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PAPER

Towards biodegradable elastomers: green synthesis of carbohydrate functionalized styrene–butadiene–styrene copolymer by click chemistry†

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Random attachment of sugar molecules to synthetic polymers is an important strategy to induce biodegradability in these polymers. The present study successfully employs “click” chemistry to introduce low levels of sugar molecules onto styrene–butadiene–styrene (SBS) copolymer, a widely used commodity polymer which is not biodegradable. Spectral, morphological and thermal studies of the modified polymers were carried out to show the dramatic changes in the properties of these modified polymers. Thermal stability of glucose linked SBS had onset of degradation at 428 °C, down from 478 °C observed for SBS. Morphology studied by WAXRD and SEM showed destructuring of the polymer domains of SBS, which is beneficial for biodegradation of these polymers. Previous studies showed that sugars anchored by hydrolysable ester groups onto polystyrene were biodegradable; current studies show that sugars anchored by unhydrolyzable C–C bonds on the butadiene component of SBS copolymer are also significantly biodegradable.

Introduction

Click reaction, that is Cu(I) catalyzed Huisgen 1,3-dipolar cycloaddition of azides and alkynes, has attracted more and more attention because of its high selectivity, mild reaction conditions, quantitative yields and almost no by-products. This has led to its application in many processes, including the synthesis of therapeutics,^{1,2} protein-based biohybrids,^{3,4} sugar arrays,⁵ dendrimers,⁶ functional polymers^{7,8} and nanotube functionalization.⁹ In particular the “click” process has become an invaluable tool for the synthesis of carbohydrate-based polymers. For example, Liebert *et al.* employed click chemistry in the modification of polysaccharides¹⁰ and Sun *et al.* immobilized carbohydrates and proteins onto solid surfaces.¹¹ One advantage of click chemistry is that the azide and alkyne groups can, in some cases, be introduced on the polymer backbone, and if these compounds are stable in common organic reagents and can coexist with other functional groups, such as hydroxyl, amino and carboxyl, then the click reaction can be successfully accomplished. The triazole ring thus formed is generally stable, besides the copper(I) catalyst system is easily available and is not sensitive to solvent and pH. Thus, the remarkable functional group tolerance of click reactions has enabled the facile introduction of reactive groups, such as hydroxyl and

carboxyl, through conventional pre- or post-polymerization modification.^{12,13} However, the number of examples of click chemistry reactions in polymer systems is still limited, but the technique remains a potent tool for further exploitation for developing new functional groups onto hydrophobic polymers.

Cell surface saccharides of glycolipids, glycoproteins and glycans participate in numerous biological phenomena in which there is mediation by carbohydrate–protein interactions. Carbohydrate chains are involved in various recognition phenomena, such as fertilization, cell adhesion, tissue formation, antigen–antibody reaction, cancer metastasis and infection of viruses and bacteria. Carbohydrate-carrying polymers have been used as cell-specific culture substrata, in human vaccines, for tumor diagnosis, as probes for receptors and in targeted drug delivery systems.¹⁴

Therefore, greater attention has recently been paid towards synthetic polymers with pendant carbohydrate chain moieties. We decided to use a click chemistry approach for the functionalization of polystyrene–polybutadiene–polystyrene (SBS) copolymer with carbohydrates, as it eliminates the need to protect the sugar hydroxyl groups which otherwise becomes necessary; thereby we also avoid use of several reagents and work-up procedures leading to a greener process to make a greener polymer molecule. Complete quantification of all functional groups is not reported in this paper as this study is just a model study to ascertain the synthesis methodology as well as preliminary studies on biodegradation and changes in morphological properties and thermal properties which affect the applications of the modified elastomer. SBS is an important synthetic elastomer, and incorporation of carbohydrate moieties

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along the SBS chain has the potential to render it biodegradable as well as biocompatible. Our previous work has shown that synthetic polymers (like polystyrene) with pendant sugar groups have significant biodegradable properties.¹⁵ It is possible to conceive that in bulk applications of SBS (such as certain types of shoe soles), there will not be significant biodegradation whilst in active use, since contact with soil will be occasional; loss of physical properties would entail long term immersion in soil bacteria environment for several days at a stretch. Needless to say that more research will be needed to develop products with appropriate degradation profiles. This can be achieved by varying the type of sugar molecules as well as their content. In a forthcoming publication we will present our results on the effect of different sugar molecules (mannose, galactose, fructose, xylose, lactose, *etc.*) on the rates of biodegradation. The current study shows the application of click chemistry to achieve the synthesis of such polymer molecules.

Experimental

Materials

Polystyrene-*block*-polybutadiene-*block*-polystyrene (Aldrich, M_w 140 000, 30% polystyrene, 70% polybutadiene) was used as a starting material. 3-Chloroperoxybenzoic acid, 77% max. (Aldrich Chemicals, USA), methanol LR (Ranbaxy, India), toluene GR, pyridine GR, *N,N*-dimethylformamide GR and 4-dimethylaminopyridine (DMAP) were purchased from Merck and used as such without further purification. Dextrose anhydrous GR was obtained from Merck. Ammonium chloride AR and sodium ascorbate were obtained from Ranbaxy and sodium azide GR was obtained from Merck. All the sugars were used as received.

Analytical methods

¹H and ¹³C NMR analysis. ¹H and ¹³C spectra of all the samples were recorded on a Bruker 200 MHz with CDCl₃ as the solvent and tetramethylsilane as external reference. The solid state ¹³C NMR spectra were recorded at 300 MHz. All the spectra are referenced at $\delta = 77$ ppm for ¹³C and $\delta = 7.25$ ppm for ¹H with respect to CDCl₃.

FTIR analysis. Spectra were recorded with a Perkin Elmer 1 FTIR instrument with a resolution of 4 cm⁻¹ in transmission mode, in which the samples were cast onto a KBr disk from a solution of the elastomer dissolved in chloroform.

Thermogravimetric analysis (TGA). The thermogravimetric analysis (TGA) was performed on a Perkin Elmer TGA-7 in N₂ atmosphere at heating rate of 10 °C min⁻¹.

Scanning electron microscopy (SEM). The surface morphology of SBS and functionalized SBS was investigated using a Leica SEM stereoscan 440, Cambridge, UK. The polymeric samples in the form of thin films, before analysis were coated with gold in a sputter coater, in order to achieve conducting surface and were analyzed at an accelerated voltage (potential) of 10 kV.

WAXRD. Wide Angle X-Ray Diffraction (WAXRD) analysis was carried by using a powder XRD Xpert-1217 diffractome-

ter. The scanning speed was 4° min⁻¹, with CuK α radiation. The samples were scanned from 2 θ values of 3° to 30°.

Synthesis of carbohydrate functionalized SBS by click chemistry

Synthesis of 22 mol% partially epoxidized SBS. We performed the epoxidation of SBS with a peracid as a homogenous reactant. Partial epoxidation of polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) was performed using 3-chloroperoxybenzoic acid, mCPBA (amount used appropriate for the desired percentage of epoxidation) in toluene at room temperature.

In a 250 mL round-bottomed flask, 10 g SBS, Aldrich (13 mmol g⁻¹ unsaturation) was dissolved in 100 mL toluene at room temperature. 6.25 g of mCPBA (75% Aldrich) dissolved in 40 mL of toluene was added dropwise with a dropping funnel over a time of 20 min. The reaction mixture was maintained at room temperature and the reaction was continued for 3.5 h after which it was precipitated in 1 L methanol. The precipitated polymer was washed many times with methanol. The polymer was then dried in a desiccator under vacuum at room temperature.

Thus, various degrees of epoxidized SBS (7, 13, 22 and 46 mol% epoxidized) could be synthesized using the appropriate amount of mCPBA with (SBS:toluene) ratio of 1:10 (w/v) using the above procedure.

¹H NMR [200 MHz, CDCl₃, δ ppm] showed signals of different protons at δ values of 7.05–6.57 (10H), 5.40 (2H), 4.99 (3H), 2.92 (2H), 2.68 (2H), 2.03(1H), 1.61, 1.58 and 1.55

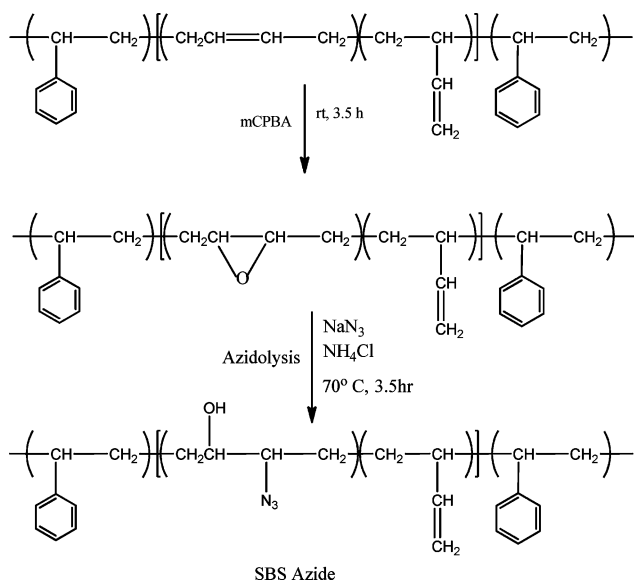
¹³C NMR [400 MHz, CDCl₃, δ , ppm] showed values at 145.26, 142.6, 131.22–127.61, 114.20, 58.42, 56.73, 43.54, 40.28, 38.13, 33.90, 32.66, 27.35 and 24.34

FTIR: (KBr, cm⁻¹) 3080, 3060, 3025, 3004, 2920, 2846, 1639, 1601, 1493, 1452, 1404, 1386, 1352, 1312, 1260, 1071, 1028, 967, 910, 841 and 804.

Synthesis of SBS azide from partially epoxidized SBS. In a 250 mL round-bottomed flask maintained under nitrogen, 2 g of epoxidized SBS (13 mol%) was dissolved in 20 mL pyridine. After the epoxide dissolved completely, 40 mL of dry DMF was added slowly at 50 °C to ensure that the epoxide does not precipitate. The reaction mixture was stirred for some time and the temperature was increased to 70° C. Sodium azide 1.5 g, and ammonium chloride 1.5 g (1:1 wt%) was added to the reaction mixture (Scheme 1). The reaction mixture was heated at 70 °C for 3.5 h, after which the product was precipitated in 500 mL water and was washed until free from pyridine. The final wash was carried out with methanol and the product was dried in a desiccator under vacuum at room temperature. This compound was characterized using FTIR spectroscopy (Fig. 1 and 2), which clearly showed the presence of azide peak at 2104 cm⁻¹ (increasing azide peak with increasing epoxide content of SBS).

Synthesis of sugar derivatives for click reaction

Synthesis of β -D-glucopyranose pentaacetate. This derivative was synthesized following the procedure of Wolfrom *et al.*¹⁶ In a 2 L flask containing 350 mL of acetic anhydride, dextrose (50 g) was added and the reaction mixture was heated to 50 °C.



Scheme 1 Synthesis of SBS azide from SBS.

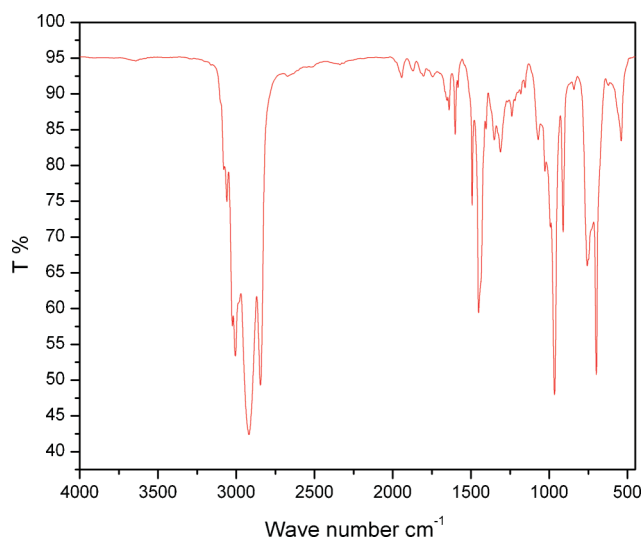


Fig. 1 FTIR spectra of unmodified SBS.

Anhydrous sodium acetate (25 g) was added and the mixture was stirred until a clear solution was obtained. The temperature was increased to 90 °C and the reaction was continued for 2.5 h at this temperature. It was then cooled and poured with stirring onto 2 L of ice water. After 3 h the crystalline material was filtered and crystallized from hot methanol. The product is further purified by recrystallization (¹H NMR spectra of the purified product is presented in the ESI, Fig. (i),† the clean spectrum confirming the purity of the product).

Synthesis of 2-propynyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside from β-D-glucopyranose pentaacetate. 2-Propynyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (**2**) as shown in Scheme 2, was synthesized following the method reported by Mereyala *et al.*¹⁹ To a solution of β-D-glucopyranose pentaacetate (10 g, 25.6 mmol) in dichloromethane (200 mL) was added propargyl alcohol (1.8 mL, 30.7 mmol) and BF₃·Et₂O (4.8 mL, 38.4 mmol) at 0° C and the reaction mixture was

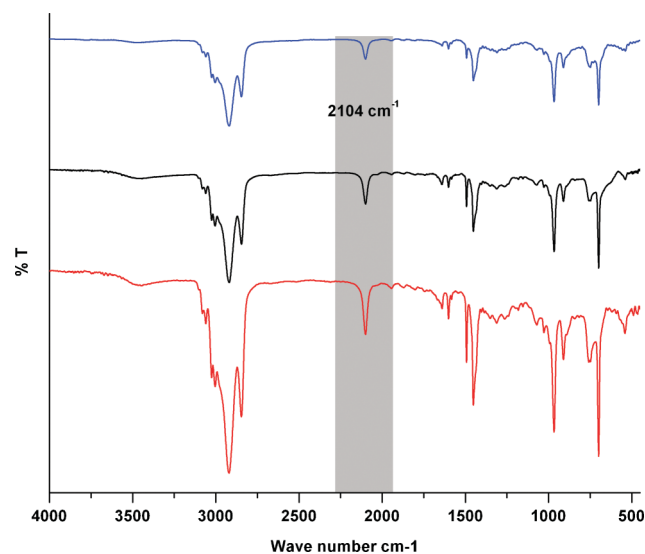


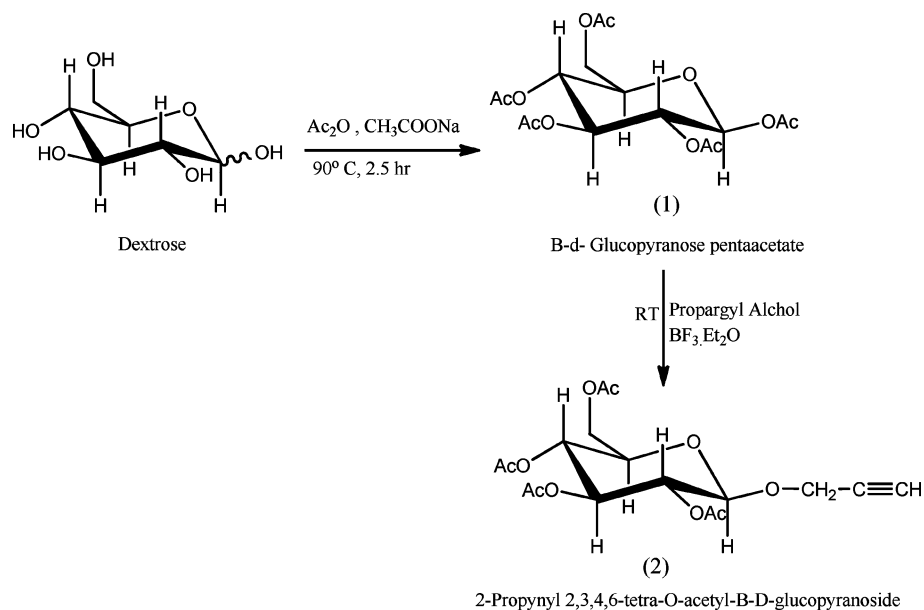
Fig. 2 SBS azide with different degrees of azidation (increasing intensity of N₃ peak at 2104 cm⁻¹).

stirred at room temperature for 2 h. After the completion of the reaction, anhydrous K₂CO₃ (4.8 g) was added and stirring was continued for an additional 30 min. The reaction mixture was filtered and washed with dichloromethane. The filtrate was washed with water (2 × 150 mL), the aqueous phase was separated and extracted with dichloromethane (2 × 50 mL) and the combined organic phase was dried over anhydrous sodium sulphate (Na₂SO₄) and concentrated to yield a solid which was crystallized in dichloromethane–hexane to obtain the derivative **2** (9 g, 90%) as a crystalline compound.

NMR: ¹H (CDCl₃) δ 5.28–4.9 (m, 3H, H-2,3,4), 4.75 (d, 1H, H-1), 4.35 (d, 2H, H-1), 4.4–4.09 (m, 4H, H-1,6), 3.76–3.67 (m, 1H, H-5), 2.46 (t, 1H, H-3), 2.09, 2.05, 2.01 and 2.0 (4 s, 12 H, OCOCH₃). FTIR: 3278 (≡CH), 2118 (C≡C) and 1749 cm⁻¹ (C=O). The clean NMR spectrum along with matching proton integrations proved the purity of the compound (Fig. 3).

Synthesis of 2-propynyl-β-D-glucopyranoside. These sugar derivatives were synthesized following the procedure of Roy *et al.*¹⁷ D-Glucose (7.2 g, 40 mmol) was suspended in propargyl alcohol (11.6 mL, 200 mmol) and stirred at 65 °C. H₂SO₄–silica was prepared as follows: to a slurry of silica gel (10 g, 200–400 mesh) in dry ethyl ether (50 mL) was added commercially available conc. H₂SO₄ (3 mL) with shaking for 5 min. The solvent was evaporated under reduced pressure resulting in free flowing H₂SO₄–silica which was then dried at 110 °C for 3 h. 200 mg of this catalyst was added to the propargyl alcohol and stirring was continued for 2.5 h until all the solids had dissolved. The reaction mixture was then allowed to stir at room temperature for another 12 h. TLC (CH₂Cl₂–MeOH; 5 : 1) showed complete conversion of D-glucose. The reaction mixtures were transferred to a silica gel column and the excess propargyl alcohol was eluted with CH₂Cl₂ followed by elution of the product glycoside with CH₂Cl₂–MeOH (15 : 1) to afford the propargyl derivative in 80% yield (Scheme 3). This product was used as such for the succeeding click chemistry step.

Synthesis of 2-propynyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside functionalized SBS. SBS azide (**2** g) was dissolved



Scheme 2 Synthesis of 2-propynyl-2,3,4,6-tetra-*O*-acetyl- β -D-glucopyranoside.

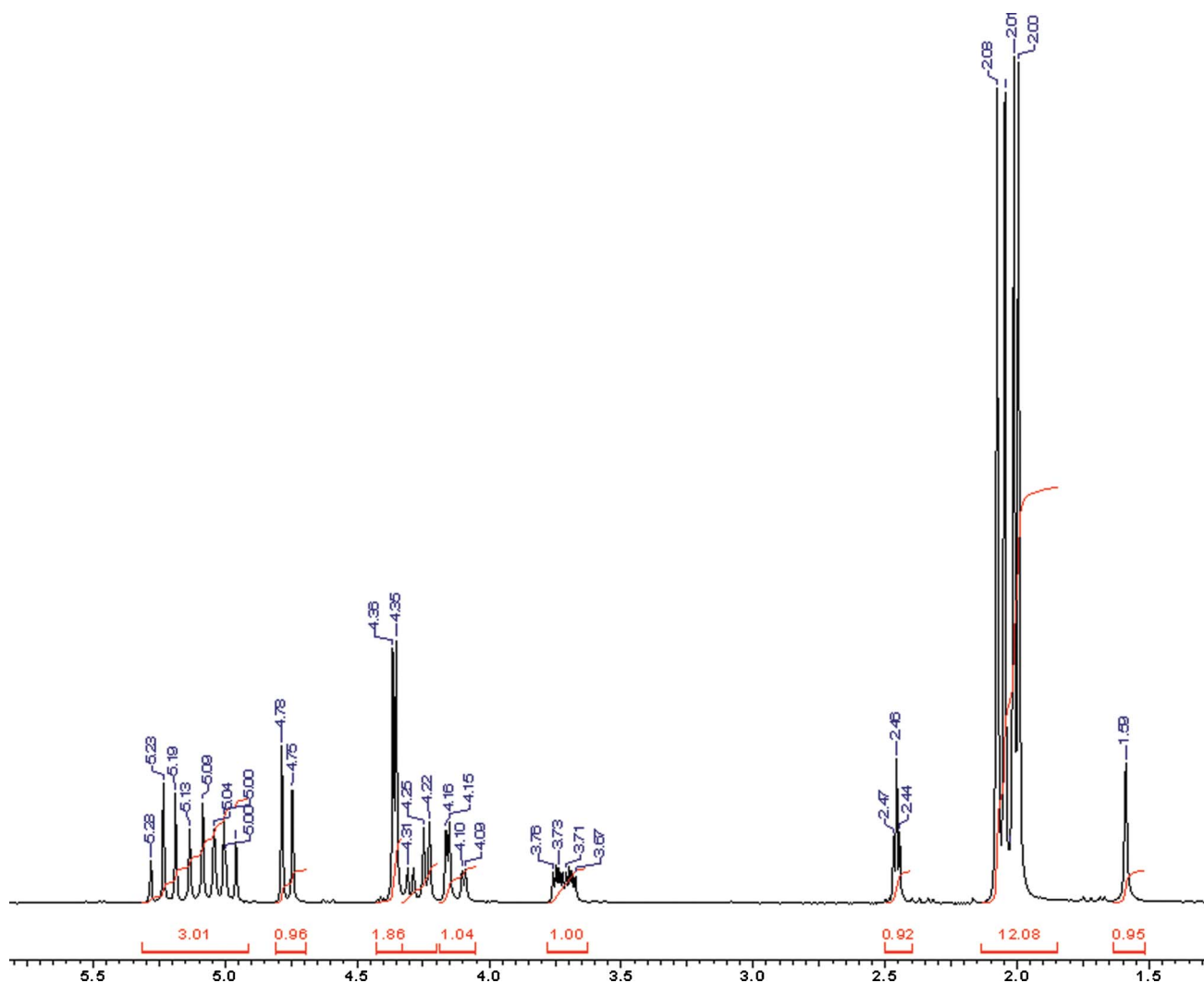
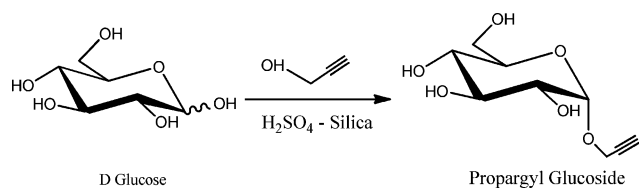
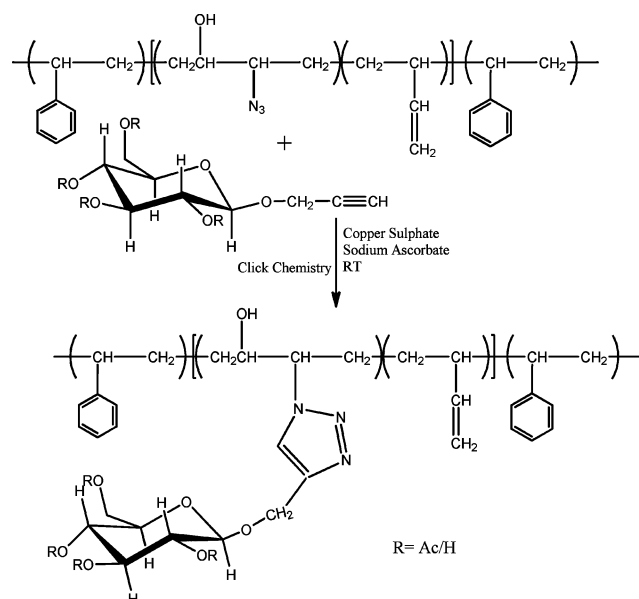


Fig. 3 ^1H NMR of 2-propynyl-2,3,4,6-tetra-*O*-acetyl- β -D-glucopyranoside.



Scheme 3 Synthesis of propargyl glucoside from D-glucose.

in 30 mL dichloromethane. Propargyl-2,3,4,6-tetra-*O*-acetyl- β -D-glucopyranoside (500 mg) dissolved in 20 mL of DMSO was slowly added to the SBS azide polymer solution to avoid precipitation. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (8 mg) dissolved in 1 mL of water and sodium ascorbate (13 mg) dissolved in 1 mL of water were added to the reaction mixture at room temperature (Scheme 4). The reaction was continued for 3 h at the end of which it was precipitated in methanol. The product was washed with methanol and finally with water. The FTIR spectrum (Fig. 4) showed the disappearance of the azide peak at 2104 cm^{-1} , and appearance of a carbonyl peak at 1759 cm^{-1} .



Scheme 4 Synthesis of carbohydrate functionalized SBS using click chemistry approach.

Synthesis of 2-propynyl glucose functionalized SBS. SBS azide (2 g) was dissolved in 30 mL dichloromethane. Sugar derivative (2-propynyl glucose, 230 mg) dissolved in 15 mL of DMSO was slowly added to the SBS azide polymer solution to avoid precipitation. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (8 mg) dissolved in 1 mL of water and sodium ascorbate (13 mg) dissolved in 1 mL of water were added to the reaction mixture at room temperature. The reaction was continued for 3 h at the end of which it was precipitated in methanol. The product was washed with methanol and finally with water. The product was characterized by FTIR spectroscopy (Fig. 5), the disappearance of the azide peak signifying completion of the reaction. This reaction was very facile in our hands and appears to be easy to scale up. Scale-up studies will be taken up as we prepare more such modified polymers for developing applications.

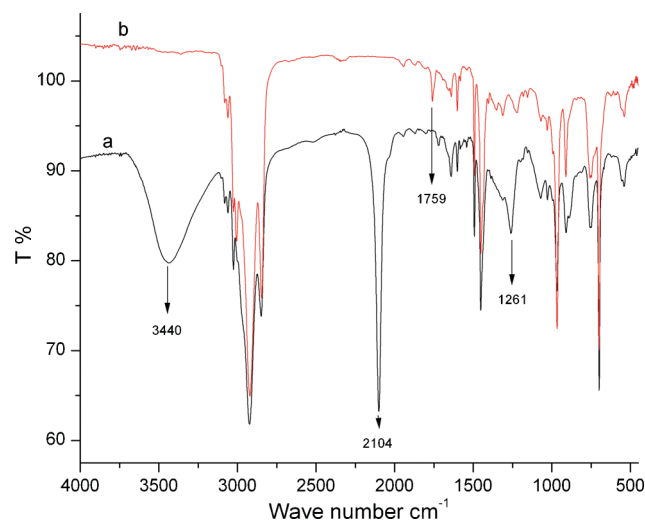


Fig. 4 Overlapped FTIR spectra of (a) SBS azide and (b) 2,3,4,6-tetra-*O*-acetyl- β -D-glucopyranoside linked SBS by click chemistry.

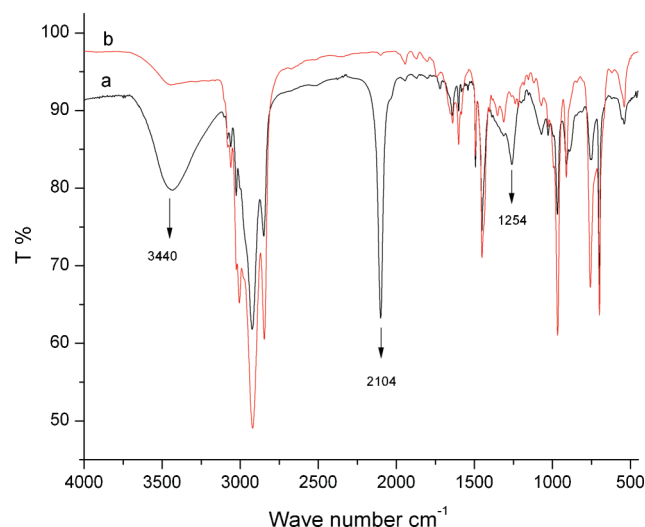


Fig. 5 Overlapped FTIR spectra of (a) SBS azide and (b) glucose linked SBS by click chemistry.

Results and discussion

Synthesis

The overall synthesis strategy, as presented in the reaction schemes above, is based on the azidation of epoxidized SBS followed by coupling with carbohydrate alkyne partner using click chemistry to yield carbohydrate functionalized SBS.

Click reaction is the Cu(I) catalyzed cycloaddition of azides and alkynes. This reaction can be performed in a number of solvents including water or other polar solvents and is not affected by presence of functional groups. In addition, the copper(I) catalyst system is easily available and insensitive to solvent and pH.¹¹ In our experiments, the copper(I) catalyst system was introduced to the reaction system by reducing copper(II) sulphate pentahydrate with sodium ascorbate. The reaction was performed in CH_2Cl_2 -DMSO solution at room temperature for 3 h. We do not perceive any difficulty in scale up of this reaction since the reaction proceeded smoothly at room temperature.

Fig. 2 shows facile formation of azide groups on epoxidized SBS. Fig. 4 shows the overlapped FTIR spectra of SBS azide and the click reaction product of SBS azide with propargyl acetyl protected glucose. It can be observed from the above spectra that after click reaction the peak at 2104 cm^{-1} , corresponding to azide, completely disappears. The acetyl protected glucose shows a new peak at 1759 cm^{-1} due to the carbonyl stretching of acetyl group. The simultaneous disappearance of the azide peak and appearance of carbonyl peak in the FTIR spectra of the product clearly proves that functionalization of SBS with protected glucose has been successful. We might add here that had we carried out the other possible synthetic strategy – *i.e.* sugar azides to react with propargyl SBS – then the sugar azide may have become an explosive molecule. It is well known that six carbon atoms per azide groups is approximately the threshold for safety of azides. However, by attaching azide on the SBS polymer chain, and also in very low concentration, we make the process very safe. We selected the sample with 13% epoxy content of the butadiene component of SBS to prepare the azide, and only a fraction of this epoxy was converted to the azide. We estimate less than 5% of the SBS chain to have azide linkages, which makes for a large interval between azides, and correspondingly they are very safe. Our synthesis procedures lead us to believe that the synthesis of the azide as well as the click reaction were very safe, and amenable to scale up.

Fig. 5 shows the overlapped FTIR spectra of SBS azide and the click reaction product of SBS azide with propargyl glucose. It can be observed from the above spectra that after click reaction the peak at 2104 cm^{-1} , characteristic of azide (N_3), disappears completely due to the cycloaddition of azide and alkyne leading to the formation of a 1,2,3-triazole linkage. Thus FTIR clearly shows the successful anchoring of glucose units to SBS by click chemistry. In this reaction it is not necessary to protect the hydroxyl groups of the glucose because hydroxyl groups do not interfere with the formation of the triazole ring.

Thermogravimetric analysis (TGA)

TG curves of various sugar linked SBS were studied under pure nitrogen atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$ from 50 – 600°C .

Fig. 6(a) shows the comparative thermal stabilities of SBS, SBS azide and glucose linked SBS synthesized by click reaction. It is clear that the thermal stability of the three polymers is in the order of $\text{SBS} > \text{SBS azide} > \text{glucose linked SBS}$. SBS is stable up to 400°C , after which it starts degrading rapidly. The rate of degradation reached a maximum at 525°C and at 600°C it degrades almost completely leaving behind only $\sim 0.63\text{ wt\%}$ residue. It is seen from Fig. 6 that sugar linked SBS samples shows higher residue at 600°C , as compared to unmodified SBS, with SBS azide being in between the two. Clearly, chemical modification affects the thermal stability of the SBS. The tetraacetyl glucose linked SBS is even more thermally unstable than the (unprotected) glucose linked SBS (Fig. 6(b)). Acetyl groups may be the cause of lower thermal stability, since these groups dissociate at low temperatures. The onset of degradation of SBS was $\sim 478^\circ\text{C}$, while it was $\sim 450^\circ\text{C}$ for SBS azide, 428°C for glucose linked SBS and 426°C for tetraacetyl glucose linked SBS (Fig. 6).

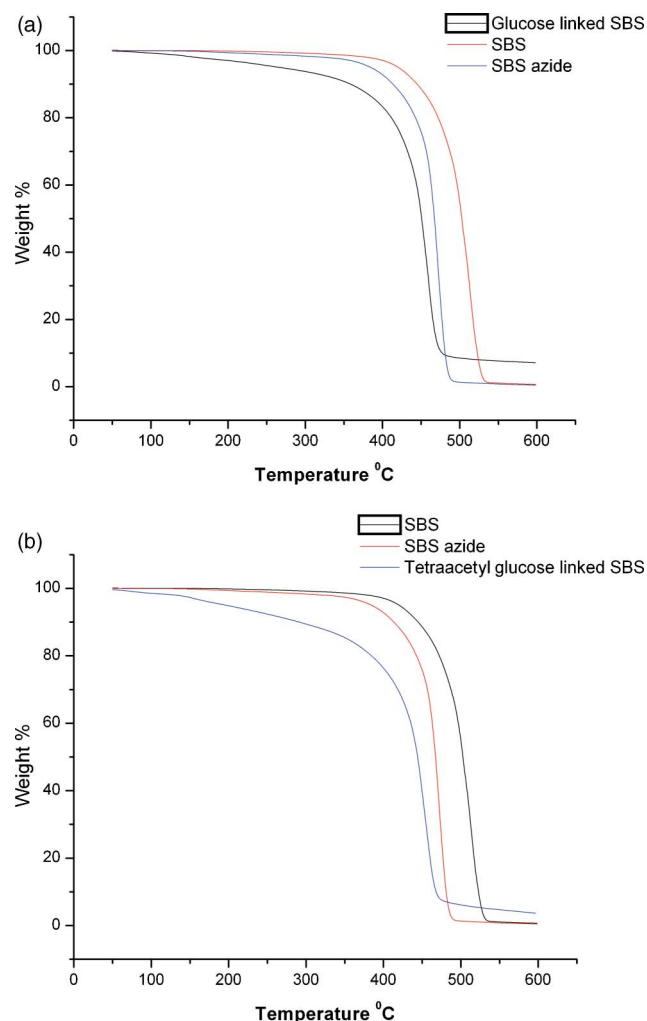


Fig. 6 (a) Overlapped TGA curves of SBS, SBS azide and glucose linked SBS by click reaction. (b) Overlapped TGA curves of SBS, SBS azide and tetraacetyl glucose linked SBS by click reaction.

These results are also borne out from the differential thermogravimetry (DTG) studies (Fig. 7). The DTG curve of SBS is clearly differentiated from those of chemically modified SBS

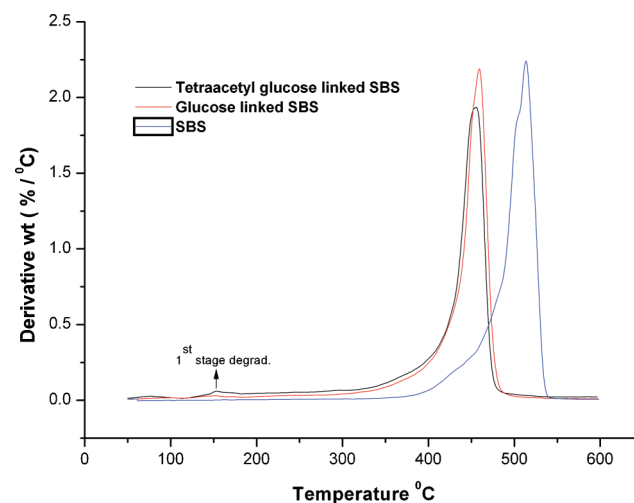


Fig. 7 Overlapped DTG curves of SBS by click reaction.

samples by its main exothermic peak at a significantly higher temperature than the modified SBS samples.

Thus we can say that functionalization of SBS with sugar leads to a decrease in thermal stability.

Morphology by wide-angle X-ray diffraction studies

SBS is an amorphous thermoplastic elastomer, hence broad peaks corresponding to polybutadiene and polystyrene are observed in the wide-angle X-ray diffraction of unmodified SBS.¹⁸ All the samples synthesized were scanned from $2\theta = 3\text{--}30^\circ$ at room temperature. Fig. 8(a) shows the wide-angle X-ray diffraction plots of unmodified SBS and azidated SBS. The more intense peak is centered at $2\theta = 19.7^\circ$ and corresponds to amorphous polybutadiene, the weaker one is centred at $2\theta = 9.5^\circ$ and corresponds to polystyrene. It can be observed from Fig. 8 that after azidation of SBS there is significant decrease in intensity of the peak at $2\theta = 19.7^\circ$ associated with the polybutadiene domain. The peaks at $2\theta = 9.5^\circ$ and 28.7° associated with polystyrene disappear.

Fig. 8(b, c) shows the wide-angle X-ray diffraction plots of tetraacetyl glucose and glucose linked SBS by click reaction. It can be observed that after functionalization of SBS with sugar there is a significant decrease in intensity of the peak at $2\theta = 19.7^\circ$ associated with the polybutadiene domain. This decrease in intensity is more pronounced in tetraacetyl glucose linked SBS. Thus, there is significant disruption of the polybutadiene domain upon attaching sugar moieties. These could be important sites for biodegradation of the SBS polymer chain.

Morphology by scanning electron microscopy (SEM)

Thin films of the polymer samples were prepared from chloroform solutions for examining their surface morphology by SEM. The SEM images are shown below in Fig. 9(a–d), which shows the surface morphology of SBS, SBS azide, glucose linked SBS and tetraacetyl glucose linked SBS, respectively, by click reaction. SBS is considered a two-phase thermoplastic block copolymer in which spherical polystyrene (PS) domains are dispersed in a continuous polybutadiene (PB) phase. It is observed from Fig. 9 that there is not much change in morphology after azidation of SBS, but after functionalizing with sugar by click reaction the morphology changes. The glucose linked SBS shows significant destructuring of the two polymer domains, and this is even more accentuated in the tetraacetyl glucose linked SBS, due to the bulky acetyl groups. These morphological studies show that the destructured polymers are more likely to biodegrade than the parent unmodified polymer, since they have greater surface area and more functional groups for the soil microbes to latch on to.

Biodegradation studies

Preliminary studies were carried out on quantification of the sugar units attached to SBS, using the phenol–sulfuric acid method, and the same protocols were followed for assessing biodegradability as in our studies with sugar-linked polystyrene.¹⁵ It was found that incorporation of 0.09% glucose onto SBS resulted in a weight loss of 3.3%, *i.e.* 36.6 times more than the weight of sugar incorporated. These studies are

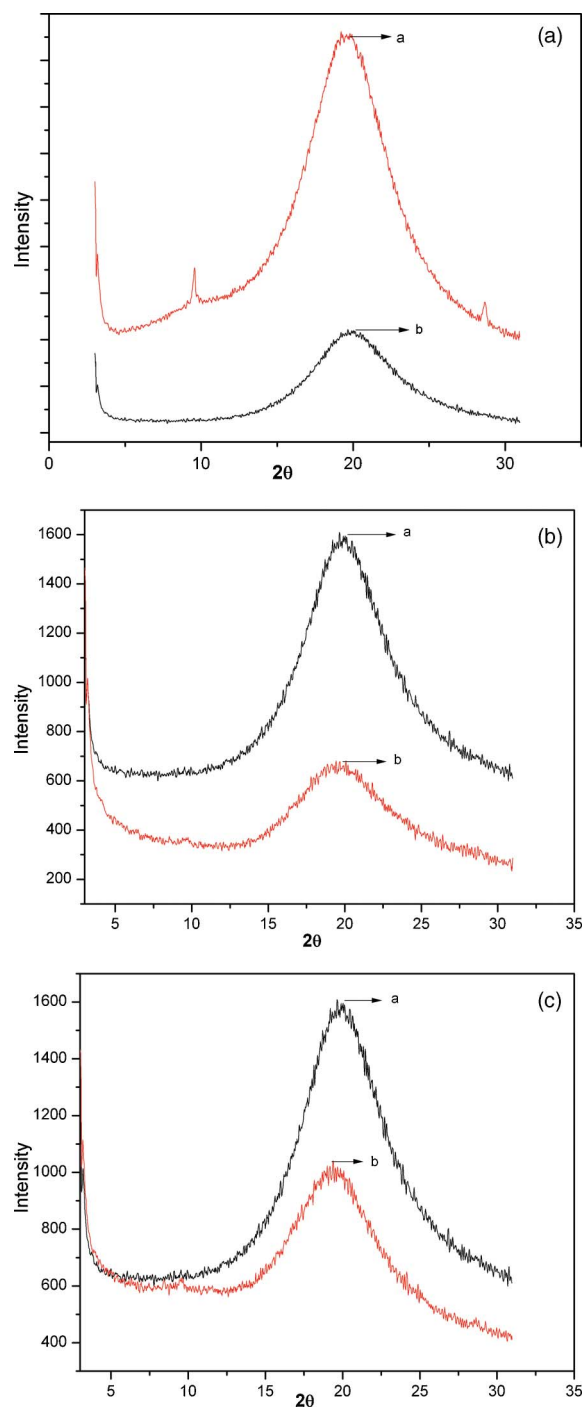


Fig. 8 (a) WAXRD diffraction plots of curve a (unmodified SBS) and curve b (SBS azide) (b) WAXRD diffraction plots of curve a (SBS azide) and curve b (tetraacetyl glucose linked SBS by click reaction) (c) WAXRD diffraction plots of curve a (SBS azide) and curve b (glucose linked SBS by click reaction).

being supplemented by studies with several bacterial and fungal cultures, and also by incorporation of a variety of sugars such as xylose, lactose, mannose, *etc.* The detailed studies will be published independently.²⁰ Suffice to say, incorporation of even minute quantities of sugar units onto hydrophobic polymers like SBS significantly affects its thermal, morphological and biodegradation properties. While we have not presented any

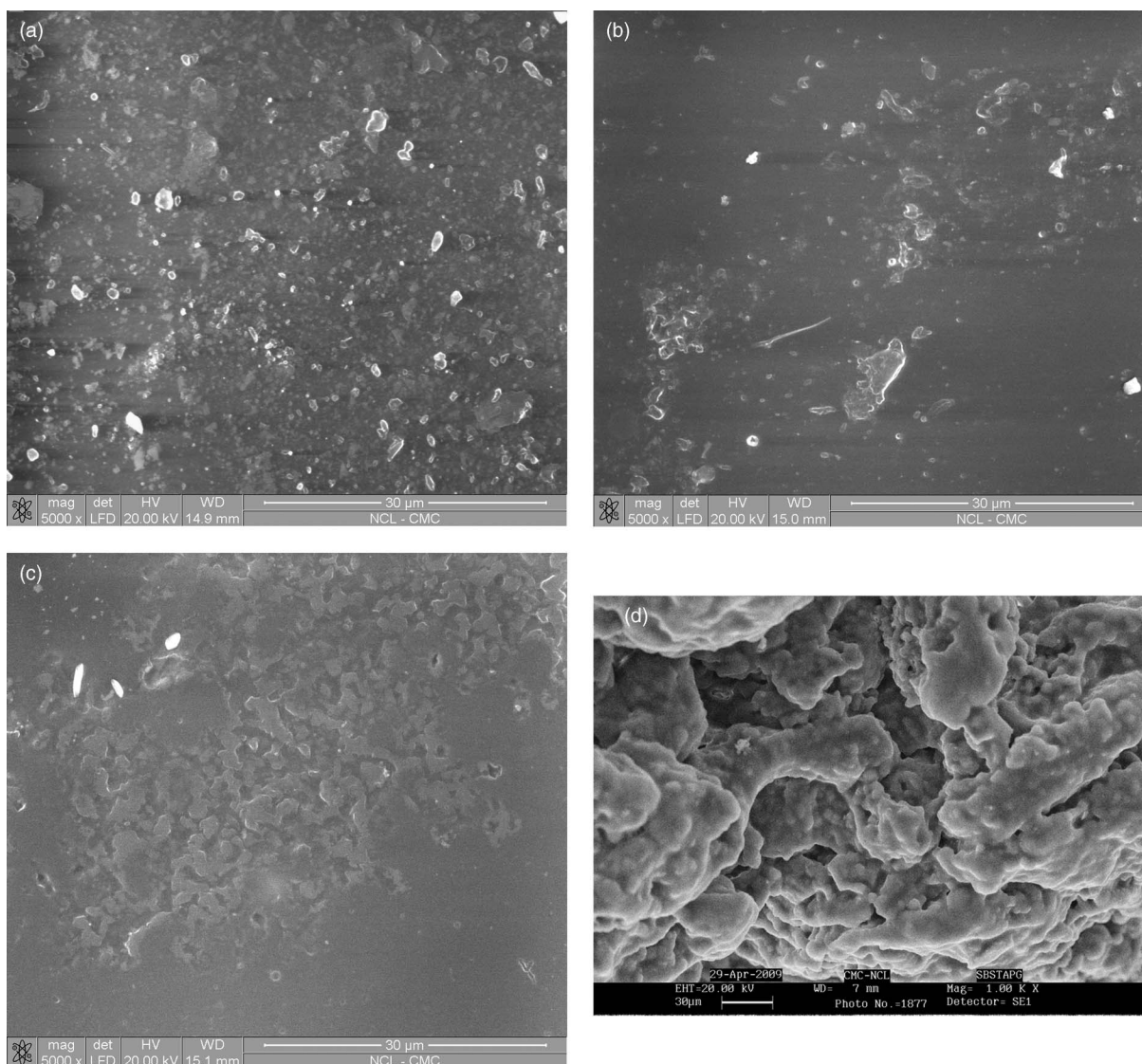


Fig. 9 (a) SEM micrographs of SBS. (b) SEM micrographs of SBS azide. (c) SEM micrographs of glucose linked SBS. (d) SEM micrographs of tetraacetyl glucose linked SBS.

spectral evidence to show biodegradation occurs on the polymer chain, we feel that this can easily be speculated to be so, since a 36.6 fold weight loss (based on sugar content) of the sugar containing SBS polymer cannot be explained simply on the basis of sugar content; some part of the polymer has also to be lost. Our detailed forthcoming paper on spectral analysis of biodegraded samples will shed more light on this aspect. This work is currently ongoing.

Conclusions

In our previous study,¹⁵ we had shown the effect of attachment of a few sugar molecules onto styrene–maleic anhydride copolymer by simple esterification reaction and proved the dramatic improvement in its rate and extent of biodegradation. In this study, we have used click chemistry to incorporate non-hydrolysable sugar units (C–C bonds), and shown that even here the degree of biodegradation (in terms of weight loss per

unit weight of sugar incorporated on SBS) is much higher than expected. Thus, it can be considered to be a general result that random attachment of sugar molecules on to synthetic polymers is an important strategy to induce biodegradability in these polymers. The present study successfully shows that low levels of sugar molecules anchored onto styrene–butadiene–styrene copolymer, a widely used commodity polymer which is not biodegradable, biodegrades to a larger than expected extent. Spectral, morphological and thermal studies of the modified polymers were carried out to show the dramatic changes in the properties of these modified polymers. Thermal stability of glucose linked SBS had onset of degradation at 428 °C, down from 478 °C observed for SBS. Morphology studied by WAXRD and SEM showed destructuring of the polymer domains of SBS, which is beneficial for biodegradation of these polymers. These results are in tandem with those earlier reported for polystyrene-linked sugars, which were found to be biodegradable.

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