# Modification of Cross-Linked Rubber Particles by Free Radical Polymerization

*Serena Coiai,*[*1] *Elisa Passaglia,*[1] *Francesco Ciardelli,*[1,2] *Diego Tirelli,*[3]
*Franco Peruzzotti,*[3] *Emiliano Resmini*[3]

**Summary:** The synthesis of polystyrene chains covalently bound to the surface of cross-linked rubber particles from recycled tires (ground tire rubber, GTR) was investigated via free radical polymerization in situ by using azobisisobutyronitrile (AIBN) and dibenzoyl peroxide (BPO) as initiators. Indeed, the graft polymerization provides a significant route to modify the physical and chemical properties of these particles allowing to improve their compatibility with other polymers. Polymerization reactions were carried out in bulk by changing the styrene/GTR ratio as well as the amount of free radical initiator. Appreciable amounts of polystyrene (PS) were grafted on GTR when BPO was used as confirmed by particle characterizations.

**Keywords:** cross-linked rubber particles; graft polymerization; polystyrene

## Introduction

Population growth, rapid industrialization and increase in living standards have caused extensive use of rubber producing proportional quantities of related wastes. Particularly, vehicular tires constitute the most important single item in terms of volume. Therefore, in industrialized countries creative and technologically sophisticated projects have been launched to use huge quantities of waste rubber. The objective of these projects is the reclaiming of vulcanized rubber material from used tires into a product which can be advantageously reused. Nevertheless, the recycling and reshaping of the vulcanized waste rubber is difficult to achieved because of its complex nature based on partially cross-linked rubber (natural rubber NR, styrene-butadiene rubber SBR and polybutadiene BR), carbon black, silica and other inorganic substrates with different ratio and composition depending on the type of tire (for cars or trucks).

Nowadays tire rubber granulates and powders, often called with the pseudonym of GTR *"ground tire rubber"*, are products commercially available on the market, which are usually produced by grinding (cryogenic, ambient and wet-ambient grinding) after metallic wires separation. The use of these peculiar hybrid inorganic/organic particles as filler in thermoplastics, elastomers and thermosets has been in the last years the topic of several researches.[1–7] Indeed, the GTR could replace commercial impact modifiers in both thermoplastics and thermosets getting to impact modified materials. Unfortunately, the incorporation of GTR into polymer matrices significantly impairs the mechanical and viscoelastic properties of the resulting composites, even at low rubber content, because of the poor-matrix filler adhesion and lack of reactive sites on the GTR surface. A specific application for these rubber particles, where improvements in compound properties may arise, is the modification of brittle plastics such as polystyrene (PS).[8] Actually PS is conventionally toughened by a rubber dispersed phase. Conventional wis-

---

[1] CNR-ICCOM c/o Department of Chemistry and Industrial Chemistry, University of Pisa, Via Risorgimento 35, 56126 Pisa, Italy
E-mail: serena.coiai@dcci.unipi.it

[2] Department of Chemistry and Industrial Chemistry, University of Pisa, Via Risorgimento 35, 56126 Pisa, Italy

[3] PIRELLI Labs, Viale Sarca 222, 20126 Milano, Italy

dom holds that a good adhesion between the rubber particles and the surrounding glassy matrix is necessary to achieve enhanced impact strength. The adhesion is usually promoted by formation of PS chains grafted on the rubber, which are believed to be collected at the interface thus stabilizing the system. In the literature the free radical grafting of styrene onto unsaturated elastomers like BR, NR and SBR has been studied fairly intensively by using free radical initiators (such as peroxides and diazocompounds).[9–11] The main results evidenced that free radicals can attack the monomer or the rubber thus creating either conditions for homopolymerization or graft copolymerization: double bonds can take part to the propagation steps or initiate the polymerization themselves and the initiator structure influences the polymerization results.[12–14] In the literature, attempts were made to prepare PS/GTR composites. Tuchmann and Rosen[15] blended untreated crumb from cryogenic grinding of tires with PS showing that impact strength increased by increasing crumb particle size and this was attributed to greater crack deviation. They also found that grafting even a small amount of PS to the surface of the crumb led to greater impact strength, but no details are reported in this paper about the polymerization reactions (i.e., initiators, temperature, time of reaction, monomer conversion, grafting efficiency, etc.). A method was patented in 1979 by Air Products[16] to produce high-impact thermoplastics by polymerization of vinyl monomers in the presence of swollen crumb. The produced materials showed high impact strength, but only few experimental details are given in this patent about polymerization reactions: no evidence of grafting was shown and tests were restricted to crumb modified solely by benzoyl peroxide (BPO). In 1986 Pittolo and Burford[17] checked the possibility to polymerize styrene in the presence of a peroxide-cured BR/SBR blend filled with carbon black to simulate the tire rubber. The particles were swollen with styrene and later polymerizations were performed by using BPO or azobisisobutyronitrile (AIBN). The authors observed that BPO allowed to obtain a partially PS grafted product, whereas AIBN independently polymerized styrene thus producing free polystyrene chains, but no details or deeper characterizations were reported in the paper.

The present work dealt with the investigation of the preparation of PS chains covalently bound to the surface of GTR particles by conventional free radical polymerization. Specifically this work is an attempt to clarify the mechanism of styrene free radical grafting onto GTR particles by measuring the monomer conversion and the grafting efficiency (GE is the percentage of grafted polymer over the total weight of polymer formed) as function of the initiator type as well as of the monomer to rubber weight ratio.

## Experimental Part

### Materials

Styrene (Sty, Aldrich) was distilled under vacuum before use. Dibenzoyl peroxide and 2,2′-azodi(isobutyronitrile) (Aldrich) were re-crystallized from methanol and acetone respectively.

Two commercial kinds of ground tire rubber (GTR) particles collected by tires recycling and kindly supplied by PIRELLI Labs were used. The former powder, P1, was obtained by means of a cryogenic grinding process and is characterized by particles with a maximum diameter of 100 μm (135 mesh), according to the manufacturer; the later, P2, obtained by means of a thermo-mechanical grinding process is composed by particles with a maximum diameter of 425 μm (40 mesh), according to the manufacturer. Powders P1 and P2 were extracted with acetone before the use in order to remove plasticizing oils and other types of additives used during the vulcanizing process of the rubber for the production of tires, and finally dried under vacuum until constant weight. The chemi-

***Table 1.***
Average composition of GTR particles P1 and P2 determined by TGA.

| Ingredient | Constituent | GTR particles | |
|---|---|---|---|
| | | P1[a)]<br>(% by weight) | P2[a)]<br>(% by weight) |
| Polymer | NR/BR | 30.8 | 34.8 |
| | SBR | 23.9 | 24.2 |
| Fillers | Carbon black | 32.6 | 32.2 |
| Calcined residue | $SiO_2$, metal oxides | 12.7 | 8.8 |

[a)] Powder extracted with acetone to remove low-molar components.

cal composition of the two powders in terms of rubbers and fillers was determined by TGA analysis after the removing of low-molar components by acetone extraction (Table 1). Differential thermogravimetric (DTG) curves were deconvoluted to calculate the amount of each polymer in the blend.[18,19]

The two powders showed the presence of double bonds on the surface as it was evidenced by ATR analysis and confirmed by an indirect titration method usually used to measure the content of double bonds in oils and in fats[20] according to the following equations:

$$R\text{–}CH{=}CH\text{–}R + I\text{–}Cl \Leftrightarrow R\text{–}CI\text{–}CCl\text{–}R$$

$$ICl + KI \rightarrow KCl + I_2$$

$$2\,Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6$$

The titration results highlighted that P1 particles had a concentration of C=C double bonds on the surface of $10.5 \cdot 10^{-4}$ mol/g and P2 particles of $7.6 \cdot 10^{-4}$ mol/g.

### Polymerization Procedure

All the polymerizations were carried out in bulk in small glass tubes (25 ml) under heterogeneous and quiescent conditions by using a larger amount of styrene with respect to GTR. No solvent was used for the simplicity of execution and to avoid side reactions with the solvent or suspending medium. The monomer/rubber ratio was maintained high to partially hinder the further cross-linking of the rubber particles since both the type of GTR particles still contain reactive double bonds at least on the surface. First a solution of styrene and initiator was prepared inside the tube and latter the GTR powder was added under nitrogen flow. The content was stirred for 2–3 hours to get an adequate mixing then before starting the polymerization reactions the reaction mixture was exposed to three repeating freezing-pump cycles. The polymerization temperature was 70 °C by using AIBN and 85 °C by using BPO as radical initiators. The reaction was maintained at the temperature for 24 hours and then the product was suspended in chloroform, precipitated in methanol three times and dried under vacuum until constant weight. In order to separate the free PS (soluble in chloroform) from the grafted PS the polymerization products were extracted with boiling chloroform for 8 hours in kumagawa. The insoluble residue was dried under vacuum until constant weight.

### Characterization Methods

IR measurements were carried on a Perkin Elmer FT-IR 1760-X equipped with ATR accessory and microscope. All TGA thermograms were recorded by a Mettler Toledo Stare System TGA/SDTA 851$^e$ Module. Samples (5–10 mg) were placed in an alumina sample pan and runs were carried out at a standard rate of 10 °C/min. The GTR and PS-grafted-GTR particles were analyzed both in nitrogen atmosphere from 25 to 600 °C and under air flow from 600 to 1100 °C. SEM micrographs were performed with a Jeol 5600-LV instrument equipped with an Oxford X-ray energy dispersive spectrometer (EDS) microprobe.

## Results and Discussion

Tests performed by using powder P1 can be collected in three different groups. In the first polymerization reactions were carried out by using BPO and ranging its concentration between 0.2 to 1.6 mol%, compared to the monomer in the feed, and keeping constant the ratio between the monomer and the GTR (90:10 wt/wt) (BP1-01 ÷ BP1-04). In the second series the concentration of BPO was kept constant with respect to the styrene (0.4 mol%), while the ratio between the monomer and P1 was raised from 90/10 to 70/30 wt/wt (BP1-02, BP1-05, BP1-06). Finally, a single run by using AIBN was achieved (AP1-01). The powder P1 was preferentially used here because of its low particle size, relative narrow particle size distribution and a more extended surface area accessible for grafting (see Experimental Part). Nevertheless, with the aim to compare these results with those obtained by using a powder with different particles size and composition, a few experiments were also carried out by using the powder P2 (BP2-01 ÷ BP2-03). Table 2 summarizes feed conditions, styrene conversion and grafting efficiency (GE), where this last was calculated as follows after removal of the ungrafted PS by extraction with chloroform:

$$GE = \frac{\text{amount of grafted (unextractable) PS (g)}}{\text{amount of total formed PS (g)}} \times 100 \qquad (1)$$

Conversion in the presence of GTR with BPO was never complete and depending on feed composition and type of powder used (P1 or P2). On the other hand without GTR (B-00) a very high monomer conversion (99.6%) was obtained thus suggesting that the presence of the tire powder strongly inhibited the styrene polymerization. By using AIBN as initiator (run AP1-01) total conversion of styrene was obtained but the recovered composite was extremely heterogeneous with a clear phase separation and the extraction with boiling chloroform did not indicate formation of grafted polymer.

All the polymerizations carried out by using BPO led to powdered apparently homogeneous products. SEM analyses of sample BP1-01 and powder P1 (Figure 1) indicated that all the particles are homogeneously coated by the new PS phase, as it is more easily detectable by the blow up of the SEM micrograph.

***Table 2.***
Grafting reactions of styrene on GTR particles by using BPO and AIBN as radical initiators.

| Sample[a)] | Styrene (g) | GTR (g) | Initiator[b)] (% mol) | Styrene Conversion (% wt) | Product insoluble in $CHCl_3$ (% wt) | PS in the $CHCl_3$ insoluble fraction (% wt) | GE[c)] (%) |
|---|---|---|---|---|---|---|---|
| B-00 | 4.5 | — | 0.2 | 99.6 | — | — | — |
| BP1-01 | 4.5 | 0.5 | 0.2 | 21.0 | 17.4 | 42.4 | 39 |
| BP1-02 | 4.5 | 0.5 | 0.4 | 54.3 | 22.2 | 55.0 | 25 |
| BP1-03 | 4.5 | 0.5 | 0.8 | 15.1 | 13.9 | 28.0 | 29 |
| BP1-04 | 4.5 | 0.5 | 1.6 | 50.8 | 20.5 | 51.2 | 23 |
| BP1-05 | 4.0 | 1.0 | 0.4 | 48.6 | 21.1 | 35.7 | 29 |
| BP1-06 | 3.5 | 1.5 | 0.4 | 30.0 | 39.4 | 23.9 | 45 |
| BP2-01 | 4.5 | 0.5 | 0.2 | 29.2 | 18.1 | 44.9 | 31 |
| BP2-02 | 4.5 | 0.5 | 0.4 | 26.5 | 16.4 | 39.2 | 27 |
| BP2-03 | 4.5 | 0.5 | 0.8 | 38.1 | 18.1 | 44.6 | 23 |
| AP1-01 | 4.5 | 0.5 | 0.8 | 97.3 | 10.0 | — | <1 |

a) The experiments performed with BPO are coded as BPx-y, with x = 1 or 2 is depending on the type of GTR used (P1 or P2); the AIBN-based experiment done is coded AP1-1 and was performed by using the P1 powder.

b) The amount of free radical initiator is expressed as % by mol with respect to the amount of styrene in the feed.

c) The grafting efficiency (GE) is the percentage of grafted polymer over the total weight of polymer formed.

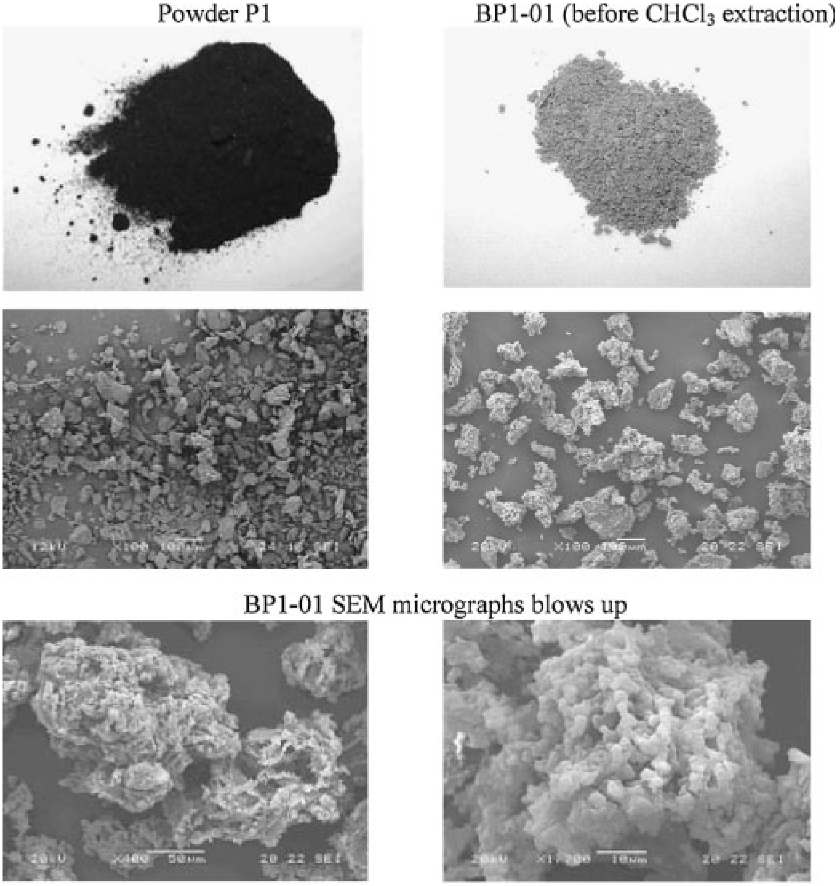
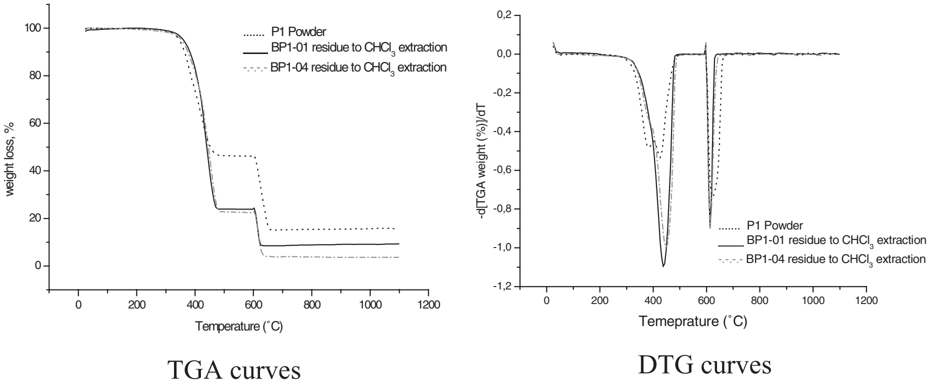


***Figure 1.***
SEM micrographs of powder P1, BP1-01 sample and BP1-01 blows up.

The free (ungrafted) PS was removed from the grafted product (PS-g-GTR) by extraction with boiling chloroform and the grafting efficiency (GE) was gravimetrically evaluated by calculating the amount of grafted PS. The data reported in Table 2 demonstrated that BPO was efficient in ensuring considerable yields of grafted PS (GE = 23–45 %) unlike AIBN ($GE < 1\%$). GE seemed to largely depend on the initial monomer/rubber ratio. In fact an increase of GE values was detected for higher GTR/monomer ratios, while the monomer was more readily transformed into homopolymer than in a grafted product in case of lower GTR/monomer ratio values. By keeping constant the monomer/GTR ratio (90/10 wt/wt) and decreasing the BPO concentration the GE raised, except for one point in the case of the powder P1 (1% wt of BPO with respect to the monomer). Small differences of GE were observed by going from powder P1 to powder P2.

The thermal degradation of the powder (P1 or P2) was composed by three principal steps as evidenced in the Experimental Part: the first two, under nitrogen flow, were correspondent to NR/BR and SBR mass loss respectively and the later one, under air flow, was due to the pyrolysis of CB. In the thermograms of the PS-g-GTR samples the PS degradation step (around 410–420 °C maximum of the DTG curve) resulted overlapped to the rubbers, as visible also on DTG thermograms reported in Figure 2. Instead the CB degradation step was well detectable (around 630 °C maximum of DTG). Therefore, by knowing the amount



TGA curves

DTG curves

***Figure 2.***
TGA and DTG curves of pure P1 powder, PS-grafted-GTR samples BP1-01 and BP1-04.

of CB present in the powders (Table 1) and by calculating with the TGA analysis its mass loss after the PS grafting, it was possible to detect the amount of GTR in the composites and so the grafted PS percentage. From the obtained results, this methodology appeared consistent with the mass balance derived from the solvent extraction. ATR-IR spectra performed on $CHCl_3$ extraction residues demonstrated that the new polymer was present on the surface of the GTR particles. Among the characteristic bands of silica filler present in the GTR substrate, additional absorption bands corresponding to PS (3062, 3026, 758 and 697 $cm^{-1}$) are clearly visible in the ATR spectra (Figure 3).

Furthermore, the surface composition data of the sample BP1-04 with the 51% by weight of PS in the $CHCl_3$ insoluble fraction was determined by EDXS analysis as summarized in Table 3.

EDXS data indicated, by the relative increase and decrease in C and Si content respectively, that the rubber particles sur-

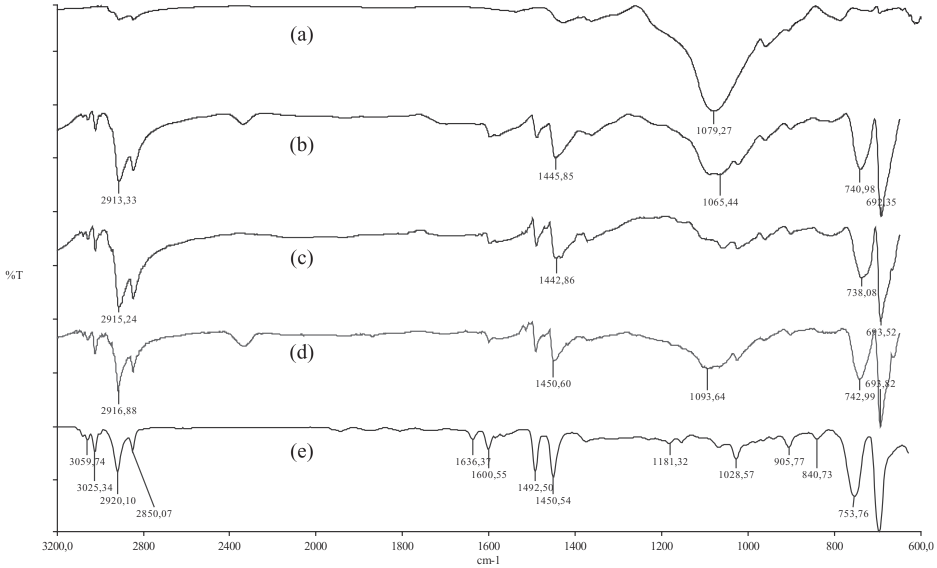


***Figure 3.***
ATR-IR spectra of P1, PS and PS grafted rubber particles (residues to chloroform extraction): P1 (a), BP1-03 (b), BP1-01 (c), BP1-04 (d) PS (e).

***Table 3.***
Average surface atomic composition of powder P1 and powder BP1-04, after $CHCl_3$ extraction, determined by EDXS analysis.

| Powder | Atomic composition (%) | | | | | |
|---|---|---|---|---|---|---|
| | C | O | Si | S | Ca | Zn |
| P1[a)] | 70.3 | 22.3 | 4.3 | 1.2 | 0.4 | 1.5 |
| BP1-04[b)] | 89.2 | 10.1 | 0.2 | 0.3 | — | — |

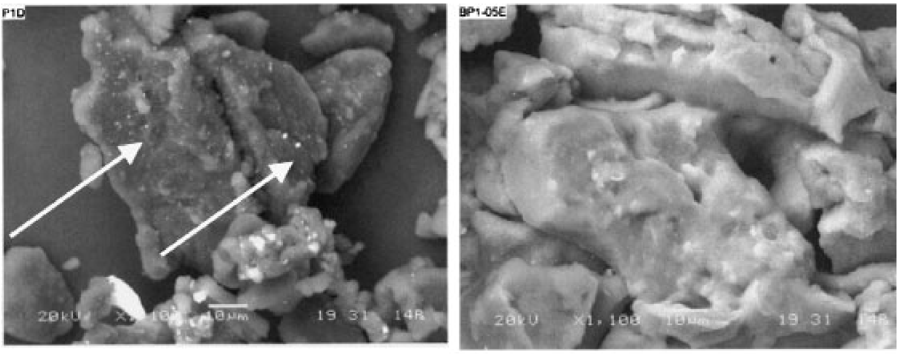
[a)] Particles extracted with boiling acetone to remove low-molar components.
[b)] Particles extracted with boiling chloroform to remove free PS.

face for the sample BP1-04 was covered with a layer of grafted PS. On the basis that EDXS sampling depth is typically less than a few nanometers, this analysis was a clear indication of the presence of an outer layer of grafted polymer which masked the underlying GTR. Moreover a backscattered electron imaging analysis was achieved for the pure P1 powder and for the grafted sample BP1-04 (Figure 4). The backscattered electron imaging provides elemental composition variation as well as surface topography since the efficiency of production of backscattered electrons is proportional to the average atomic number of the material (higher atomic number material appears brighter than low atomic number material). In our case, the backscattered electron images provided a further confirmation of the existence of the PS layer since, while for the powder P1 it was possible to observe points at elevate brightness (Figure 4) probably due to zinc atoms, they were not detectable in the case of the sample BP1-04 because the backscattered electrons were not able to reach this depth due to the PS layer presence.

Since it was not clear whether the graft-polymerization was purely interfacial or it took place also in the bulk of GTR particles, an attempt was made to analyze by IR (ATR) the cross-section of PS-g-GTR particles in order to get more insight about the PS distribution. BP1-04 particles (after $CHCl_3$ extraction) were embedded in a frozen polyester resin and then 7 μm-thick slices were cut by using a ultramicrotome and successively analyzed.

Despite the polyester resin covers all the original particles signals, the comparison between ATR spectra recorded on several cross-sectional slices via IR microscopy showed the presence of the grafted PS (bands at 3083, 3062, 3026 $cm^{-1}$) in increasing quantity by raising the distance from the centre of the particle [from spectrum (e) towards (c)] by considering a spherical shape for GTR particles (Figure 5).

All the experimental evidences collected in this work clearly demonstrated the formation of PS strongly grafted/interpenetrated in the GTR. This result can be tentatively rationalized by considering: (a) the presence of polymerization/grafting sites on GTR and (b) the nature of the initiator.



(a) (b)

***Figure 4.***
Backscattered electron imaging of (a) unmodified P1 powder and (b) sample BP1-04 after $CHCl_3$ extraction.

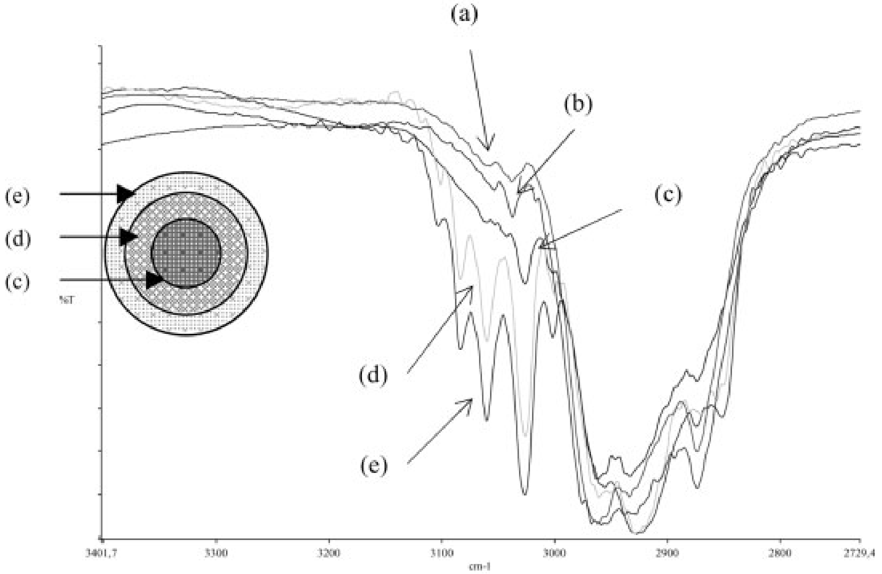
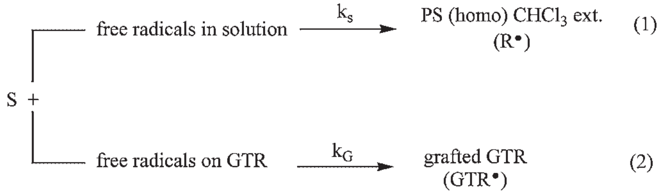


***Figure 5.***
Comparison of IR spectra for assessing the distribution of the grafted PS on cross-sectional slice of PS-g-P1 particles (sample BP1-04 after $CHCl_3$ extraction): polyester resin (a), pure P1 (b), spectra at different distance from the centre of the PS-g-P1 particles (c), (d) and (e).

(a) implies the formation of free radicals on the GTR network (through H-abstraction by the primary radical deriving from the initiator), but the possible copolymerization reaction among styrene and the vinyl double bond of 1,2-butadiene units in the cross-linked elastomer chains cannot be excluded. In particular, the double bonds of the GTR elastomer fraction could have taken part to the propagation step or initiated the polymerization themselves as literature reports suggest.[13,14] In addition primary radicals can react directly with the monomer thus initiating homopolymer formation in solution. This last reaction is not giving any grafting apart a very improbable termination coupling with grafted growing chainsorotherfreeradicalonGTR.

While for preparation of HIPS the total PS formed is relevant, the main objective of this paper is the understanding of the grafting process. However even if the formation of PS in solution was considered being useful to understand initiation inhibition connected to the GTR presence. Accordingly, the partial conversion of the styrene by using BPO in the presence of GTR was probably due to the competition between the monomer and the GTR versus the free primary radicals. Specifically (point b) the higher chemical affinity of BPO primary radicals ($C_6H_5COO\bullet$ and $C_6H_5\bullet$) towards the GTR powder as well as their different reactivity compared to AIBN ones $[(CH_3)_2(CN)C\bullet]$ can explain the results in terms of conversion. The peroxide radicals generally react by hydrogen abstraction with macromolecular chains whereas carbon radicals (such as the primary radicals generated by AIBN decomposition) are more reactive towards the monomer double bond. Most likely in our case by using BPO there was a lower concentration of free radicals available for the monomer because of the strong interaction with the GTR powder. Therefore, the process can be drawn as described in Scheme 1 where the two principal reactions involved are considered: (1) homopolymerization and (2) graft-polymerization.

Because of steric reasons it is likely that $k_s \geq k_G$ independent of initiatior; therefore



$$v_1 = k_s[S]\cdot[R\bullet]$$

$$v_2 = k_G[S]\cdot[GTR\bullet]$$

***Scheme 1.***
Rationalization of the process.

the ratio between homo and grafted PS is determined by the ratio [R•]/[GTR•]. By using BPO the macroinitiator formation by allylic H-abstraction from elastomer chains is more probable thus favoring polystyrene grafting. The lack of grafted PS observed by using AIBN as radical initiator with respect to BPO suggests that the mechanism of grafting is principally due to the formation of GTR macroradicals by H-abstration promoted by free radicals rather than to copolymerization of styrene with GTR vinyl double bonds which should be initiator independent. Therefore the [R•]/[GTR•] ratio should be lower by using BPO compared to AIBN.

Another aspect that cannot be neglected is the presence of carbon black (CB) in the rubber particles and its influence on the process. In the literature it is in fact reported that when CB is treated with a conventional radical initiator[21,22] the corresponding free radicals are bonded onto its surface by addition reaction with polycondensed aromatic rings and quinonic oxygen groups. The radicals formed on the CB surface are stabilized by the polycondensed aromatic rings, which act as strong radical trapping-agents. Particularly it has been underlined that by using BPO the styrene polymerization is intensively retarded by GTR while a moderate inhibition appeared if the polymerization is initiated by AIBN.[23] As confirmation of the fact that the CB presence (inhibition on $k_G$, see Scheme 1) can affect the grafting process particularly by using BPO an experiment of styrene polymerization in the presence of CB by using BPO as initiator (monomer/CB 90/10 by weight and 0.4% mol of BPO with respect to the monomer) at 85 °C was carried out: neither free nor grafted polymer were obtained.

## Conclusive Remarks

The process of PS grafting on GTR particles was studied in this work by styrene free radical polymerization initiated by BPO or AIBN, respectively. Results concerning monomer conversion and GE were rationalized by considering both the influence of polymerization/grafting sites on GTR and initiator nature. Specifically experimental data suggest that two main parallel reactions happen: the homopolymerization, which produces free PS, and the graft-polymerization, which allows to obtain PS chains grafted to the particles. The competition between the two reactions which establishes the ratio between the homo and grafted PS is determined by the [R•]/[GTR•] ratio which was lower in the case of BPO compared to AIBN. Actually the H-abstraction capability of bezoyloxy and phenyl radicals from BPO should be higher than RC• free radicals from AIBN therefore the amount of GTR macroradicals (GTR•) should be higher. Due to this last feature appreciable GE values were obtained by using BPO despite the monomer conversion was lower.

*Acknowledgements:* The authors gratefully acknowledge PhD Catherine Hirel, Mr. Piero

Narducci (Ingegneria Chimica, Università di Pisa) and the CNR-ISMAC Section of Genova for their cooperation to GTR particles titration, SEM analyses and PS-g-GTR particles cutting with ultramicrotome. Fondazione Silvio Tronchetti Provera, PIRELLI Labs and Polylabs are acknowledged for financial support.

[1] I. Fuhrmann, J. Karger-Kocsis, *Kautschuk Gummi Kunststoffe* **1999**, *52*, 836
[2] P.K. Pramanik, W.E. Baker, *Plast. Rubber Comp. Process. Applic.* **1995**, *24*, 229
[3] A.K. Naskar, S.K. De, A.K. Bhowmick, *J. Appl. Polym. Sci.* **2002**, *84*, 370
[4] K. Oliphant, W.E. Baker, *Polym. Eng. Sci.* **1993**, *33*, 166
[5] A.K. Naskar, A.K. Bhowmick, S.K. De, *Polym. Eng. Sci.* **2001**, *41*, 1087
[6] C.R. Kumar, I. Fuhrmann, J. Karger-Kocsis, *Polymer Degradation and Stability* **2002**, *76*, 137
[7] P. Rajalingam, W.E. Baker, *Rubber Chemistry and Technology* **1992**, *65*, 908
[8] M. Pittolo, R.P. Burford, *Rubber Chemistry and Technology* **1984**, *58*, 97
[9] A. Brydon, G.M. Burnett, G.G. Cameron, *J. Polym. Scie. Polym. Chem. Ed.* **1973**, *11*, 3255
[10] A. Brydon, G.M. Burnett, G.G. Cameron, *J. Polym. Scie. Polym. Chem. Ed.* **1974**, *12*, 1011
[11] G.G. Cameron, M.Y. Qureshi, *J. Polym. Scie. Polym. Chem. Ed.* **1980**, *18*, 3149
[12] P.W. Allen, G. Ayrey, C.G. Moore, *J. Polym. Sci.* **1959**, *36*, 55
[13] N.J. Huang, D.C. Sundberg, *J. Polym. Sci.: Part A: Polym. Chem.* **1995**, *33*, 2551
[14] N.J. Huang, D.C. Sundberg, *J. Polym. Sci.: Part A: Polym. Chem.* **1995**, *33*, 2571
[15] D. Tuchman, S.L. Rosen, *J. Elastom. Plast.* **1978**, *10*, 115
[16] G.F. Freeguard, Air Products Ltd, British Patent Application 2 022 10512, 1979
[17] M. Pittolo, R.P. Burford, *J. Mater. Scie.* **1986**, *21*, 1769
[18] D. Brück, *Kautschuk Gummi Kunststoffe* **1988**, *41*, 875
[19] E. Bilgili, H. Arastoopour, B. Bernstein, *Powder Technology* **2001**, *115*, 277
[20] S.G. Gallo, H.K. Wiese, J.F. Nelson, *Ind. Eng. Chem.* **1948**, *40*, 1277
[21] N. Tsubokawa, K. Fujiki, Y. Sone, *Polymer Journal* **1988**, *20*, 213
[22] K. Fujiki, N. Tsubokawa, Y. Sone, *Polymer Journal* **1990**, *22*, 661
[23] Y. Hu, J. Liu, H. Dong, *Coll. Chem. Eng.* **1998**, *14*, 59