

# Accelerated Natural Aging of Styrene-Isoprene Block-copolymers

PAUL GHIOCA\*, LORENA IANCU, BOGDAN SPURCACIU, RAMONA MARINA GRIGORESCU, AUGUSTA-RALUCA GABOR, CRISTIAN-ANDI NICOLAE

The National Research & Development Institute for Chemistry and Petrochemistry ICECHIM - Bucharest, 202 Splaiul Independentei, 060021, Bucharest, Romania

*The paper presents the effect of poly (vinyl-phenyl-ketone) used as prodegradant for styrene-isoprene block-copolymers exposed at natural aging.*

*Keywords: styrene-isoprene block-copolymers, poly (vinyl-phenyl-ketone), physico-mechanical properties, photo-oxidative degradation*

Styrene-isoprene block-copolymers (SIS) are obtained through sequential anionic polymerization of monomers, in hydrocarbons, the reaction being initiated by n-butyl lithium [1-3]. Their sequential structure and the thermodynamic incompatibility between polystyrene and polyisoprene blocks lead to phase separation of the two different polymeric species [4-7]. Their morphology consists in a polyisoprene continuous, elastomeric (when it is majority) phase, in which the polystyrene domains are dispersed. Polystyrene blocks from different macromolecules are contained in these plastomeric domains, thus ensuring the polymer physical crosslinking that gives it vulcanized rubber properties. At temperatures above the glass transition temperature ( $T_g$ ) for polystyrene blocks (approx.  $100^\circ\text{C}$ ), the polymer gets softer and the material as a whole presents plastic properties, and it can be processed in similar conditions to plastics. At cooling, phase separation occurs and the block-copolymer shows again vulcanized elastomer properties [2, 8-10].

Due to their thermoplastic behaviour, SIS block-copolymers are mainly used for plastomers and bitumen modification, for a variety of adhesives production, and as hoses, sheets and elastic bands for packaging.

The bands obtained from SIS block-copolymers present a higher elasticity and can be used to fix the scion to the rootstock in fruit trees orchards. This attachment must be ensured a limited time and then the material must be removed, which involves significant labor consumption. The accelerated degradation can lead to advanced

deterioration of physical and mechanical properties so that to produce the unattended detachment of SIS block-copolymers bands.

This paper presents the natural degradation study for SIS block-copolymers, process initiated by ultraviolet radiation from sunlight (280-400 nm), in poly (vinyl-phenyl-ketone) (PPVK) presence used as prodegradant.

## Experimental part

Linear SIS block-copolymers used in this natural aging study were obtained by sequential anionic polymerization in three steps, in cyclohexane solution, using n-butyl lithium as initiator [1-3, 11, 12]. The thermoplastic elastomers were stabilized with 2,6-di-tert-butyl-4-methyl phenol 1%, separated from the synthesis solution by desolvation with hot water and steam stripping and then dried in an oven under reduced pressure at a temperature of  $60^\circ\text{C}$ . Physico-mechanical properties for the SIS block-copolymers are presented in table 1.

Poly (vinyl-phenyl-ketone) used as prodegradant (supplied by Aldrich) had an average molecular weight of 11,000 Da (SEC, in THF) and  $T_g$   $56.15^\circ\text{C}$  (DSC, 2<sup>nd</sup> heating).

SIS block-copolymers and PPVK were compounded by dissolving the components at a concentration of about 25 % in toluene solution. PPVK concentration in SIS block-copolymer varied between 1 and 10 %. Composite polymer films with about 1 mm thickness were obtained from toluene solution, using a centrifugal casting process in which the desolvation is performed at low temperature

| Crt. No. | Property                                    | SIS - 20 | SIS - 30 |
|----------|---|----------|----------|
| 1.       | Polystyrene content, %                      | 19.9     | 29.8     |
| 2.       | Total molecular weight, g/mole              | 86.800   | 101.200  |
| 3.       | Polystyrene block molecular weight, g/mole  | 8.600    | 15.100   |
| 4.       | Polyisoprene block molecular weight, g/mole | 69.600   | 71.000   |
| 5.       | Tensile strength, MPa                       | 12.4     | 18.2     |
| 6.       | Elongation at break, %                      | 940      | 950      |
| 7.       | Remanent elongation, %                      | 10       | 28       |
| 8.       | Hardness, °Sh A                             | 44       | 54       |
| 9.       | $T_g$ of the polystyrene block, °C          | 86       | 91       |
| 10.      | $T_g$ of the polyisoprene block, °C         | -61.2    | -61.8    |

**Table 1**  
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CHARACTERISTICS OF LINEAR  
STYRENE-ISOPRENE BLOCK-  
COPOLYMERS

\* email: pghioca@yahoo.com

(max. 50 °C), thus avoiding their thermal degradation. This method for obtaining polymer films ensures a uniform dispersion of PPVK, providing materials with constant composition and reducing the experimental errors. From these films type 5A specimens for measurements of mechanical properties were stamped.

The exposure to natural aging of styrene-isoprene-styrene/poly(vinyl-phenyl-ketone) (SIS-PPVK) compounds was performed according to STAS 9554-87 (Plastic Materials. Methods of exposure to natural aging) and ASTM D5272-08 (Standard Practice for outdoor Exposure Testing of Photodegradable Plastics).

Differential scanning calorimetric (DSC) analysis was carried out on a DSC Q2000 (TA Instruments) in inert atmosphere (purge gas: helium 30 mL/min) and in a temperature range between -110 and 155 °C, with a heating rate of 20 °C/min.

Physico-mechanical properties of the specimens were carried out using a FPZ 100 dynamometer, with an elongation rate of 500 mm/min, according to ISO 527.

The specimens of elastomers having dimensions of 10×10×1 mm were subject to dynamic mechanical analyzer (DMA-Q 800 TA Instruments). The measurements were carried out in DMA Multifrequency-strain mode (shear sandwich clamp), the corresponding viscoelastic properties being obtained as a function of temperature. The temperature range was up to 160°C with a heating rate of 3°C/ min in air. The samples were scanned at a fixed frequency of 1 Hz and amplitude of 15 microns.

Hardness Shore was tested according to ISO 868 using a Shore A durometer.

## Results and discussions

SIS block-copolymers were synthesized with different polystyrene content (20 and 30 %) as can be seen from table 1, in order to study the effect of elastomers composition to their natural aging process.

SIS block-copolymers with different total molecular weight were obtained by adjusting the n-butyl lithium dosage, but there was maintained constant the molecular weight of polyisoprene blocks which is the continuous phase of the elastomers. The polyisoprene phase is the main responsible for obtaining PPVK composites, maintaining constant its molecular weight, and minimizing the misinterpretation of changing the physico-mechanical properties depending on the compounds composition and their degradation level [13].

SIS block-copolymers / PPVK composites show a complex tetra-phase modification because PPVK is distributed both in polyisoprene and polystyrene phase, in different proportions depending on its compatibility degree with these elastomers.

PPVK presence in the dense polystyrene domains is emphasized by the decrease of polystyrene phase Tg depending on the PPVK content in the composite material, as can be seen from figure 1, thus observing also a compatibility between these polymers.

In case of polyisoprene phase the Tg does not vary significantly with PPVK dosage, fact that highlights the components incompatibility (fig. 2). Thus we can conclude that PPVK acts as an inactive batch dispersed into the polyisoprene matrix as shown by typical modification of mechanical properties of composites: decrease in tensile strength (fig. 3) and elongation at break (fig. 4) and the simultaneous increase in remanent elongation (fig. 5) and hardness (fig. 6).

The effect of photo-thermo-oxidative natural aging was pursued using the modification of physico-mechanical

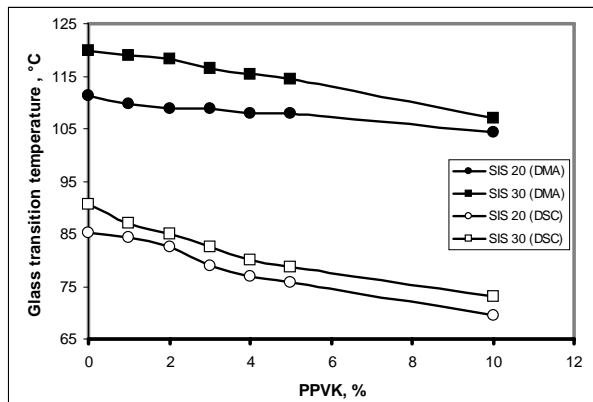


Fig. 1. Tg variation for polystyrene phase (Tan  $\delta$  peak max) of unexposed samples depending on PPVK content

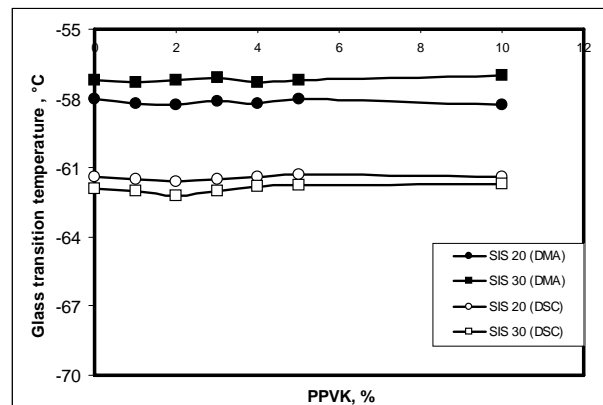


Fig. 2. Tg variation for polyisoprene phase (midpoint in first heat) of unexposed samples depending on PPVK content

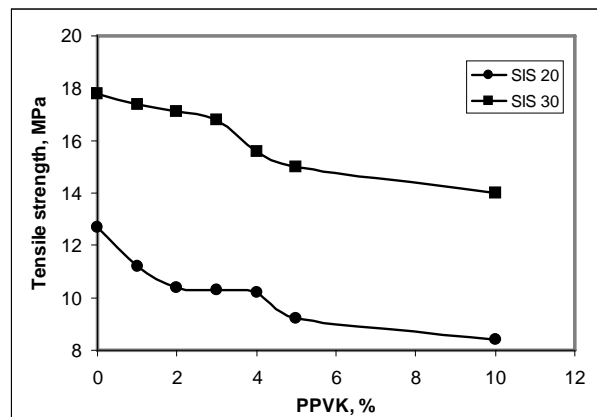


Fig. 3. Tensile strength of SIS/PPVK composites vs. PPVK content

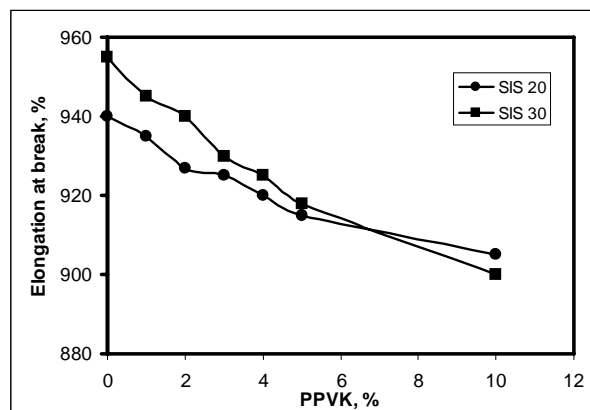


Fig. 4. Elongation at break of SIS/PPVK composites vs. PPVK content

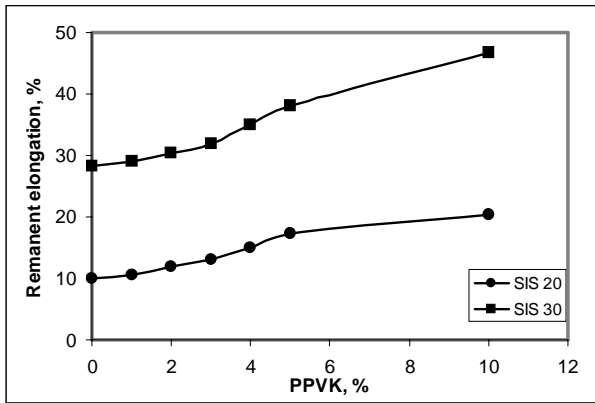


Fig. 5. Remanent elongation of SIS/PPVK composites vs. PPVK content

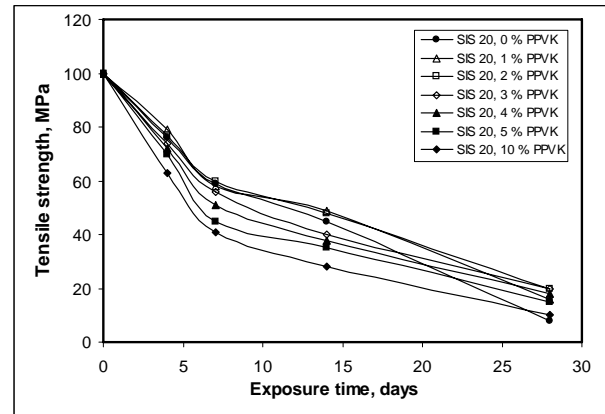


Fig. 9. Tensile strength of SIS 20/PPVK composites vs. exposure time

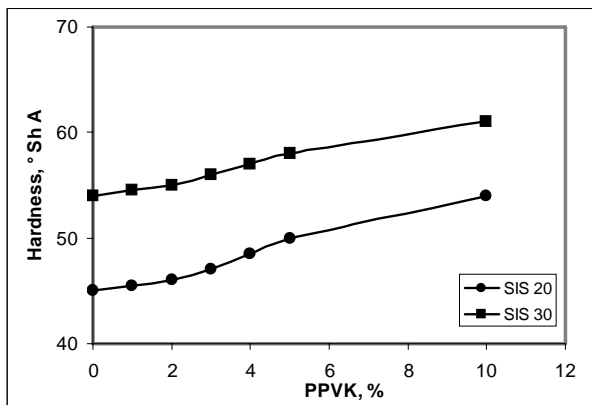


Fig. 6. Hardness of SIS/PPVK composites vs. PPVK content

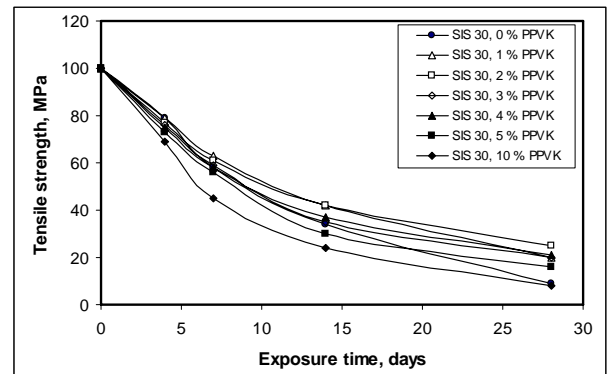


Fig. 10. Tensile strength of SIS 30/PPVK composites vs. exposure time

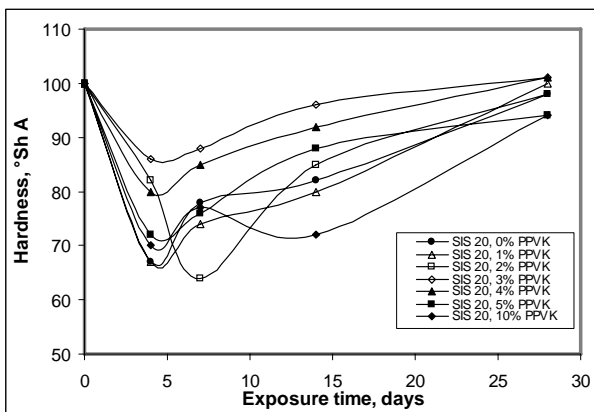


Fig. 7. Hardness of SIS 20/PPVK composites vs. exposure time

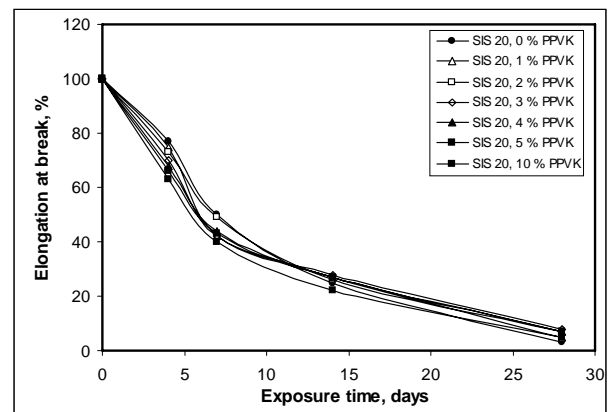


Fig. 11. Elongation at break of SIS 20/PPVK composites vs. exposure time

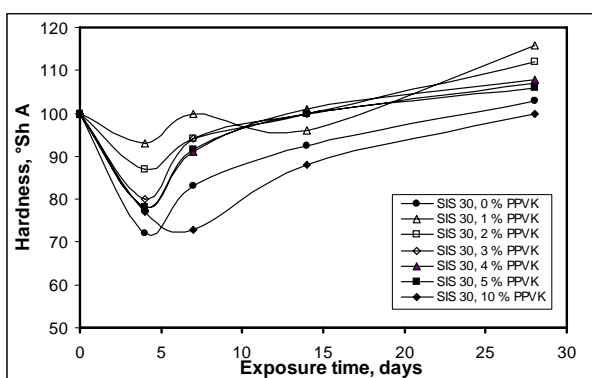


Fig. 8. Hardness of SIS 30/PPVK composites vs. exposure time

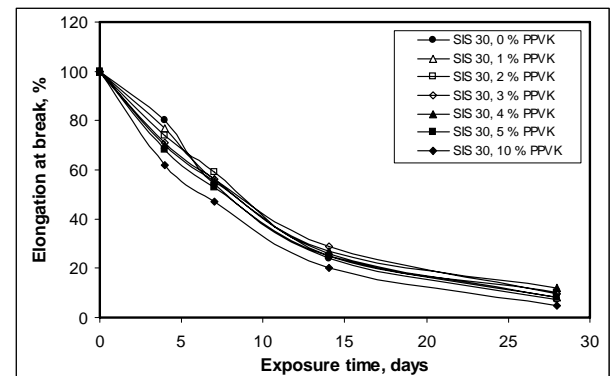


Fig. 12. Elongation at break of SIS 30/PPVK composites vs. exposure time

properties on which depends the decision to use the SIS/PPVK composites in pomiculture. Thermo-oxidative degradation under ultraviolet radiation of SIS block-copolymers and their composites has been extensively studied and the destruction mechanism involves in the first stage a predominant scission of polyisoprene chains [14-20].

The variation of SIS/PPVK composites hardness depending on the degradation time, presented in figures 7 and 8, highlights the very pronounced aging degree that occurs in the first days of exposure, marked by its significant decrease. The effect of the polyisoprene chain scission affects the tensile strength (figs. 9 and 10) and the elongation at break (figs. 11 and 12), their decrease being more pronounced in this first step of degradation.

The hardness is a measure of the whole material resistance although it must be considered that the continuous phase has the main contribution to this parameter size. As a result to oxidation advancement, the number of hydroxyl, carbonyl, epoxide,  $\alpha$ ,  $\beta$  unsaturated ester reactive groups increases [16, 20] and because of them, the crosslinking reactions have a more important share, partially restoring the integrity of the polyisoprene continuous phase. The phenomenon is pointed for increasing the hardness and decreasing the slope of tensile strength and elongation at break decrease.

SIS block-copolymers without PPVK show a less important hardness rebound in the second stage of aging due to a lower crosslinking degree caused by a smaller number of reactive groups produced during the oxidation in the absence of photo-degradation initiator.

It should be emphasized that the polystyrene phase dispersed in the polyisoprene one plays the insulator role in oxygen penetration, does not suffer significant degradation, a phenomenon mentioned in the literature [16-21]. The fact that the polystyrene domains are not degradable increases the crosslinking degree of polyisoprene network in the second stage of aging in case of the block-copolymers with 30% styrene, compared to the elastomer with a content of 20%. This explains the higher final values of hardness for SIS-30 block-copolymers.

The values of tensile and break strength decrease relatively uniform in the second stage of aging, more pronounced in correlation with PPVK concentration, indicating an isotropic degradation independent of the block-copolymers composition [16,17].

The study of SIS block-copolymers natural aging confirms the accelerating effect of the phenomenon produced of PPVK presence in the polymer, its dosage being chosen in correlation with the wanted destruction time of the material.

## Conclusions

The accelerated natural aging study of the SIS block-copolymers lead to the following conclusions:

- degradation occurs in polyisoprene continuous phase of block-copolymers by chain scission mainly in the first stage, in the second one increasing the crosslinking degree due to the appearance of hydroxyl, carbonyl, epoxide,  $\alpha$ ,  $\beta$  unsaturated ester groups in polyisoprene chains.

- SIS block-copolymers aging is accelerated only by the PPVK fraction distributed in polyisoprene phase.

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