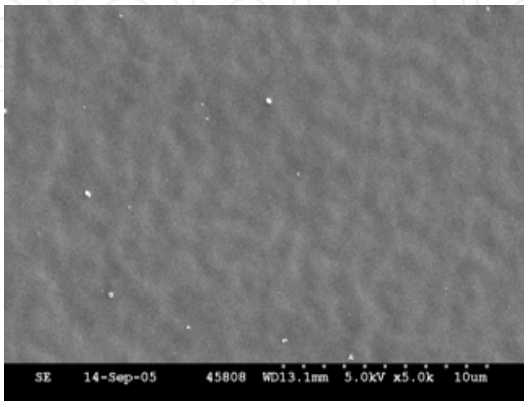
Fig. 17. A white light profilometry scan for a SBS-g-NVP coating illustrating 2D and 3D surface profiles as well as the PV value, 6.896μm and the RMS parameter, 0.859μm.

11.2 Scanning electron microscopy

SEM micrographs of SBS, selected grafted polymers are illustrated in Figures 18 to 20.



(a)



(b)

Fig. 18. SEM images of SBS at resolutions of 50μm (a) and 10 μm (b).

Mohammady et al., (2002) has confirmed that SBS, kraton D1101, exhibits a mixture of PS cylinders and lamellae embedded in the PB matrix when analysed by SEM. These findings correspond with observations made by the Authors, as shown in Figure 18, where SBS exhibits a uniform and dense structure with no pores present whereas the remaining grafted samples illustrated in Figures 19 and 20 revealed porous sponge like membranes due to the migration of chloroform during the UV polymerisation process.

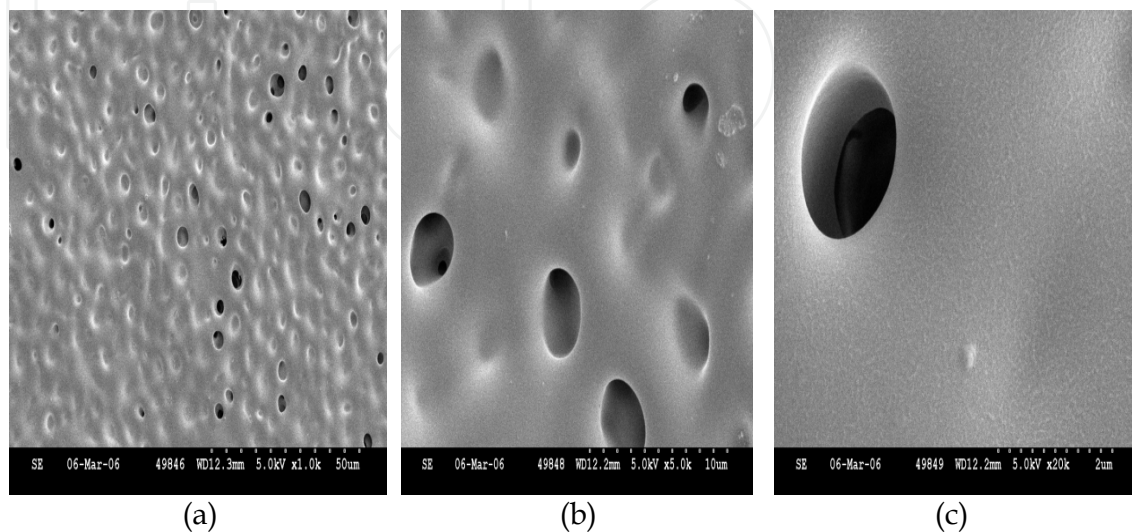


Fig. 19. SEM images of SBS-g-NIPAAm at resolutions of 50μm (a), 10μm (b) and 2μm (b).

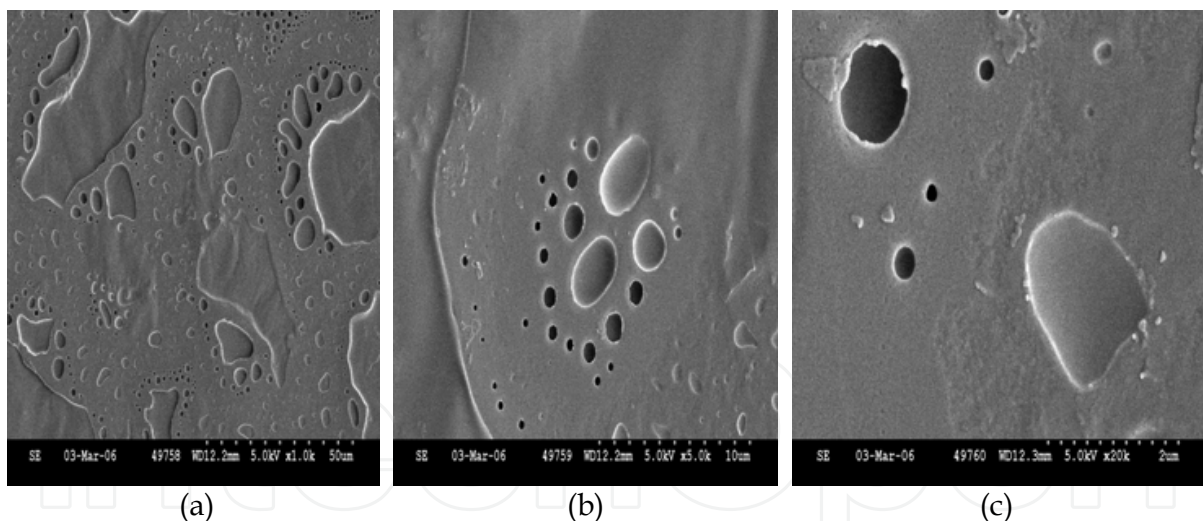


Fig. 20. SEM images of SBS-g-NVP at resolutions of 50μm (a), 10μm (b) and 2 μm (c).

11.3 Contact angle analysis of SBS and grafted SBS copolymers

For the fabrication of biomedical coatings coming into contact with blood and tissue, it is usually desirable to create or utilise materials which exhibit high degrees of wettability. One technique used to predict wetting properties of biomedical polymers is the use of contact angles. When a droplet impacts onto a solid surface, a liquid film is formed which spreads out with a retarding velocity, due to the influence of both the surface tension and surface forces, resulting in the liquid film attaining a maximum spread when it comes to a stop. Young's law provides a relation between those forces outlined in equation 3.

$$\sigma_{lv} \cdot \cos \theta + \sigma_{ls} = \sigma_{sv} \quad (3)$$

where θ is the angle of contact the liquid makes on the solid, σ_{lv} , σ_{ls} , and σ_{sv} represent the interfacial tensions at the boundaries between liquid (l), solid (s) and vapour (v). The contact angle, θ , is usually referred as the wettability of a surface. The liquid is non-wetting when $90^\circ < \theta < 180^\circ$ and wetting when $0^\circ < \theta < 90^\circ$ (Moite & Moreira, 2003). Wettability can be assessed directly using goniometry by measuring the angle formed between a solid surface and the tangent to the drop surface. A graphic illustrating the concept of wettability is shown in Figure 21.

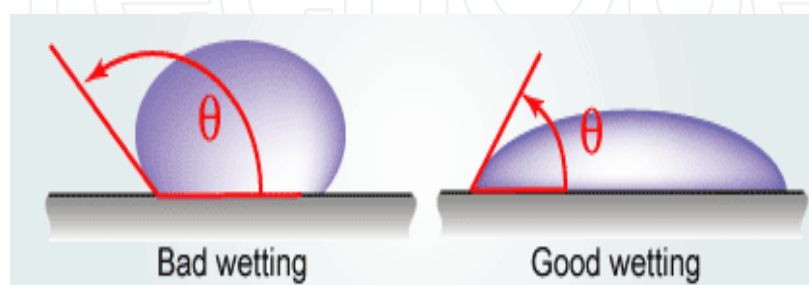


Fig. 21. A graphical representation of wettability.

Therefore, wettability is often referred to as hydrophilicity and is considered to be a surface property of a material as opposed to true hydrophilicity, which is considered to be a bulk property. A caveat to this design criterion is the fact that polymers are generally hydrophobic in nature due to their generally low surface tensions, resulting in polymers exhibiting poor wettability. For visual purposes, to illustrate principles of wettability, a digital goniometer was used and the results are illustrated in Figure 22, these images best demonstrate the affect of wettability on SBS as well as grafted SBS copolymers.

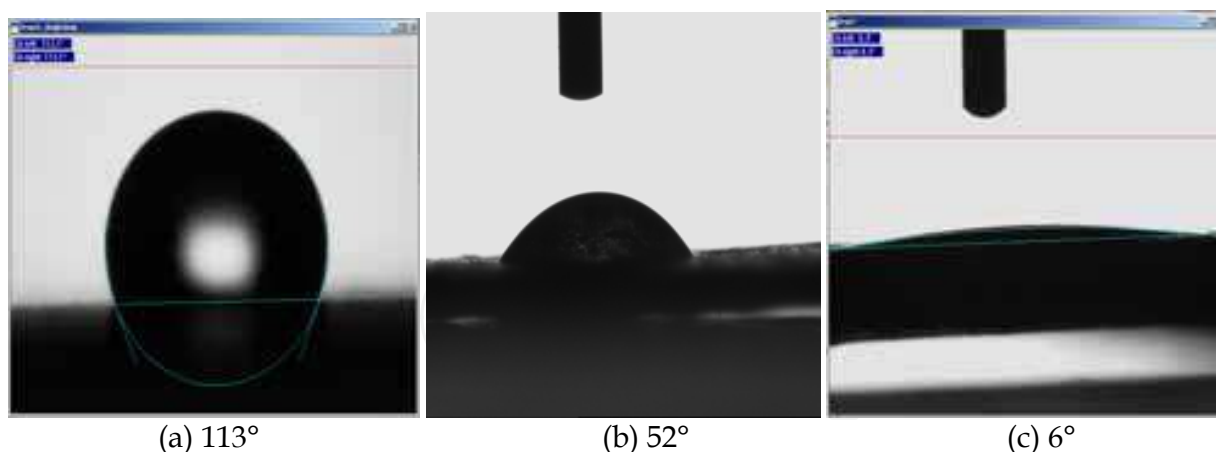


Fig. 22. Contact angles representing the copolymers, where (a) SBS, (b) SBS-g-NIPAAm and (c) SBS-g-NVP.

From the images obtained the modification in the surface chemistry and wettability is reflected by the dramatic reduction in the contact angles as shown in Figures 22. Lassalle *et al.*, (2004) has found a contact angle of 95° when 1% of N-carbamyl maleamic acid was grafted onto SBS. Whereas, Yang *et al.*, (Yang 7Hsiue, 1996; Yang *et al.*, 1997; Yang *et al.*, 1998) reported similar trends when vinyl pyridine was grafted onto SBS and when dimethyl amino ethyl methacrylate was grafted onto SBS, contact angles of 77° and 76° were obtained.

Therefore, by grafting a hydrophilic monomer/polymer onto a hydrophobic backbone the wettability of the material is increase. It is important to note, that the samples tested where not washed and the low contact angle for the SBS-g-NVP copolymer was in part due to the migration on polymerised poly *N*- vinyl-2-pyrrolidone which is an excellent hydrophilic hydrogel, but the principle still applies whereby a hydrophobic material such as SBS can be made into a hydrophilic compound via grafting technologies.

12. Conclusion

Polymer science is by nature an interdisciplinary field, where it has found refuge in the traditional domains of engineering, chemistry and physics. However, the importance of this branch of science has now expanded and by the further integration of other disciplines such as biology, medicine and computing, new innovations have emerged resulting in opportunities which very much find itself in the fields of biomaterials. This chapter looked at such possibilities, where the tradition SBS copolymer (a thermoplastic elastomer) was modified into a grafted copolymer utilising hydrogel technology to create a potential medical application in the area of biomedical coatings.

To truly appreciate the breath and depth of the opportunities one must have a detailed understanding of the fundamental principles which occur within the materials such as phase separation, the domain theory, topography and reaction kinetics to name but a few. Only then can new materials be commercialised which capture the needs society has place on them.

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Biomedical Engineering, Trends in Materials Science

Edited by Mr Anthony Laskovski

ISBN 978-953-307-513-6

Hard cover, 564 pages

Publisher InTech

Published online 08, January, 2011

Published in print edition January, 2011

Rapid technological developments in the last century have brought the field of biomedical engineering into a totally new realm. Breakthroughs in materials science, imaging, electronics and, more recently, the information age have improved our understanding of the human body. As a result, the field of biomedical engineering is thriving, with innovations that aim to improve the quality and reduce the cost of medical care. This book is the second in a series of three that will present recent trends in biomedical engineering, with a particular focus on materials science in biomedical engineering, including developments in alloys, nanomaterials and polymer technologies.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

James E. Kennedy and Clement L. Higginbotham (2011). Synthesis and Characterisation of Styrene Butadiene Styrene Based Grafted Copolymers for Use in Potential Biomedical Applications, Biomedical Engineering, Trends in Materials Science, Mr Anthony Laskovski (Ed.), ISBN: 978-953-307-513-6, InTech, Available from: <http://www.intechopen.com/books/biomedical-engineering-trends-in-materials-science/synthesis-and-characterisation-of-styrene-butadiene-styrene-based-grafted-copolymers-for-use-in-pote>

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