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Abstract

Poly(styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene) (SEBS) is functionalized via radical grafting with 4-vinyl-1-cyclohexene 1,2-epoxide (VCHO) initiated using 2,5-Bis(tert-butylperoxy)-2,5-dimethylhexane. The existence of the epoxide group on the SEBS backbone is evidenced by ^{1}H-NMR. A SEC study reveals some chain coupling and this phenomenon is limited by controlling the quantities of peroxide and monomer reagents used during the radical grafting. Photocrosslinking of SEBS-*g*-VCHO under UV irradiation in the presence of a cationic initiator is then successfully performed with resultant gel contents higher than 85 %. Mechanical

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properties of SEBS and crosslinked materials are measured by tensile tests on thin films. On the one hand, those tests reveal a significant increase of the Young's modulus of the crosslinked materials. On the other hand, the diminution of elongation at break is much more limited; crosslinked materials retain their elastomeric properties with an elongation at break greater than 200 %. Finally, the photo-sensitive SEBS-*g*-VCHO is used to show the adhesion performance of the photo-crosslinking coating as well as a resin for stereolithography process.

1. Introduction

Copolymers based on styrene and butadiene monomers are an important class of thermoplastic elastomers. Among them, poly(styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene) (SEBS) has gained interest over the last decades and has found various applications in the industry. SEBS is traditionally produced by hydrogenation of poly(styrene-*b*-butadiene-*b*-styrene) (SBS) copolymers leading to ethylene and butylene units. SEBS is characterized by phase separation in which the high modulus polystyrene phases are incompatible with the low modulus ethylene-butylene phases. The polystyrene hard block brings to SEBS its thermoplastic behaviour while the ethylene-butylene soft block mainly contributes to the elastomeric behaviour of the SEBS. Thanks to its composition, excellent aging resistance and moisture resistance compared to other thermoplastic elastomers such as polyurethanes (TPU) or amide block polyethers (PEBA) are observed and SEBS has been widely used as shock absorbing material, cable insulants and in adhesive and sealant formulations. Moreover, while SEBS possesses good chemical resistance to water and alcohol, it remains soluble in ketones, esters and hydrocarbons. However, if its high elongation at break and high resilience properties make it very interesting for toughening coatings, the absence of crosslinkable groups greatly limits its use compared to acrylate functionalized polyurethane or SBS in coating or adhesive applications.

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Post-polymerization modification of SEBS appeared to be a solution of interest to obtain a functionalized or reactive SEBS. For instance, these modified copolymers could be grafted with functional chains such as fluorinated ones, liquid crystals or could interact with other polymers to lead to compatibilized polymers blends. Although SEBS is widely used today, few studies have focused on the modification of SEBS by radical grafting. Like for polyolefins such as polyethylene, Passaglia and Rosales reported in 2000 a duality between the degree of grafting and the risk of β-scission or even crosslinking of SEBS polymer chains [1, 2]. These two phenomena can lead to a degradation of the mechanical properties of the material and especially its elongation at break and resilience. Most post-polymerization modifications of SEBS therefore occur at high temperature; in the molten state during reactive extrusion to favour the radical grafting reaction rate using appropriate peroxides with short half-life such as dicumyl peroxide. Although the reactivity of dicumyl peroxide and aryl type peroxides has been proven to modify SEBS, other peroxides should be considered of interest. "*ter*-butyl" peroxides have the ability to split into methyl radicals during their homolytic cleavage. These radicals are very reactive and can therefore easily abstract hydrogen from ethylene-butylene block of SEBS.

Despite the difficulty of functionalization, Passaglia *et al.* succeeded to graft in the molten state up to 8,1 wt.% of diethyl maleate and 8,9 wt.% of maleic anhydride onto SEBS [1]. SEBS-*g*-MA is mainly used as compatibilizing agent for blends of SEBS with PA11 or ABS, or as interfacial agent for polypropylene filled with wood fibers or polyurethane [3-6]. SEBS-*g*-MA has also been obtained using ultrasound initiation [7] or in solution [8]. Glycidyl methacrylate (GMA) was successfully grafted alone or with the assistance of N-vinyl pyrrolidone by Pracella *et al.* up to 6 wt.% to be used for reactive blending with polyethylene terephthalate or polypropylene [9-11]. Sugar based surfactants [12] or hyaluronic acid [13] were reacted onto SEBS-*g*-GMA surfaces and found applications as biomaterials. N-vinyl pyrrolidone were grafted on the surface of SEBS using UV radical grafting and benzoyl peroxide [14]. More recently SEBS

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was successfully grafted with 2,6 wt.% of itaconic acid and was then used as compatibilizing agent with $BaTiO_3$ particles [15]. Some more unique monomers like ricinoloxazoline maleate and allyl (3-isocyante-4-tolyl) carbamate have been melt radical grafted as well [16, 17].

In summary, only few molecules have been grafted onto SEBS. None have been reported to lead to a crosslinking of this copolymer in the presence of a stimulus like UV light, contrary to SBS or EPDM which are well known to react via UV light when activated by peroxides with or without mercaptans [18-20].

The grafting of SEBS with cycloaliphatic epoxide has never been reported previously to our knowledge. In this study, a two step approach was considered: first a free radical grafting of a vinylic monomer onto SEBS polymer chains with peroxide and then the crosslinking of the functionalized SEBS in the presence of UV-light as illustrated in Figure 1. A bifunctional molecule was used: 4-vinyl-1-cyclohexene 1,2-epoxide (VCHO); this molecule has a vinyl group for the grafting step and an epoxy group for the crosslinking step. This monomer has already been photocrosslinked in stereolithography after having been grafted via its vinyl bond by hydrosilylation onto silicones [21]. However, the radical reactivity of VCHO vinyl group has not been described in the literature to our knowledge since it is not very reactive with the double bond being not activated[22].
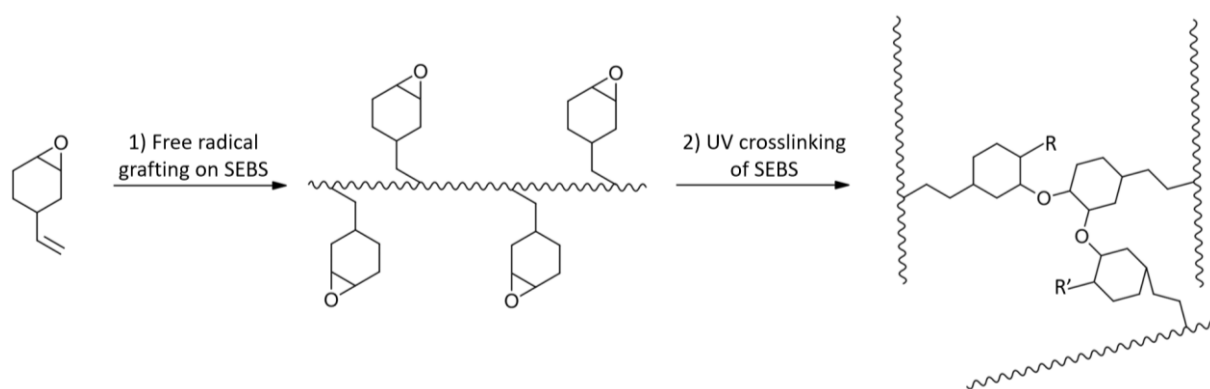
Figure 1: Proposed post-polymerization modification strategy to obtain a UV crosslinkable SEBS (with R and R' being groups of initiating and terminating species from cationic polymerization with onium salts).

Photo-crosslinking reactions induced by UV light are of growing interest in various fields, such as protective coatings, graphic arts, microelectronics, dental applications, and can find applications in various polymer processes such as stereolithography [23-25]. This chemical crosslinking technique has a number of economic advantages in comparison to thermal crosslinking systems. Among those advantages, rapid curing, chemioselectivity and low energy requirements are most cited [25].

Photo-induced cationic polymerization is nowadays expanding and many routes have been developed [26-28]. It was discovered by Crivello[29, 30] at the end of the 1970s. He observed that under UV irradiation, onium salts (triphenylsulfonium or diarylsulfonium) generate Brönsted acids able to undergo cationic polymerization of vinyl and epoxy monomers [30]. The efficiency of these onium salts mainly depends on their nucleophilicity, degree of acidity, and solubility in the particular polymer resin, which is directly linked to the polymer resin polarity and the anion's charge. The solubility of the salt generally increases with an increasing anion size which allows the charge to be dissipated. Thus, the solubility of the onium salt in the resin increases as follows: $BF_4^-<PF_6^-<AsF_6^-<SbF_6^-$. For this reason, antimony salts are used more often as cationic photoinitiators [30]. Beside solubility, spectroscopic properties such as light absorption and bond cleavage efficiency of the onium salt should be considered. In this study, we investigated the photo-polymerization of functionalized SEBS with VCHO groups using triarylsulfonium hexafluorophosphate salt. This photoinitiator is known to have a good UV absorption at a wavelength of $\lambda=300$ nm [29, 31]. This salt helps open the epoxy rings with subsequent polymerization, hence allowing UV selective crosslinking of the cycloaliphatic epoxide functionalized SEBS network. With the photo-crosslinkability demonstrated, the SEBS

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based resin was then tested as adherent coating and also for its potential in additive manufacturing by stereolithography.

2. Materials and methods

2.1. Materials

4-vinyl-1-cyclohexene 1,2-epoxide, 2,5-Bis(tert-butylperoxy)-2,5-dimethylhexane and cationic triarylsulfonium hexafluorophosphate photo-initiator mixed 50 % in propylene carbonate were purchased from Sigma-Aldrich (France) and used as received. Vikoflex® 7190 epoxidized linseed oil (ELO) was purchased from Arkema. Poly(styrene ethylene butylene styrene) SEBS Kraton™ G 1650 ES (30 wt.% of styrene) was kindly provided by Kraton™ Corporation (Netherlands).

2.1.1. Free radical grafting of 1,2-epoxy-4-vinylcyclohexane onto SEBS procedures

Grafting was performed in the bulk. Before grafting, SEBS (as fluffy crumb with very low density) was compressed in 2 mm thick sheets at 200 °C under 100 bar. They were then cut in squares of 5 mm × 5 mm and 1 g was added to the Schlenck tube. The solution of 4-vinyl-1-cyclohexene 1,2-epoxide and 2,5-Bis(tert-butylperoxy)-2,5-dimethylhexane was then slowly added with a syringe which swelled the copolymer. The Schlenck tube was then cooled down with liquid nitrogen for 5 min while applying vacuum and nitrogen. All syntheses were carried out in the Schlenck tube under nitrogen at 135 °C for 4 h. At the end of the reaction, the product was solubilized in 30 mL of toluene at 80 °C for 2 h and then slowly precipitated in 300 mL of cold methanol. This step was repeated 3 times to assure the excess of 1,2-epoxy-4-vinylcyclohexane was entirely removed. The obtained product was then dried in vacuum oven at 60 °C during 24 h and analyzed by ^{1}H nuclear magnetic resonance (NMR) and steric

chromatography (SEC). No homopolymer of VCHO was observed after evaporation of the solvents[22].

2.1.2. Irradiation of grafted SEBS

0.500 g of SEBS and SEBS-*g*-VCHO samples were solubilized in 5 mL of dichloromethane at room temperature overnight. Then 0.015 g of triarylsulfonium hexafluorophosphate were added to the solution. A part of the solution was deposited on a glass surface. In the presence of dichloromethane, the irradiation was performed immediately after. Also, without dichloromethane, the solvent was evaporated at room temperature overnight before performing the irradiation. Then, the samples were immersed again in 5 mL of dichloromethane to evaluate if they were soluble (not crosslinked) or swollen (crosslinked).

2.1.3. Preparation of thin film surface coatings

Solutions of SEBS in toluene were prepared in the absence of light as follows: 5 g of SEBS were incorporated into 30 mL of toluene at 80 °C for 4 h with stirring and 1 h without stirring in order to limit the presence of bubbles in the material. In the case of sample SB-VCHO$_1$-P$_{0.075}$, 0.075 g of triarylsulfonium hexafluorophosphate was added with a syringe after the first 4 h of mixing at 80 °C. Then, solutions were processed as films with an Elcometer 4340 Automatic Film applicator, with a 0.5 µm spiral bar coater. The obtained films were slowly dried in a vented oven at room temperature in the dark during 24 h to remove toluene without creating bubbles or cracks in the material. After evaporation of solvent, the films exhibited a thickness of 0.140 ± 0.003 mm. Samples were exposed to the radiation of a mercury lamp for 0, 1, 5 or 10 min in air and at room temperature.

2.1.4. Built samples by stereolithography DLP

3D objects were printed from a liquid resin composed of SEBS/ELO/Anisol at 1/1/4, including triarylsulfonium hexafluorophosphate as photo-initiator and 2-Isopropylthioxanthone (ITX) as

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photo-sensitizer in proportion 6 % and 3 %, respectively regarding the amount of polymer and oil. A Digital Light Processing (DLP) Max X27 apparatus (Asiga, Australia) with a UV light projector at 385 nm and light intensity of 40 mW/cm² was used. An irradiation time of 80 s was necessary to cure 100 µm thick layers. After fabrication, the 3D objects were washed with dichloromethane (DCM) and dried at room temperature.

2.2 Instruments and characterization

2.2.1. 1H-NMR Analyses

Nuclear Magnetic Resonance (NMR) analyses were performed at the Laboratoire de Mesures Physiques of the University of Montpellier, France. ^{1}H NMR Spectrometry was performed on a 400 MHz Brüker Aspect Spectrometer (Brüker, Germany) with $CDCl_3$ as deuterated solvent. The determination of the grafting rate was performed on a 600 MHz ^{1}H NMR Brüker Avance III. The reference peak was residual $CDCl_3$ at 7.26 ppm.

2.2.2. Size Exclusion Chromatography Analyses

Number-average (Mn) and weight-average (Mw) molar masses, as well as the dispersity Đ were obtained by size exclusion chromatography (SEC) at a flow rate of 1.0 mL/min at 30 °C. SEBS and SEBS-g-VCHO samples were first solubilized at 1 mg.mL^{-1} in HPLC grade tetrahydrofuran (THF, Fisher Scientific, Hampton, NH). Solutions were filtered through a 0.2 µm syringe filter. The SEC apparatus was composed of (a) a Varian 290-LC pump injection module, and a 1260 Infinity II degasser (Agilent Technologies, Santa Clara, CA); (b) a PL-AS RT sample changer (Polymer Laboratories, Shropshire, UK); (c) one PLgel 5 µm guard precolumn and two PLgel 5 µm Mixed-D columns (Agilent Technologies) maintained at 30 °C; (d) a Smartline UV Detector 2500 (Knauer, Berlin, Germany) set at 254 nm; and (e) a refractive index (RI) detector and a Varian 390-LC (Multi Detector Suite) viscosimeter maintained at 30 °C. The RI and

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viscosity data were acquired using Cirrus Multi GPC/SEC software. Universal calibration was performed using polystyrene standards from Agilent Technologies (EasiVial).

2.2.3. UV irradiation

Irradiations of SEBS and SEBS-*g*-VCHO formulations were performed in air at room temperature (23 °C) with a Crosslinker box UVP, CL-1000, 365 nm, 100 J.cm^{-2} (VWR International SAS France).

2.2.4. Gel Content and swelling ratio measurements

UV irradiated SEBS-g-VCHO samples were weighed (m_1) before being swollen in dichloromethane at room temperature for 24 h. They were after carefully removed from solution using tweezers, and weighed immediately after (m_2).

The samples were then dried at room temperature under vacuum until a constant mass (m_3) was reached. Gel content and swelling ratio were calculated respectively from equation (1) and (2):

$$gel\ content\ = \frac{m_3}{m_1} \times 100 \quad (1)$$

$$swelling\ ratio\ = 1 + (m_2 - m_3) \times \frac{\rho_{SEBS}}{\rho_{DCM}} = q \quad (2)$$

with respectively ρ_{SEBS} and ρ_{DCM} the density of SEBS (0.91) and the density of dichloromethane (1.33).

2.2.5. Tensile tests

Stress-strain measurements were performed at room temperature (23 °C) and 50 % of relative humidity on an Instron 3366L5885 tensile test machine with a 10 N load cell with a preload of 0.1 MPa and. Data were directly obtained from the cross head displacement.

The ISO 527-2 5B-type specimens were 2 mm wide and 60 mm long and were cut from thin films. Before testing, the dimensions of each specimen were measured three times. Tensile tests were carried out at a strain rate of 50 mm/min and a preload of 0.1 MPa was applied. Young's moduli were calculated from the slope of the stress-strain curves according to ISO 527-1 standard. The reproducibility was evaluated over 5 samples.

2.2.6. Cross-cut adhesion tests

This method is inspired from ISO 2409 standard devoted to the evaluation of the adhesion of paint coatings. A cross-cut grid was realized on the SEBS, SEBS-*g*-VCHO and the UV irradiated SEBS-*g*-VCHO coatings using a scalpel. Parallel cuts at 5 mm spacing were made in the direction of coating application, followed by perpendicular cuts (also at 5 mm spacing) to form a cross-cut grid. The resistance of the coating to removal from the substrate was then evaluated. A tape was firmly placed over the cross-cut grid, parallel to one set of cuts. After 5 min, the tape was quickly pulled off the coating. The cross-cutted surface on the coating was then visually examined to assess the extent to which the coating had been removed off the metal plate. The coating's removal was evaluated according to cases presented in Figure 2, a high score indicating a poor adhesion to the substrate.

Score	Cross-cut surface appearance	Evaluation of adhesion

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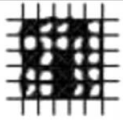|		
0	Surface unaffected	
1		Small flakes of coating are detached at intersections. Less than 5 % of the area is affected
2		Small flakes of coating are detached along edges and at intersections of cuts. The area affected is 5 % to 15 % of the lattice.
3		The coating has flaked along the edges and at parts of the squares. The affected area is 15 % to 35 % of the lattice.
4		The coating has flaked along the edges of cuts in large ribbons and entire squares have detached. The area affected is 35 % to 65 % of the lattice.
5	Flaking and detachment in excess of 65 %	

Figure 2: Scoring patterns classification of the cross-cut adhesion test (according to ISO 2409 standard).

3. Results and discussion

Radical grafting of SEBS has been investigated after swelling of the copolymer with the monomer and initiator mixture. Low quantities of added monomer in respect to copolymer were not tested since in these conditions since all the copolymer was not homogeneously swollen by the monomer. Various experimental parameters and characterizations of the functionalized SEBS were conducted using various techniques:

3.1. ^{1}H-NMR Analyses

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The ^{1}H NMR analyses of the purified copolymer demonstrated the grafting of the VCHO monomers onto the SEBS backbone (the ^{1}H NMR spectrum S1 of pristine SEBS is given in E.S.I.). The spectra exhibit two peaks at δ = 3.13 ppm and δ = 3.18 ppm which correspond to the protons bound to the epoxide ring. On the other hand, no peak was detected at δ = 4.93 ppm and δ = 5.69 ppm showing the total disappearance of the vinyl bonds, and their reactivity in radical grafting onto SEBS (see Figure 3).
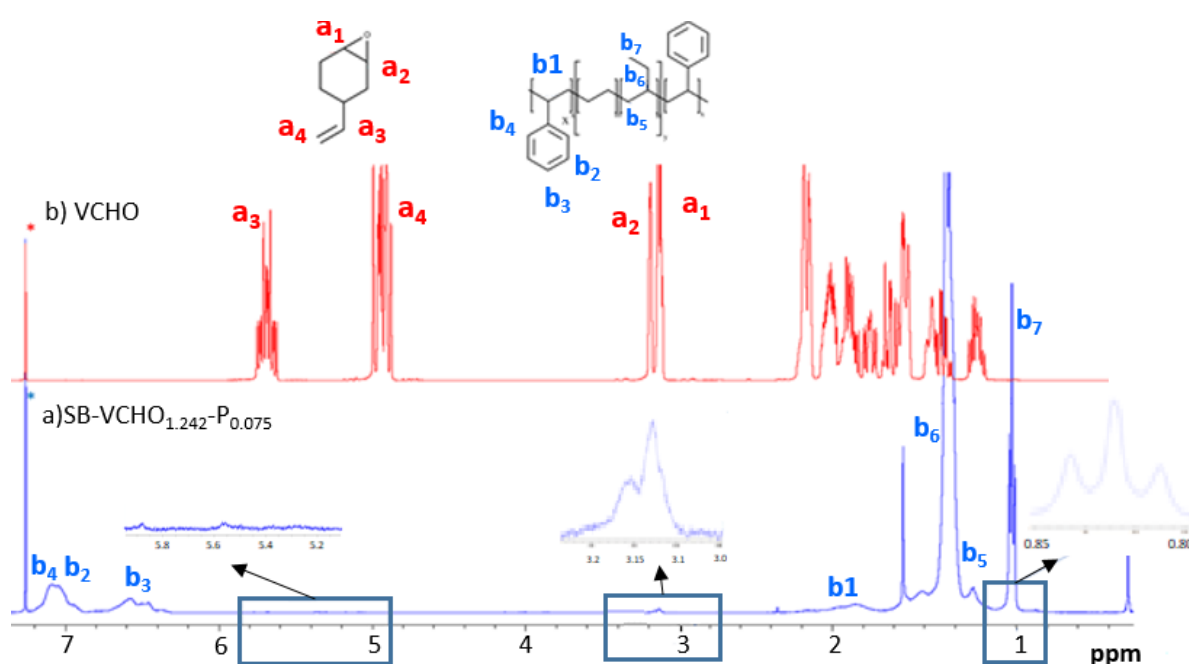

Figure 3: ^{1}H NMR Spectrum of VCHO monomer (above) SB-VCHO$_{1.242}$-P$_{0.075}$ polymer (below) (*CDCl$_3$).

Various experiments were conducted to highlight the suitable peroxide/monomer ratio for successfully carrying out the grafting without crosslinking SEBS copolymer (Table 1). According to experiments, SB-VCHO$_{1.242}$-P$_{0.05}$, SB-VCHO$_{0.75}$-P$_{0.05}$ and SB-VCHO$_{0.5}$-P$_{0.05}$, an amount of peroxide of 2.10^{-4} mol per gram of copolymer or less do not allow grafting of the monomer regardless of the quantity of monomer added. On the other hand, SB-VCHO$_1$-P$_{0.15}$, SB-VCHO$_{0.75}$-P$_{0.15}$ and SB-VCHO$_{0.5}$-P$_{0.15}$ with a large amount of peroxide higher than 5.10^-

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[4] mol per gram cause an unwanted in-situ crosslinking of the SEBS. In summary, 3.10^{-4} mol of peroxide per gram of SEBS allows successful grafting of VCHO. The grafting rate was calculated from integrations of protons a_1 and a_2 in respect to aromatic protons (Figure 3).

Table 1: Comparison of the different grafting procedures of VCHO onto SEBS using various amounts of peroxide and VCHO

Experiment	VCHO (g)	VCHO (mol)	Peroxide (g)	Peroxide (mol)	Result	Grafting rate (wt.%)
SB-VCHO$_1$-P$_{0.15}$	1.00	0.008	0.150	0.0005	Crosslinking	-
SB-VCHO$_{0.75}$-P$_{0.15}$	0.75	0.006	0.150	0.0005	Crosslinking	-
SB-VCHO$_{0.5}$-P$_{0.15}$	0.50	0.004	0.150	0.0005	Crosslinking	-
SB-VCHO$_{7.45}$-P$_{0.075}$	7.45	0.060	0.075	0.0003	Grafting	2.7
SB-VCHO$_{1.242}$-P$_{0.075}$	1.24	0.010	0.075	0.0003	Grafting	2.6
SB-VCHO$_1$-P$_{0.075}$	1.00	0.008	0.075	0.0003	Grafting	2.8
SB-VCHO$_{0.75}$-P$_{0.075}$	0.75	0.006	0.075	0.0003	Grafting	2.8
SB-VCHO$_{0.5}$-P$_{0.075}$	0.50	0.004	0.075	0.0003	Grafting	2.5
SB-VCHO$_{1.242}$-P$_{0.05}$	1.24	0.010	0.050	0.0002	No grafting	-
SB-VCHO$_{0.75}$-P$_{0.05}$	0.75	0.006	0.050	0.0002	No grafting	-
SB-VCHO$_{0.5}$-P$_{0.05}$	0.50	0.004	0.050	0.0002	No grafting	-

Surprisingly, the results show that the grafting rate is close to 2.7 wt./wt.% regardless of the monomer quantity in the mixture. In our experimental conditions, that is to say with SEBS swollen with monomer, the quantity of grafted monomer is limited to this percentage. However,

removing excess monomer is challenging and a reaction operated in an extruder could permit to eliminate excess monomer avoiding also subsequent purification steps[32, 33].

A grafting test was also performed in the same experimental conditions (135 °C, 4 h) with the same amounts of monomer and peroxide as SB-VCHO$_{1.242}$-P$_{0.075}$ and in the presence of 0.075 g of triarylsulfonium hexafluorophosphate salt, the cationic photoinitiator used for the subsequent UV crosslinking of the modified SEBS. The ^{1}H NMR spectrum confirmed the efficient grafting of VCHO without crosslinking SEBS at the same time. Triarylsulfonium hexafluorophosphate salt did not disturb the grafting reaction. It is therefore possible to incorporate all the reagent at the same time, which is very interesting for reaction in the molten state and hot melt adhesives applications for example.

To be sure that VCHO was grafted onto SEBS copolymer, 2D DOSY ^{1}H NMR of VCHO and grafted copolymers was investigated (Figure 4).
The ^{1}H NMR spectrum shows without any doubt that the purified copolymer exhibits only one diffusion coefficient for VCHO (blue spots, 10^{-11}m^2.s). This coefficient is very different from that of pure VCHO (red spots, 10^{-8}m^2.s) meaning that VCHO is linked to the SEBS confirming its efficient grafting.
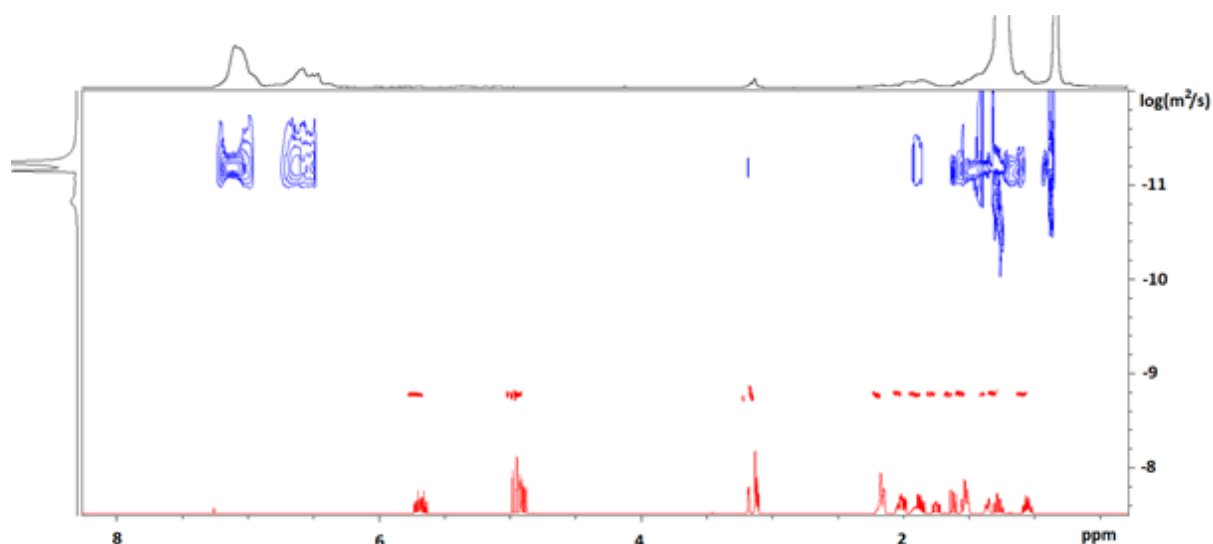
Figure 4: 2D DOSY^{1}H NMR spectrum of VCHO (below) and grafted copolymers (top).

3.2. Size Exclusion Chromatography Analyses

SEC results are gathered in Table 2 and Figure 5. A notable increase of Mn can be observed with decreasing quantity of monomer. Dispersity indexes regarding those trials confirmed coupling reactions. From a mechanistic point of view, it seems that when high quantities of VCHO are used, the grafting reactions are favoured instead of chain coupling.

Table 2: Evolution of molecular weight

Experiment	SEBS (g)	VCHO (g)	VCHO (mol)	ROOR (g)	Mn (g.mol^{-1})	Mw (g.mol^{-1})	Đ
SEBS Kraton G1650	-	-	-	-	94000	99900	1.06
SB-VCHO$_{7.45}$-P$_{0.075}$	1	7.45	0.0600	0.075	93600	104000	1.11
SB-VCHO$_{1.242}$-P$_{0.075}$	1	1.24	0.0100	0.075	97000	115500	1.22
SB-VCHO$_1$-P$_{0.075}$	1	1.00	0.0080	0.075	108100	157000	1.45
SB-VCHO$_{0.75}$-P$_{0.075}$	1	0.75	0.0060	0.075	109300	160000	1.46

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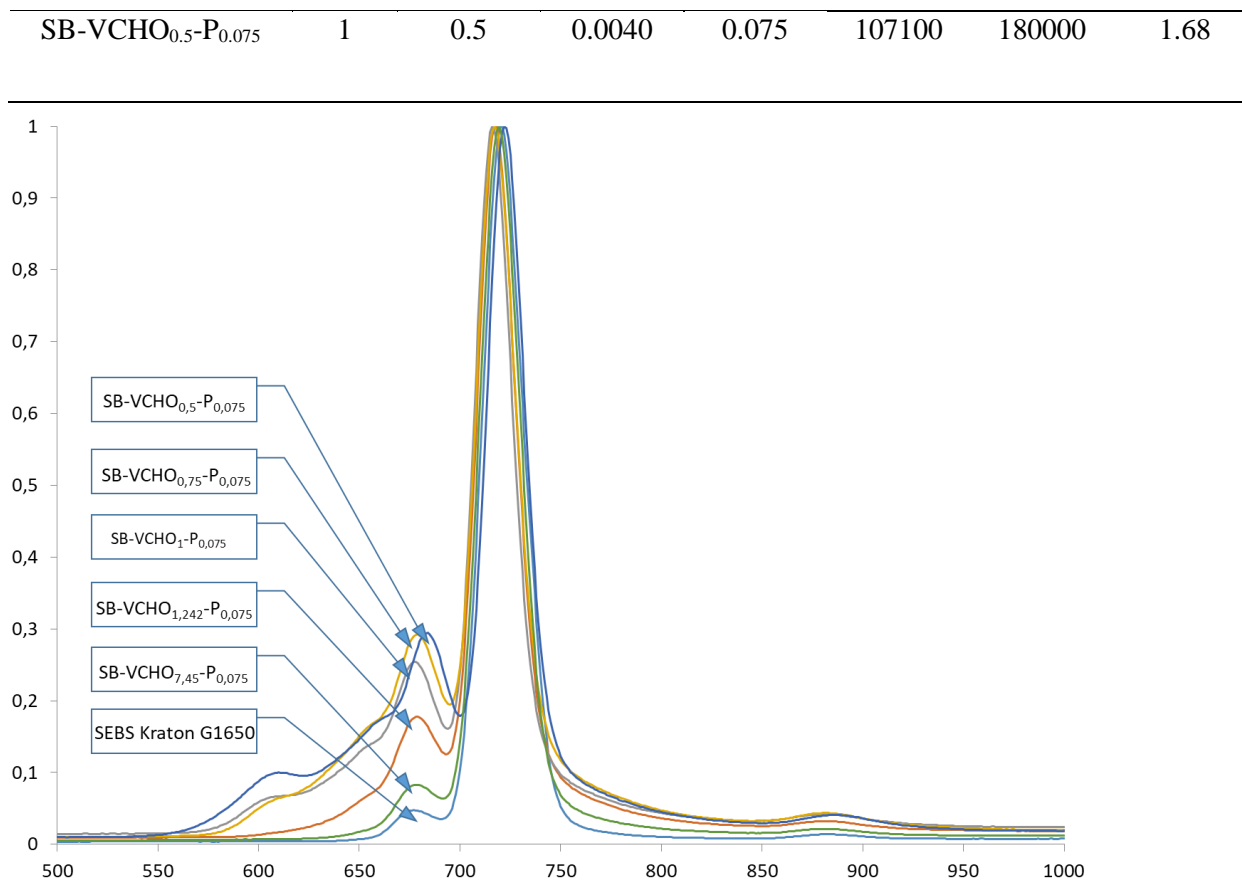|							
SB-VCHO$_{0.5}$-P$_{0.075}$	1	0.5	0.0040	0.075	107100	180000	1.68

Figure 5: SEC traces of the various grafted copolymers from experiments of Table 1.

3.3 UV irradiation and evaluation of the gel content and swelling ratio

Prior to the study of polymer crosslinking, the reactivity of monomer alone was studied. Polymerization and conversion rate of VCHO monomer in the presence of 1.5 wt.% of triarylsulfonium hexafluorophosphate salt under UV light was assessed via ^{1}H NMR by comparing the integration areas of the signals from protons close to the epoxide ring with those close to ether links after ring opening (Figure 6 and 7). We observed a rapid conversion of the epoxide ring which reached 92 % after 1 min. A plateau was reached for longer irradiation times with a maximum of 94 % conversion rate. This reactivity is drastically higher than for glycidyl based epoxides making them useful for industrial photopolymerization processes requiring fast curing [34].
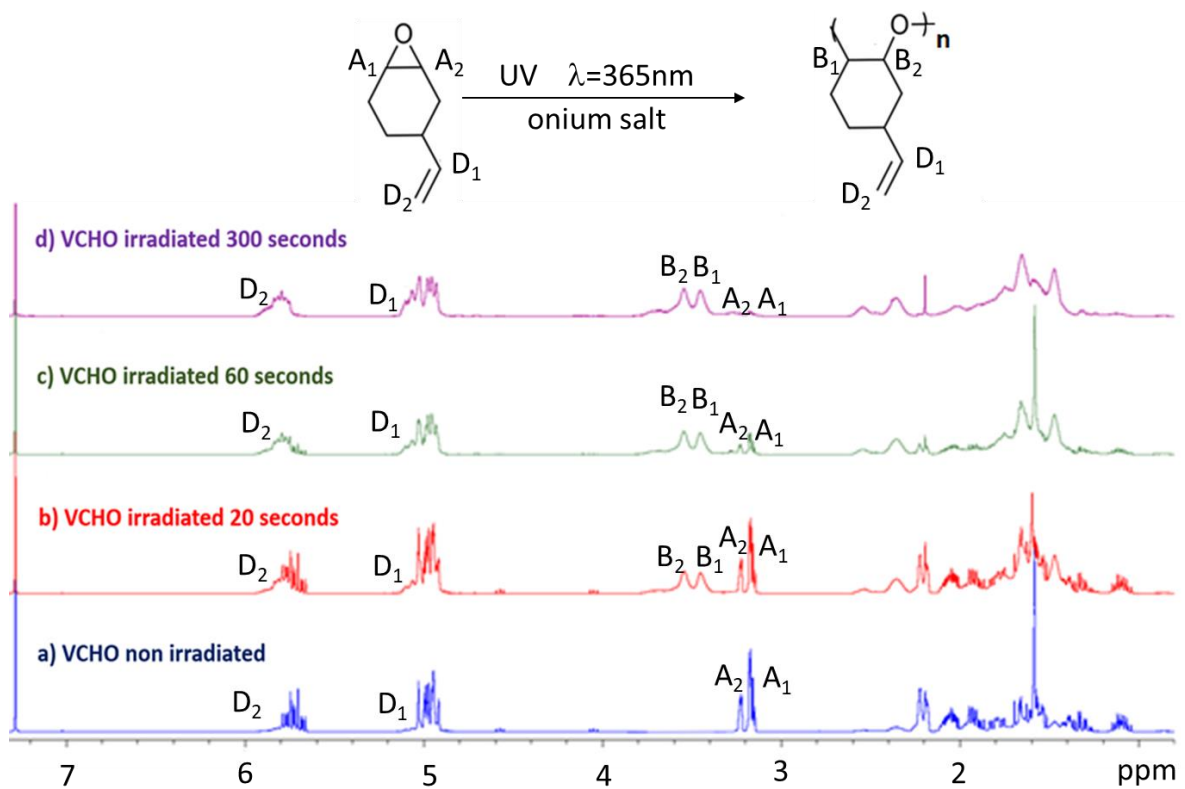
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Figure 6: ^{1}H NMR Spectrum of VCHO monomer (above) and irradiated VCHO (below) (CDCl$_3$).
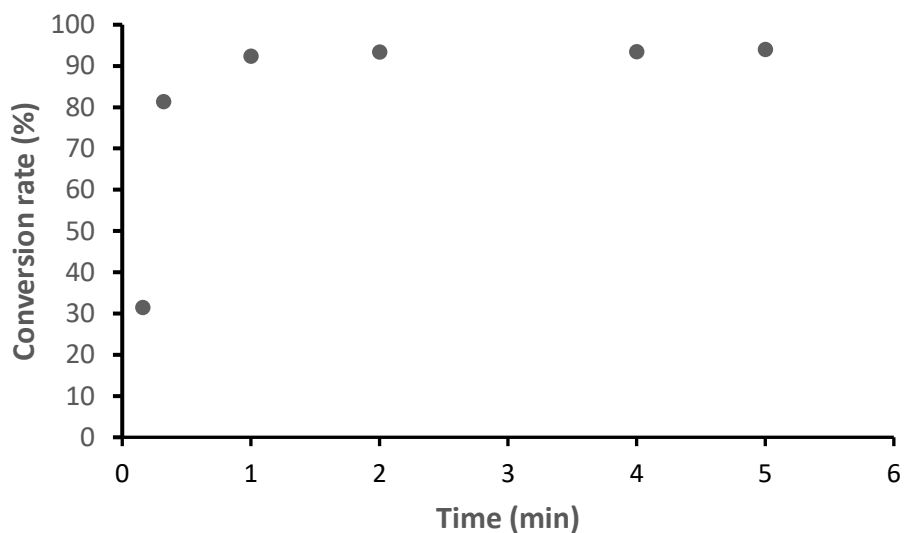

Figure 7: Evolution of conversion rate of cycloaliphatic rings with 1.5 wt.% of triarylsulfonium hexafluorophosphate as a function of irradiation time (365 nm, 100 J.cm^{-2}).

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Considering the previous results, various irradiations have been performed in bulk or in solution on virgin SEBS and SEBS-*g*-VCHO with and without triarylsulfonium hexaflurophosphate (Table 3). Those tests revealed that only SEBS-*g*-VCHO was able to be UV-crosslinked. Crosslinking occurred even in the solid state, i.e. without dichloromethane, which shows the good reactivity of the grafted cycloaliphatic epoxides.

The swelling ratio reflects the quantity of solvent absorbed by the material (here dichloromethane) which is directly related to the crosslinked network density (Table 4). The higher the swollen volume fraction, the lower the crosslinking density. This expected low crosslinking density can be attributed to the low degree of grafting of with 4-vinyl-1-cyclohexene 1,2-epoxide on SEBS and the significant distance between the crosslink junctures. After 5 min of UV exposure, the gel content of all the evaluated products were all above 85 %, meaning that the crosslinking was very efficient with a few volume of material excreted.

Table 3: Evaluation of the crosslinking ability of different SEBS formulations

	With DC		Without DCM	
UV Exposure time	5 min	1 min	5 min	1 min
SEBS	No crosslinking	No crosslinking	No crosslinking	No crosslinking
SEBS with triarylsulfonium salts	No crosslinking	No crosslinking	No crosslinking	No crosslinking
SEBS-*g*-VCHO	No crosslinking	No crosslinking	No crosslinking	No crosslinking
SEBS-*g*-VCHO with triarylsulfonium salts	Crosslinking	Crosslinking	Crosslinking	Crosslinking

Table 4: Evaluation of the gel content and swelling degree of different SEBS-*g*-VCHO

Experiment	SEBS (g)	VCHO (g)	VCHO (mol)	ROOR (g)	Gel content (%)	Swelling ratio q
SB-VCHO$_{7.45}$-P$_{0.075}$	1	7.45	0.0600	0.075	89	≈4
SB-VCHO$_{1.242}$-P$_{0.075}$	1	1.24	0.0100	0.075	86	≈4
SB-VCHO$_{1}$-P$_{0.075}$	1	1.00	0.0080	0.075	86	≈4
SB-VCHO$_{0.75}$-P$_{0.075}$	1	0.75	0.0060	0.075	90	≈4
SB-VCHO$_{0.5}$-P$_{0.075}$	1	0.50	0.0040	0.075	87	≈4

A strong excess of VCHO monomer during the grafting (see SB-VCHO$_{7.45}$-P$_{0.075}$ experiment) does not allow a significantly higher gel content to be attained. Those slight variations of the gel content suggest an equivalent grafting rate, independently of the quantity of monomer used during the grafting step. This result contradicts traditional grafting experiments which usually shows linearly increasing functionality with increasing monomer amount. The swelling ratio q is close to 4 for all products. The large uncertainty in the volume measurements of the recovered swollen SEBS fractions does not allow observation of accurate and significant differences between the various samples.

3.4. Tensile tests

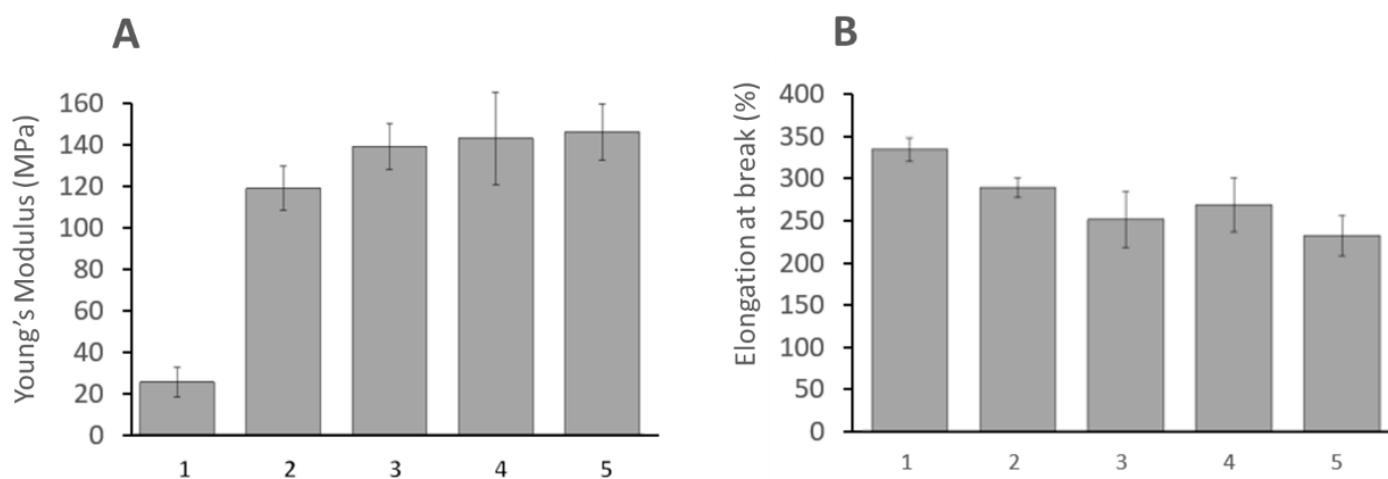Tensile tests revealed a significant increase of the Young's modulus of the modified SEBS (Figure 8A).

Figure 8: (A) Evolution of the Young's modulus of SEBS-g-VCHO regarding its UV exposure and comparison with virgin SEBS. (B) Evolution of the elongation at break of SEBS-g-VCHO

regarding its UV exposure and comparison with pristine SEBS. (1= SEBS, 2= SEBS-VCHO$_1$-P$_{0.075}$, 3= SEBS-VCHO$_1$-P$_{0.075}$-irr.1mn, 4= SEBS-VCHO$_1$-P$_{0.075}$-irr.5mn, 5= SEBS-VCHO$_1$-P$_{0.075}$-irr.10mn)

Comparing the non-irradiated SEBS-VCHO1-P0.075 sample with pristine SEBS shows a hugh increase in Young's modulus.   The irradiation of the VCHO modified SEBS does not lead to significantly higher moduli regardless of irradiation times taking into account standard deviations and the student test statistics. Thus, irradiation of the samples seems to only crosslink the materials as showed in Table 4 without a clear effect on their rigidity.

For all VCHO modified materials, the elongation at break is moderately diminished after irradiation due to crosslinking effect. Again, in view of the standard deviations, there is no significant differences for the elongation at break of SEBS-g-VCHO UV irradiated 1, 5 and 10 minutes (Figure 8B). However, the material maintains its elasticity after irradiation in respect to pristine SEBS.

The insensitivity of mechanical properties to longer irradiation times could be because traces of water inhibit cationic polymerization. However, this hypothesis was rejected because of the room temperature drying of every product.
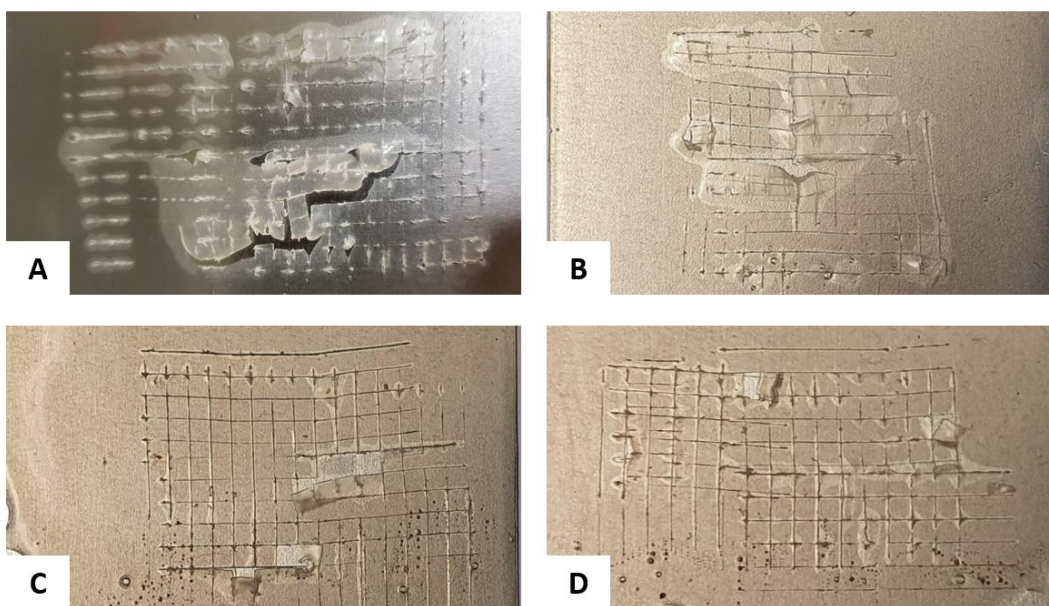
3.5. Cross-cut adhesion tests

Figure 9: Cross-cut test pattern of (A) SEBS; (B) SEBS-*g*-VCHO non UV-irradiated; (C) SEBS-*g*-VCHO UV irradiated 1 min; (D) SEBS-*g*-VCHO irradiated 10 min.

Cross-cut tests presented in Figure 9 confirm the improvement of the adhesion properties of SEBS via the grafting of VCHO and its subsequent UV-irradiation. Pristine SEBS has a poor adhesion onto the metal substrate. This formulation can be scored 5 according to the cross-cut test pattern classification. The non-irradiated SEBS-*g*-VCHO can be classified as 4 with only 50 % of the surface affected; the grafting of the epoxide group improved adhesion because the polarity of the polymer was enhanced. Crosslinking caused by UV irradiation greatly improve the adhesion properties of the coating, with a score of 2. However, there is no significant improvement of adhesion properties between formulations irradiated 1 min and 10 min confirming the fast kinetics of polymerization of VCHO reported in Figure 7 and thus, the rapid crosslinking reaction.

The ability of SEBS to photo-crosslink was also highlighted in the context of additive manufacturing. We therefore investigated the potential of the developed photosensitive SEBS to be processable by stereolithography (SLA)[35-37]. For that, the photosensitive SEBS-*g*-VCHO was dissolved in anisol, which is a non-reactive solvent, in the proportion to get a suitable

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viscosity (~5 Pa.s). However, despite the previous photo-crosslinking success of the SEBS-*g*-VCHO resin in the UV-box, the photo-polymerization in the SLA apparatus did not reach sufficient curing to build a layer. We therefore, increase the photo-reactivity by adding a biosourced epoxidized linseed oil (ELO) which has been already used for SLA [38, 39]. However, crosslinked epoxidized oils lead to stiff and brittle materials due to their high crosslink density. Therefore, in this study we combined the SEBS-*g*-VCHO with the ELO resin, which makes SEBS resin photo-processable by SLA and generates a flexible and elastic 3D object based on ELO resin.
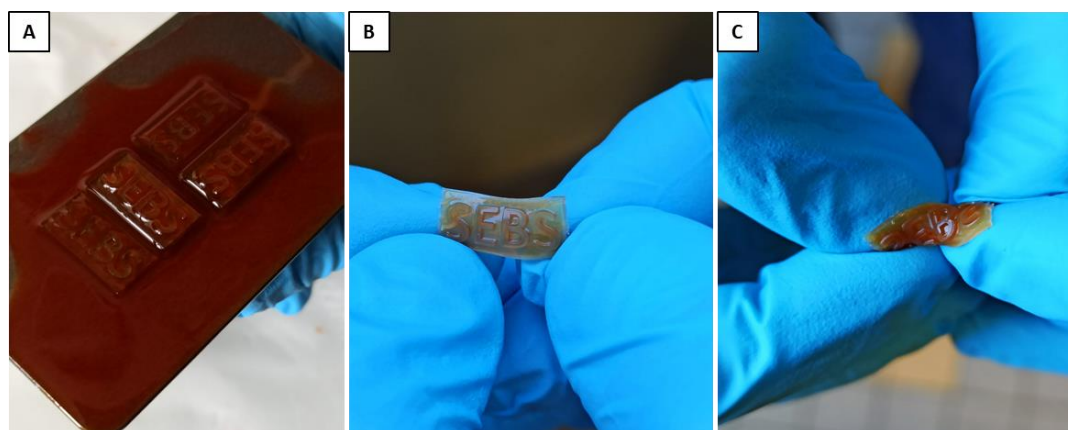

Figure 10: (A) 3D structures based on SEBS-*g*-VCHO built by SLA; (B) Hand stretching on the built 3D structure that shows the traction resistance; (C) Hand torsion on the built 3D structure that shows the flexibility.

Such SEBS-*g*-VCHO and ELO combined resin was successfully used by SLA to build a proof of concept representing "SEBS" in relief (Figure 10A). In Figure 10B and 10C, the reversible deformations achieved by manual traction and torsion highlight the compliance of the material which cannot be achieved by the sole use of the ELO resin which gives a brittle material. This proof of concept is the first demonstration of fabrication by SLA using a photosensitive resin based on SEBS.

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4. Conclusion

This study shows that radical grafting of epoxide groups onto SEBS can be achieved via free radical grafting. The functionalized copolymer was crosslinked in 1 min with UV irradiation causing cationic polymerization and produced an elastomeric material. Young's modulus and the adhesion performance onto a metallic substrate of the UV-crosslinked modified SEBS significantly increased vs SEBS alone, while the elongation at break only decreased slightly after crosslinking.

This new type of UV-curable thermoplastic elastomer could have potential applications such as coatings. Also, SEBS is of interest for additive manufacturing technologies such as laser sintering and fused filament fabrication [40, 41]. However, the implementation of high molecular weight polymers in photocuring process such as stereolithography remains challenging. Some recent attempts focused on stereolithography of non-reactive styrene butadiene rubber latex[42] dispersed in monomer precursors of a scaffold hydrogel leading after photopolymerization to a continuous bi-phasic system. Here, the formulation of SEBS-*g*-VCHO and ELO appears to be a more stable resin formulation than latex formulation overtime and therefore probably more suitable. As demonstrated with a proof-of-concept experiment, this epoxy group functionalization strategy could be an innovative opportunity to directly involve high molecular weight elastomers in a crosslinked network.SEBS-*g*-VCHO could also potentially be used for compatibilization for specialized polymers blends, similar to how SEBS modified with maleic anhydride, glycidyl methacrylate or itaconic acid are used.

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Supporting Information

Modification of Poly(styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene) via free radical grafting and its photo-crosslinking

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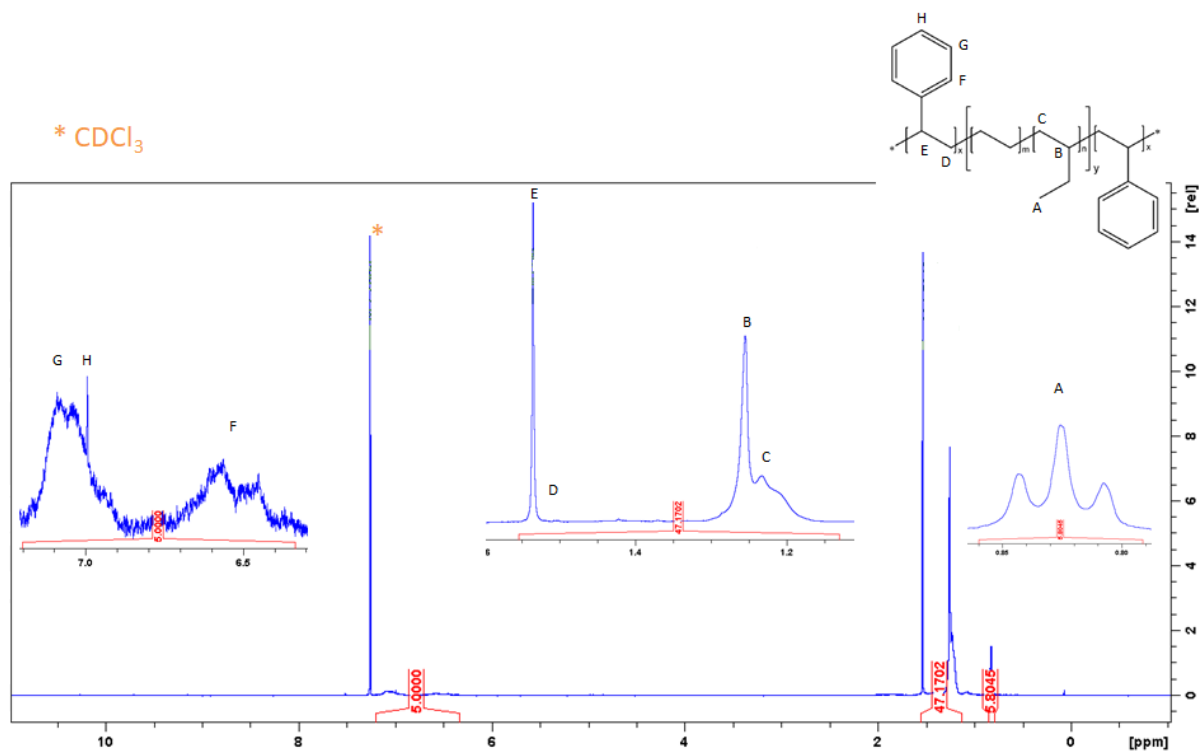

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Figure S1 : NMR Spectrum of pristine SEBS