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Photocrosslinking of functionalized rubbers IX. Thiol-ene polymerization of styrene-butadiene-*block*-copolymers

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Abstract

A thermoplastic elastomer, polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) with a high vinyl content (59%), was crosslinked within a fraction of a second by UV-irradiation in the presence of a trifunctional thiol and an acylphosphine oxide photoinitiator. The curing process was followed by IR spectroscopy, insolubilization and hardness measurements. Both the thiol and the photoinitiator concentrations were shown to affect the kinetics of the thiol–ene polymerization. Insolubilization was found to occur even at very low concentrations in thiol ($\leq$1 wt%) and in photoinitiator (0.1 wt%). The heat resistance of the photosensitive formulation is high enough at 150°C to allow this system to be used for hot-melt adhesive applications. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Photochemistry; Crosslinking; UV-curing

1. Introduction

Three-dimensional polymer networks can be readily generated by photoinitiated polymerization of multifunctional monomers or of polymers bearing reactive functions [1]. This technology has been mainly used, so far, to perform a quasi-instantaneous liquid to solid phase change, a process called UV-curing. But it can also serve to transform irreversibly a soluble polymer into an insoluble material showing improved resistance to elevated temperatures and chemicals. Among the various functionalized polymers studied so far, promising results have been obtained with rubber-type elastomers bearing epoxy rings [2–4], acrylate functions [5,6] or vinyl [7,8] double bonds on the main chain. Crosslinking was achieved within seconds upon UV exposure in the presence of a cationic type or radical-type photoinitiator, respectively. The main advantages of using light to initiate the chain reaction, besides the rapidity of the curing process, consist in the solvent-free formulations, the low energy consumption, ambient temperature operations and control of the location and time of the process, which occurs specifically in the illuminated areas.

In a recent paper [8], we have shown that styrene–butadiene-*block*-copolymers (SBS) undergo a rapid crosslinking when they are exposed to UV radiation in the presence of a radical photoinitiator. Complete insolubilization requires the reaction of 17 double bonds per polymer chain for an SBS containing 8% pendent vinyl double bonds. These thermoplastic elastomers, known under the trademark KRATON®, have a two-phase morphology and are commonly used as pressure sensitive adhesives, in combination with a tackfying resin [9,10], and as flexographic printing plates [11]. UV-curing creates covalent bonds within the elastomeric phase, thus reinforcing irreversibly the already existing physical network. As a result, the photocured SBS becomes more resistant to high temperatures, the values of the Shear Adhesion Failure Temperature (SAFT) rising from 80°C to over 160°C [10].

The crosslinking process was markedly accelerated by adding to SBS a diacrylate monomer which copolymerizes with the polybutadiene vinyl and butene double bonds [8], but at the expense of the heat resistance, thus making the photosensitive material ill-suited for hot-melt adhesive applications. Another approach, which proved to be even more effective, consisted in incorporating a trifunctional thiol into SBS to perform crosslinking through a thiol–ene photopolymerization [12,13], according to the following reaction scheme:

$$\text{Photoinitiator} + \text{RSH} \xrightarrow{h\nu} \text{RS}^{\cdot}$$

$$\text{RS}^{\cdot} + \text{CH}_2\text{=CH–R}' \rightarrow \text{RS–CH}_2\text{–}\dot{\text{C}}\text{H–R}'$$

$$\text{RS} - \text{CH}_2\text{–}\dot{\text{C}}\text{H–R}' + \text{RSH} \rightarrow \text{RS–CH}_2\text{–CH}_2\text{–R}' + \text{RS}^{\cdot}$$

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The polymerization proceeds by a step growth addition mechanism which is propagated by a chain transfer reaction involving the thiyl radical ($RS^{\cdot}$) [14,15]. A thiol concentration of 5 wt% proved to be enough to increase 10-fold the insolubilization rate [16]. The heat resistance of the uncured formulation, although superior to the acrylate–SBS system, was still not sufficient to meet the specifications required for the manufacturing of hot-melt adhesives or flexographic printing plates (stability of the unreacted sample during 20 min upon processing at 150°C) [7]. Moreover, one of the major drawbacks of the polyene–thiol system lies in the bad smell of mercaptans, which is reduced as polymerization proceeds, the thiol becoming incorporated into the polymer network.

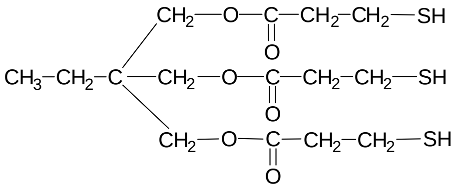
The main objective of the present study was to determine how much the thiol concentration can be reduced, without affecting substantially the reactivity, in order to improve the heat resistance of the photosensitive formulation, and reduce its smell as well. For the same reason, the concentration of the photoinitiator was also decreased, with the expected additional benefit of allowing thick samples to be deep-through cured, because of the increased penetration of UV radiation. The progress of the crosslinking reaction has been followed quantitatively through the insolubilization and hardening of the UV-exposed SBS-thiol sample, and by monitoring the disappearance of the polybutadiene double bonds by infrared spectroscopy.

2. Experimental

2.1. Materials

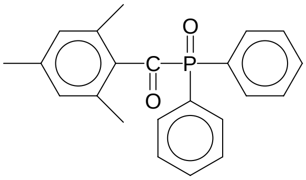
The polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) from SHELL used in this study contained 59% pendent vinyl groups, the 2-butenylene units ($-CH_2-CH{=}CH-CH_2$) located on the polybutadiene backbone representing 41% of the unsaturation content. Because of its relatively low styrene content (~15%) the SBS behaves similarly to a conventionally vulcanized rubber. A trifunctional thiol was selected as crosslinking agent, trimethylolpropane mercaptopropionate (TRIS) from Evans Chemetics. It was added to a toluene solution of SBS at concentrations between 0.2 and 5% by weight of SBS.

TRIS



Among the various radical-type photoinitiators tested, acylphosphine oxides proved to be the most efficient ones to photocrosslink SBS samples. All the experiments have been carried out by using 2, 4, 6-trimethylbenzoyl-diphenylphosphine oxide (Lucirin TPO from BASF) as photoinitiator, at a typical concentration of 1 wt%.

Lucirin TPO



2.2. Irradiation

In a typical UV-curing experiment, 20 μm thick films were cast from a toluene solution containing the SBS rubber, the thiol monomer and the photoinitiator onto either a KBr crystal for infrared analysis or a glass plate for insolubilization and hardness measurements. If a solvent-free process is required for industrial applications, the photoinitiator and the thiol can also be incorporated into the liquid resin heated at 150°C, the usual processing temperature. Samples were exposed at ambient temperature in the presence of air to the radiation of a 80 W/cm medium pressure mercury lamp (IST), at a passing speed of 60 m/min which corresponds to an exposure duration of 0.1 s per pass. The maximum light intensity at the sample position was measured by radiometry (IL-390 light bug) to be 600 mW cm^{-2} in the UV range.

2.3. Analysis

The kinetics of the light-induced crosslinking of the rubber film was studied quantitatively by FTIR spectroscopy, by following the decrease upon UV exposure of the absorption band characteristic of the vinyl double bond at 1827 cm^{-1}. The degree of conversion (x) was calculated from the ratio of the corresponding IR absorbance before and after UV exposure (A_0 and A_t) by using the following equation:

$$x(\%) = [1 - (A_t/A_0)] \times 100$$

This value was not corrected for shrinkage which was found to be insignificant, based on the invariance of the C–H peak at 2960 cm^{-1}. It should be mentioned that even very small variations of the IR band intensity can be monitored accurately, because the analysis is performed on the same sample exposed to UV light for various durations, exactly on the same spot.

The gel fraction and the degree of swelling of the irradiated polymer were determined by soaking the sample in toluene for one day at room temperature. The insoluble polymer was recovered by filtration and dried at 70°C to a constant weight. The hardness of the coating was evaluated before and after irradiation by monitoring the damping of the oscillations of a pendulum (Persoz hardness). The

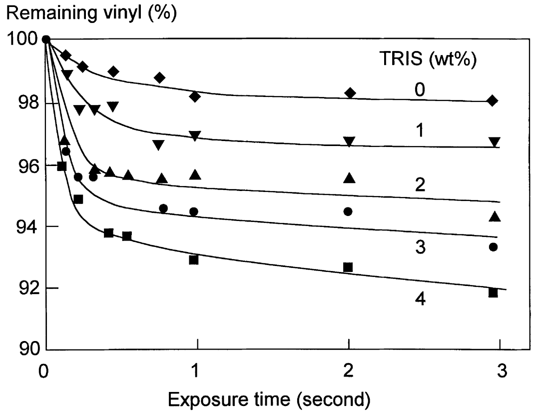
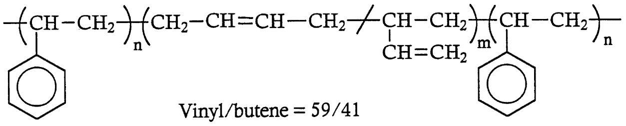


Fig. 1. Influence of the thiol concentration on the vinyl group consumption upon UV exposure of the SBS/TRIS system. [LucirinTPO] = 1 wt%.

hardness was shown to be strongly dependent on the glass transition temperature [17], with Persoz values ranging typically from 30 s for soft elastomeric materials to 300 s for hard and glassy polymers. The thermal stability of the various formulations was tested by heating the uncured sample for up to 1 h at 150°C, the processing temperature for hot-melt adhesive applications.

3. Results

In a previous study on the photocrosslinking of SBS rubber [16], we have shown that the thiol-ene polymerization proceeds much more efficiently with the pendent vinyl double bonds arising from 1-2 polymerization of butadiene than with the backbone 2-butene double bonds of the polybutadiene chain (by a factor 16). UV-curing experiments were therefore conducted on a specially designed SBS sample where as many as 59% of the polybutadiene unsaturations were vinyl double bonds.

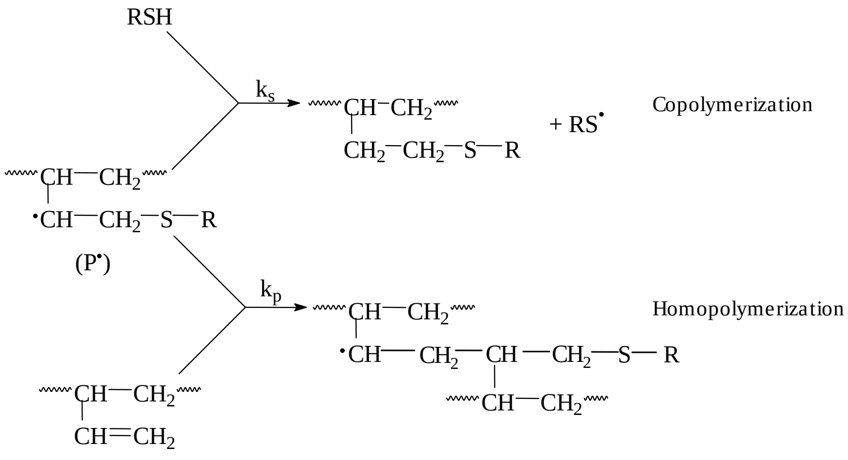


The formation of the polymer network in the elastomeric phase upon UV irradiation was followed through the vinyl group disappearance and the polymer insolubilization.

3.1. Loss of the vinyl group upon photocrosslinking of SBS

The SBS samples containing 1 wt% Lucirin TPO and various concentrations of TRIS (between 0.2 and 5 wt%) were exposed to UV radiation for different times, up to 3 s. The crosslinking reaction was monitored through the decrease of the vinyl IR band at 1826 cm^{-1}. Fig. 1 shows the influence of the thiol concentration on the decay profile of the vinyl group upon UV irradiation. The initial sharp drop which occurs within the first 0.3 s was attributed to the copolymerization with the thiol which is rapidly consumed. At a TRIS concentration of 5 wt%, as much as 90% of the thiol was found, by IR spectroscopy (band at 2566 cm^{-1}), to have reacted after this short exposure, as shown in Fig. 2.

As expected, the amount of vinyl groups polymerized $[V]_t$ after a given exposure (0.3 s) increases with the initial thiol content $[SH]_0$ (Fig. 3). Vinyl groups are also undergoing a radical induced homopolymerization reaction which can be quantified by substracting $[SH]_t$ from $[V]_t$. Fig. 3 shows how the ratio copolymerization/homopolymerization, calculated from the ratio $[SH]_t/([V]_t - [SH]_t)$, increases with the thiol concentration. The fact that the vinyl-thiol copolymerization is as important as the vinyl homopolymerization, even though the SH concentration (0.2 mol kg^{-1}) is much lower than that of the vinyl groups (9.3 mol kg^{-1}), clearly shows that the propagating alkyl radicals ($P^{\bullet}$) are much more reactive toward the thiol than toward the vinyl double bond.



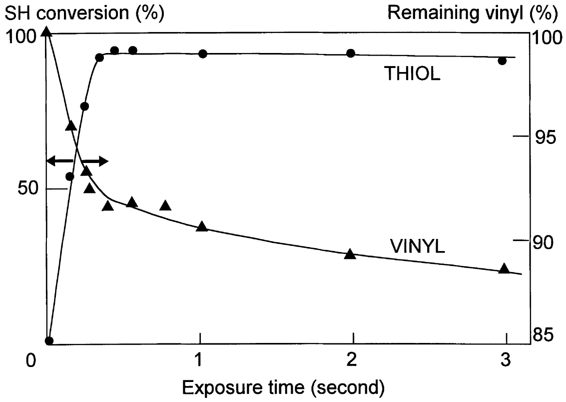


Fig. 2. Thiol conversion and vinyl loss in photocrosslinking of the SBS/TRIS system. [Thiol] = 5 wt%; [LucirinTOP] = 1 wt%.

The 2-butene double bonds of the polybutadiene chain do not contribute significantly to the crosslinking process as they were shown to be 16 times less reactive toward the thiyl radicals than the vinyl double bonds [16], and as they are in lower concentration. If allowance is made for them, the value of the copo/homo ratio in Fig. 3 would be roughly 10% lower.

3.2. Insolubilization

Both reactions of the vinyl groups, homopolymerization and copolymerization with the thiol, generate crosslinks between the polybutadiene chains, with formation of a tridimensional network which is schematically represented in Fig. 4. As a result, the UV-exposed polymer becomes insoluble in organic solvents, like chloroform or toluene. Fig. 5 shows the insolubilization profiles obtained at various concentrations of the thiol crosslinker, between 0.5 and 4 wt%. At a TRIS concentration of 1 wt%, a single pass under the lamp at a speed of 60 m/min proved to be sufficient to get a 90% insoluble material. This value did not change much upon further exposure, even when the TRIS content was increased to 4 wt%. This limiting value suggests that the SBS sample contains about 5% non polymeric materials.

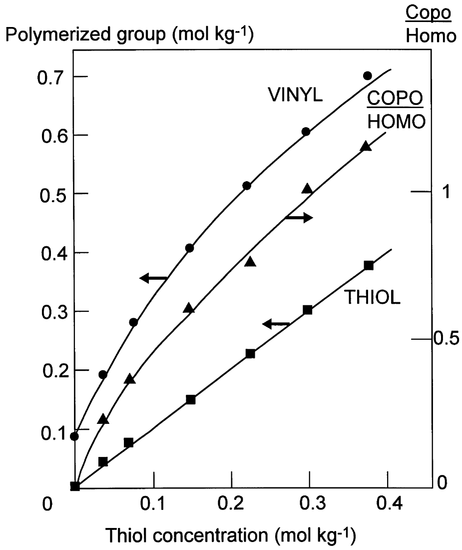


Fig. 3. Influence of the thiol concentration $[SH]_0$ on the amount of vinyl and thiol groups polymerized after a 0.3 s UV exposure of the SBS/TRIS system.

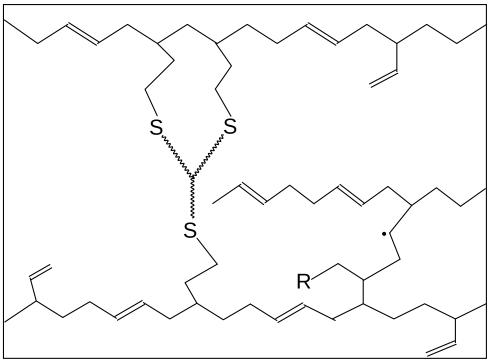


Fig. 4. Schematic representation of the photocrosslinked SBS/TRIS polymer network formed in the elastomeric phase.

In the absence of TRIS, a 30 times as long UV exposure (3 s) is needed to reach the same gel fraction, the vinyl consumption being evaluated to be only 2% of its original value, i.e. 0.18 mol kg^{-1}. This result suggests that the polymerization of the pendent vinyl double bonds is not a very effective crosslinking process in this SBS. The most probable reason is that, because of the high vinyl content (59% of the polybutadiene units), polymerization proceeds preferentially between neighboring vinyl groups to form six-membered rings along the polymer chain which remains soluble. However, because the polybutadiene chain contains 41% butene-2 units, the cyclization process will propagate along the polymer chain over only a few adjacent vinyl

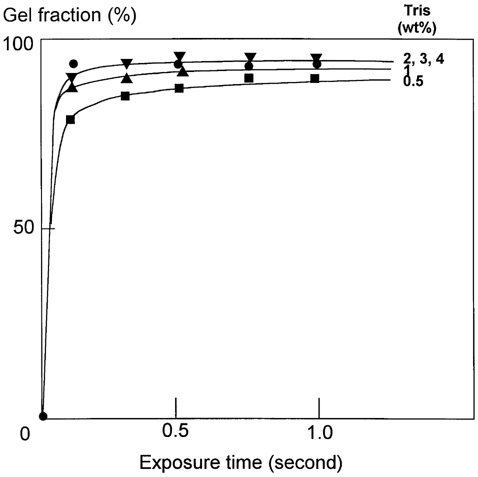


Fig. 5. Insolubilization profiles of UV-exposed SBS/TRIS films for different thiol concentrations. [LucirinTPO] = 1 wt%.

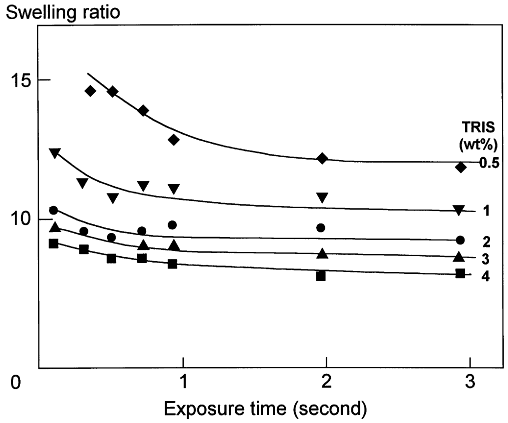


Fig. 6. Influence of the thiol concentration and the exposure time on the swelling of a photocrosslinked SBS/TRIS polymer. [LucirinTPO] = 1 wt%.

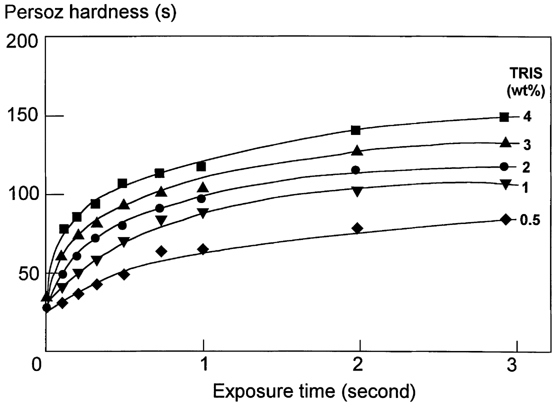
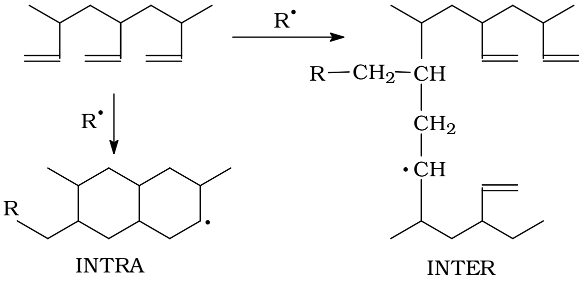


Fig. 7. Variation of the polymer hardness upon UV-exposure, for various thiol contents of the SBS/TRIS system. [LucirinTPO] = 1 wt%.

units. Larger loops can still be formed by reaction of more distant vinyl double bonds located on the same polymer chain. Such an intramolecular process was already found to occur during the cationic polymerization of epoxidized polyisoprene at high epoxy contents (>50%) [3,4]. Crosslinks will be formed and the polymer will become insoluble only if vinyl groups located on two different polybutadiene chains undergo polymerization. As a result, a very loose polymer network is generated, as shown by the high value of its swelling ratio: SR = weight of absorbed solvent/weight of polymer = 50 for UV-cured SBS [8].



In the presence of the trifunctional thiol, a branch point will be created each time a thiyl radical reacts with a vinyl double bond, which leads to a tightening of the polymer network. Indeed, the swelling ratio of the UV-exposed polymer was found to drop down to a value of 8 upon addition of as little a 1 wt% TRIS to SBS, as shown in Fig. 6. The SR value was cut by half when the TRIS concentration was further increased to 4 wt%. It should yet be noticed that, because of the high vinyl content of the SBS used, two of the three thiol groups of the TRIS molecule may typically react with two neighboring vinyl double bonds located on the same polymer chain (Fig. 4). Such an intramolecular process will have no net effect on the crosslink density, or on the polymer insolubilization.

When all the thiol crosslinker has reacted, typically after 0.3 s UV exposure, the concentration of branch points will be equal to the initial concentration of the thiol groups, e.g., $[SH]_0 = 0.075\ \mathrm{mol\ kg^{-1}}$ at [TRIS] = 1 wt%. This corresponds to 1 attachment formed for every 124 vinyl double bonds, or to 10 attachments per SBS chain. Even if this number is reduced to 7 to take into account the above mentioned intramolecular process, it is still sufficient to get total insolubilization of the rubber. After this short UV exposure, crosslinking is mainly due to the thiol–ene polymerization, the homopolymerization of vinyl groups providing only a minor contribution, as shown by the low value of the gel fraction (8%) found in the neat SBS sample UV-exposed for 0.3 s.

3.3. Hardening

While crosslinking is proceeding upon UV exposure, the amount of elastic chains which become bounded increases, and the hardness of the polymer rises consequently, as shown in Fig. 7. It is important to control precisely the crosslink density in order to obtain cohesion, but without hardening too much the polymer, which would be detrimental for its adhesion. At a low thiol concentration (<1 wt%) and short exposure (≤0.5 s), the UV-cured polymer remains still soft (Persoz value of less than 80 s) and keeps its elastomeric character. This is important if such rubbers are to be used as adhesives or as impact resistant materials to maintain the tack and wetting required to achieve a good adhesion. Harder but still flexible elastomers can be produced for flexographic printing plates or coatings applications, simply by increasing the thiol concentration up to 5 wt%, and/or the UV-exposure time up to 2 s.

The influence of the thiol concentration on the insolubilization, swelling and hardening processes is illustrated in Fig. 8 for a SBS sample UV-exposed for 0.3 s in the presence of 1 wt% Lucirin TPO. It clearly appears that a TRIS concentration of 0.5 wt% is already enough to obtain a crosslinked elastomer showing the required characteristics for adhesive applications.

The outer polystyrene segments of the block copolymer, which are phase separated, are not expected to participate to

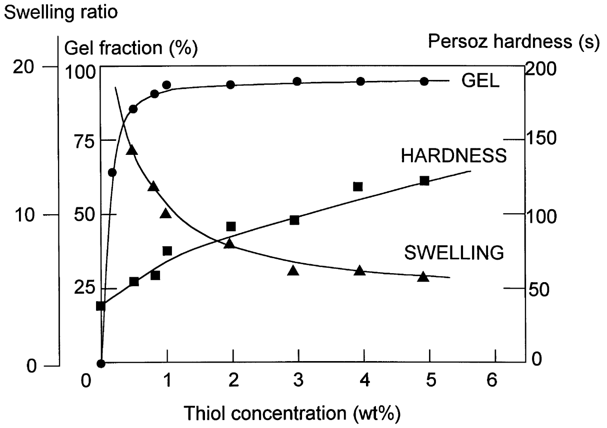


Fig. 8. Influence of the thiol concentration on the photocrosslinking of the SBS/TRIS system. UV exposure: 0.3 s; [LucirinTPO] = 1 wt%.

the crosslinking process, except by a possible chain transfer reaction if some propagating radicals succeed in abstracting a labile hydrogen on the PS chain at the interphase. Increasing the PS chain length should not affect insolubilization, which is ensured through the polybutadiene crosslinks, but it will increase the degree of swelling by lowering the crosslink density.

3.4. Influence of the photoinitiator concentration

The photoinitiator (PI) plays a keyrole by controlling both the rate of initiation and the penetration of the incident light. An increase of the PI concentration will accelerate the crosslinking reaction, but it will also steepen the cure depth gradient in the UV exposed sample and lead to insufficient polymerization at the sample/substrate interface. This radiation inner filter effect is a critical factor, specially for thick samples, because it is often responsible of the poor adhesion of UV-cured coatings or adhesives. It is therefore recommended to work at low PI concentrations, but it will be at the expense of the polymerization speed, and of the cure extent as well. Only with highly reactive systems will it be possible to achieve a fast and complete deep-through cure. In this respect, the Lucirin TPO–TRIS–SBS system shows outstanding performance because crosslinking appears to proceed efficiently even at very low concentration in photoinitiator.

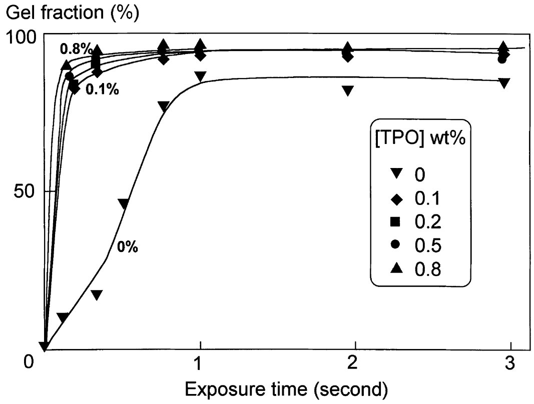


Fig. 9. Influence of the photoinitiator concentration on the insolubilization of the SBS/TRIS system upon UV exposure. [TRIS] = 1 wt%.

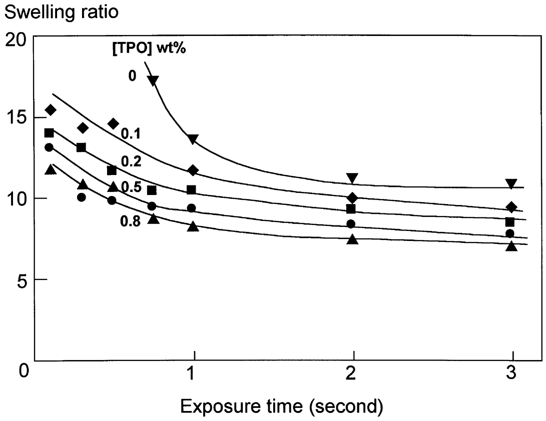


Fig. 10. Influence of the photoinitiator concentration and the exposure time on the swelling of a photocrosslinked SBS/TRIS polymer. [TRIS] = 1 wt%.

Fig. 9 shows the insolubilization profiles obtained upon UV exposure of a SBS–TRIS (1 wt%) sample containing various amounts of Lucirin TPO, between 0.1 and 0.8 wt%. It is quite remarkable that the crosslinking reaction still proceeds very rapidly at these very low PI concentrations, insolubilization being achieved in less than 1 s for a Lucirin TPO content of 0.1 wt%. The polymer network formed is almost as tight as that obtained by operating at higher photoinitiator concentrations, as shown by the swelling curves of Fig. 10. After 1 s exposure, SR values of 12 and 8 were measured at PI concentrations of 0.1 and 0.8 wt%, respectively.

An interesting feature was observed when the SBS-TRIS system was exposed to UV radiation without any added photoinitiator. After 1 s, as much as 85% of the polymer has become insoluble in toluene with formation of a relatively tight network (SR = 15), as shown in Figs. 9 and 10. This result suggests that the SBS sample contains some

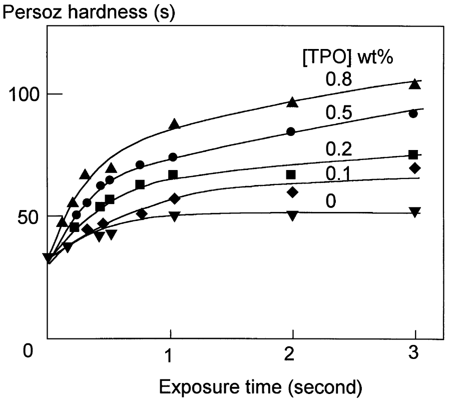


Fig. 11. Variation of the polymer hardness upon UV exposure, for various photoinitiator concentrations in the SBS/TRIS system. [TRIS] = 1 wt%.

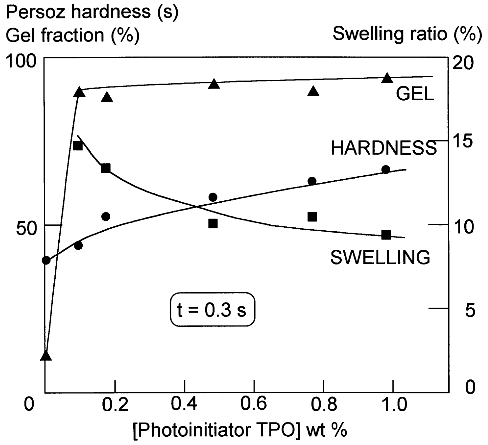


Fig. 12. Influence of the photoinitiator concentration on the photocrosslinking of the SBS/TRIS system. UV exposure: 0.3 s; [TRIS] = 1 wt%.

chromophores which absorb the UV radiation of $\lambda > 250$ nm. The free radicals generated upon photolysis would then produce the propagating thiyl radicals by abstracting an hydrogen atom from the thiol molecule.

As expected, the hardening of the polymer upon UV exposure becomes less pronounced as the photoinitiator concentration is decreased (Fig. 11). After a 1 s irradiation, the Persoz hardness value was found to increase from 40 to 55 s at [TPO] = 0.1 wt%, and up to 85 s for [TPO] = 0.8 wt%. The UV-cured elastomer remains soft and flexible, as required for adhesive applications.

The influence of the photoinitiator concentration on the properties of the polymer material obtained after a 0.3 s UV exposure of the SBS–TRIS (1 wt%) system is shown in Fig. 12. It clearly appears that a TPO concentration of 0.1 wt% is already sufficient to get the expected performance. This formulation presents a number of advantages:

- high reactivity upon UV-exposure;
- no residual thiol and photoinitiator in the UV-cured rubber;
- low cost of the tiny amounts of additives used;
- low-modulus polymer well suited for adhesives applications;
- deep through cure because of the low PI concentration;
- curing of thick samples.

For example, a 2 mm thick sample of SBS was rendered insoluble within less than 1 s, with formation of a relatively tight polymer network. Fig. 13 shows the insolubilization and the swelling profiles obtained with such a sample upon UV exposure in the presence of air, at ambient temperature. The % gel increase is slower than in thin films, as might be expected from the inner filter effect which reduces the amount of radiation received by the deep-lying layers.

More surprising is the fact that the swelling ratio of the thick UV-cured sample was found to be lower than that of the thin film (7 and 11, respectively), thus indicating that a tighter polymer network has been performed. This could be due to a less pronounced inhibitory effect of atmospheric oxygen in the thick sample. An additional reason could be the larger rise in temperature for the thick sample caused by the exothermal polymerization, as already shown in UV-curable resins [17]. The resulting increase in molecular mobility would favour intermolecular reactions and lead to a higher crosslink density.

3.5. Thermal stability

For some applications, like hot-melt adhesives and flexographic printing plates, the highly reactive SBS/thiol system is to be processed at elevated temperatures (usually 150°C). It is therefore important to assess the heat resistance of the formulation before UV-curing. In a previous study on a SBS formulation containing 5 wt% TRIS and 1 wt% Lucirin TPO, we found that about one-third of the sample has become insoluble in toluene after a 10 min heating at 150°C [16]. This poor thermal stability makes this system unfit for hot-melt adhesive applications.

We have repeated this study with a formulation containing only 0.5 wt% TRIS and 1 wt% Lucirin TPO. Under

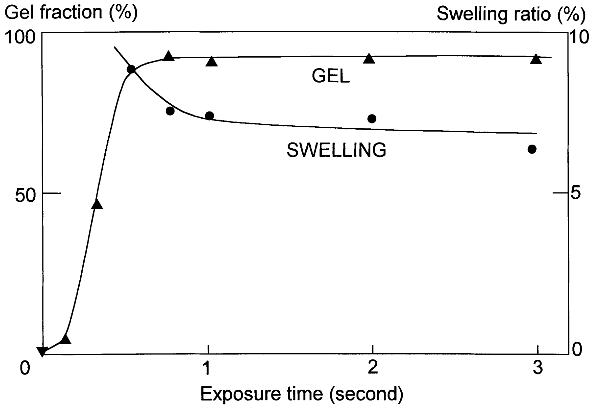


Fig. 13. Photocrosslinking of a 2 mm thick SBS/TRIS sample. [LucirinTPO] = 0.1 wt%; [TRIS] = 1 wt%.

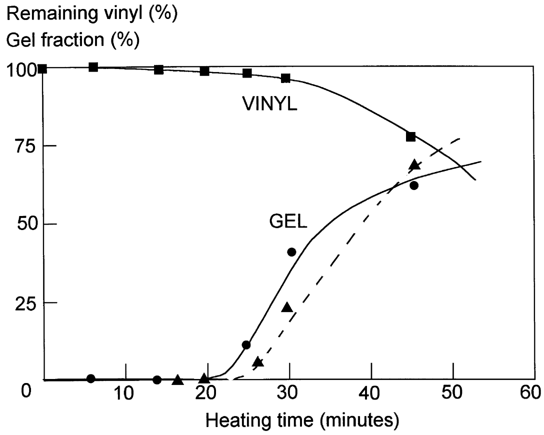


Fig. 14. Insolubilization of a SBS/TRIS upon heating at 150°C. [LucirinTPO] = 1 wt%; [TRIS] = 0.5 wt%. ---: SBS without thiol.

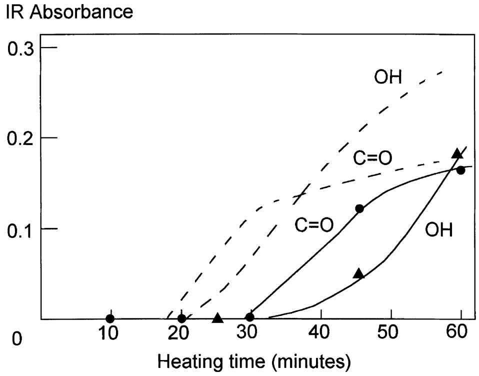


Fig. 15. Thermal oxidation of the SBS/TRIS system upon heating at 150°C. [LucirinTPO] = 1 wt%; [TRIS] = 0.5 wt%. ---: SBS without thiol.

those conditions, the vinyl content remained unchanged and no gelation was found to occur during the first 20 min of heating, very much like for neat SBS (Fig. 14). This formulation appears thus to meet the required specifications for heat resistance. The formation of insoluble polymer, which was observed upon further heating, could probably be delayed by the addition of an antioxidant, which should not interfere with the UV-curing process. Interestingly, the thermooxidation of SBS, which can be quantitatively followed by monitoring the formation of carbonyl and hydroxyl groups by IR spectroscopy, was shown to be depressed in the presence of the TPO and TRIS additives. These oxidation products are produced in significant amounts only after a 30 min heating at 150°C, as shown in Fig. 15.

4. Conclusion

The photoinduced thiol–ene polymerization has been successfully applied to crosslink at ambient temperature a styrene–butadiene rubber with a high vinyl content (59%). A very low amount of thiol crosslinker (≤1 wt%) proved to be already enough to achieve total insolubilization within less than 1 s upon intense illumination in the presence of a acylphosphine oxide photoinitiator. Crosslinking occurs predominantly by reaction of the thiyl radicals with the pendent vinyl double bonds and, to some extent, by homopolymerization of the vinyl groups.

Hardening is hardly taking place upon UV-curing, so that the thermoplastic elastomer retains its viscoelastic properties, while becoming more resistant to heat and chemicals. The photoinitiator concentration can be lowered down to 0.1 wt%, thus allowing relatively thick samples to be rapidly crosslinked because of the increased penetration of UV radiation. This UV-curable formulation exhibits a sufficiently high resistance to heating to allow its use in hot-melt adhesive and flexographic printing plate applications. Further studies on the photocrosslinking of the thiol/SBS combination are in progress, aiming at lowering the SBS vinyl content down to 8%, to be able to cure rapidly commercial styrene–butadiene rubbers.

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