Styrene-butadiene Block-copolymer Solutions for Protective Coating of Metals in the Chemical Milling Process

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This paper presents an experimental study aiming to obtain a new polymer composition by using styrene-butadiene radial block-copolymer with styrene-butadiene diblock-copolymer blend, in order to manufacture masking solution for metal protective coating in the chemical milling process.

Keywords: styrene-butadiene block-copolymers, masking solution, protective coating

The chemical milling process is used as a rule to chemically remove layers from a metal surface during manufacturing, a portion of the metal piece needing to be protected from corosive action of an etchant solution by etching resist masking material. The protective coverage surface of the metal is usually obtained by immersing the metal piece in a masking solution, and after that follows the solvent evaporation. For most applications, the masking solution contains mainly an elastomer and an organic or more often an anorganic filler and anti-setting agents, all materials being solved-dispersed in a non-inflammable solvent [1,2]. The masking formulation contains an usual elastomer (polybutadiene, styrene-butadiene rubber, nitryle rubber, natural rubber) the final coat of mask being tack free. The film need to be oven cured for 30 to 60 min at elevated temperature(80–140°C). This paper investigates the case of radial branched styrene-butadiene block-copolimers (SBS) using as elastomer component part and styrene-butadiene diblock-copolimers (RS) as fillers in masking formulation. The radial branched styrene-butadiene block-copolimers exhibit at ambient temperature many of the properties of a vulcanized rubber as a consequence of the polystyrene- polybutadiene incompatibility. Due to the thermodynamic incompatibility of the two kinds of blocks, a phase separation occurs, resulting in the formation of a glassy domain in which polystyrene blocks belong to different molecules aggregate. This virtual crosslinking is reversible by dissolvation. The elimination of the chemical cure, a notoriously energy – consuming operation, offers large energy and time savings providing a new masking solution based on SBS.

Experimental part

In the frame work of the performed experimental research study were synthesized three radial branched styrene-butadiene block-copolimers and three styrene-butadiene diblock-copolimers by means of sequential anionic polymerization of monomers. Only after the full consumption of the previous monomer the next one was added , in cyclohexane solution, initiated with butyllithium. The active diblock-copolimer polystyren-polybutadien-lithium—was finally coupled with $Si Cl_4$ to obtain radial branched styrene-butadiene block-copolimers [3-6]. The optimal polymerization periods for every step were computed by using previously established kinetic relations [7-8].

The molecular weights of polymers were measured by gel permeation chromatography (GPC) on a Waters - Millipore 244 apparatus, in tetrahydrofurane (flow rate 1mL/ min.). The GPC was calibrated with polystyrene standards.

The polystyrene content was determined by means of density-refraction index method [9].The tensile properties of synthesized SBS were obtained on films resulting by centrifugal casting from toluene solution on standard dumbbel specimens, at a jaw separation speed of 0.5 m/ min., using a Zwick 1454 tensile tester, the retractive force being recorded during extension. Hardness was measured with a dead load Zwick hardness meter in the Shore A scale.

Table 1
PROPERTIES OF RADIAL BRANCHED STYRENE-BUTADIENE BLOCK-COPOLIMERS

Nr. crt.	Property	SBS 1	SBS 2	SBS 3
1	Polystyrene content, %	30,4	30,2	30,1
2	Total molecular weight, g/ mol	149200	181600	208800
3	Polystyrene block molecular weight, g/ mol	11300	13700	15700
4	Polybutadiene block molecular weight, g/ mol	104000	126800	146000
5	Tensile strength, MPa	21.6	22.8	23.5
6	Elongation at break, %	760	780	810
7	Hardness, ° ShA	68	68	68,5

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Table 2
PROPERTIES OF STYRENE-BUTADIENE DIBLOCK-COPOLIMERS

Nr. crt.	Property	RS 1	RS 2	RS 3
1	Polystyrene content, %	80,15	80,05	80,15
2	Total molecular weight, g/ mol	79600	90800	102300
3	Polystyrene block molecular weight, g/ mol	63800	72700	80000
4	Polybutadiene block molecular weight, g/ mol	15800	18100	22300

The physical and tensile properties of polymers are presented in table 1 and 2.

The masking solutions were obtained by dissolvation of SBS and RS block-copolymers in tetrachlorethylene using a vigorous stirring. In accordance with this route all masking solutions were obtained at constant total polymers by weight of 9 %. In our research, the RS concentration was varied from 25 to 45 % as reported at total polymer content.

Results and discussion

The experimental research have been concerned to the molecular weight effect of SBS and RS block-copolymers at various RS concentrations on the masking solution characteristics and upon the protective film properties.

Masking solutions

For a safe and effective chemical milling process, the masking solution needs to assure a uniform thickness and composition protective coating without incorporating air bubbles.

Since the majority of masking solutions contain an anorganic filler having higher density as those of elastomers, after storage appear density and concentration longitudional differences as well as filler depositions. To assure uniform and reproducible results in applying mask, prior the use adequate mixing of the solution is necessary. Caution should be exercised to prevent air bubbles forming into the mask by the mixing action.

The use of RS diblock-copolymers as filler in mask recepture avoid these impediments because the densities of SBS and RS copolymers are very close , whereas polymers have a good compatibility.

The most important property of masking solution, which control this demands, is the viscosity, from field experience being estabilished, that the best results in masking operation has been obtained for a viscosity limited to the range from 25 to 50 s, Zahn, cup 5.

In figures 1 -3 are presented the effects of polymers weight in correlation with polymer mixture composition on the masking solution viscosity.

The decrease of both polymers molecular weight determines the diminution of masking solution viscosity, as it was expected.

Analizing all data, it was estabilished the composition of masking solutions which fulfilled the limitations of viscosity variation, the results being presented in table 3. The possibility to vary the masking formulation increase with the molecular weight diminution of both poymers (table 1 and 2).

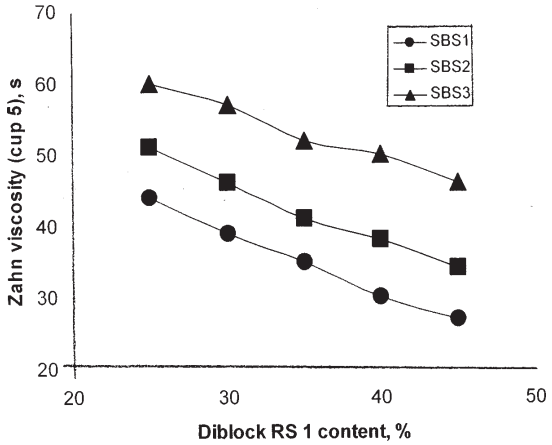


Fig. 1. Dependence of masking solution viscosity on SBS molecular weight and RS 1 content

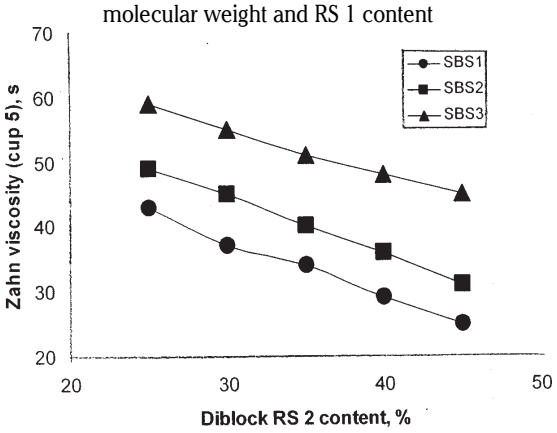


Fig. 2. Dependence of masking solution viscosity on SBS molecular weight and RS 2 content.

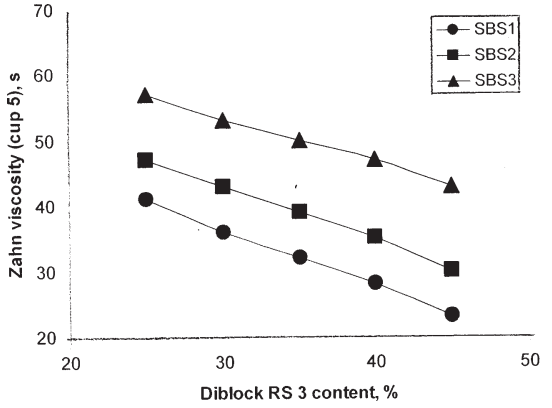


Fig. 3. Dependence of masking solution viscosity on SBS molecular weight and RS 3 content

Film properties

The protective coatings were obtained by slowly immersion in masking solution of the metal piece in order to avoid air intoduction and bubbles formation in the film. Hence , it is necessary to wait 15 – 30 min to allow to dry until the film is tack-free. The metal piece is then rotated 180°, and recoated. The immersion was 4 times repeated to obtain dessired thickness (about 0.3 mm). After the final coating, there are necessary minimum 4 h to mask drying, at normal temperature using air ventilation. The time of drying may be reduced using warm air for ventilation.

Table 3
MASKING SOLUTION COMPOSION FOR THE VISCOSITY ACHIEVEMENT LIMITED AT 25 – 50 s ZAHN, CUP 5

SBS	RS 1 content, %	RS 2 content, %	RS 3 content, %
SBS 1	25 - 45	30 - 45	40 - 45
SBS 2	25 - 45	25 - 45	40 - 45
SBS 3	25 - 40	25 - 45	35 - 45

The protective coating deposited on metal pieces looks like a film which must present very well defined properties, including :

- good tensile strength and elasticity to prevent the deformation when coated metal pieces are transported and are fasten in clips to immerse in the etching bath;
- controled moderate peel adhesion, not very high values for an easy handstrippable operation of the imprinted model. On the another hand, it is necessary to have a good peel adhesion of remained cover film to metal for a sure permanent protection against etchants.

In accordance with these requirements, it has been estabilished from field experience a value of 7 MPa for tensile strength and 500% for elongation at break as minimum protective film requirements.

The peel adhesion depends on the metal nature as well as on the surface processing degree (300 g / 25mm is generaly agred as a minimum value).

The tensile properties were determined on pulled out films from metal pieces, in accordance with standard procedure [7].

The tensile strength varied especially according to the coating film composition, and in a smaller measure with the molecular weight of polymers as it can observed in figures 4-6.

The close values of tensile strength at the same diblock content are the result of the close tensile strength values as compared with the original SBS (table 1).

It must be pointed out that all tensile strength have values higher than the minimum limit of 7 MPa.

The protective coatings present a good elastic behaviour, all films being able to support large strains, in the range of 520 to 730% elongation at rupture (fig. 7 – 9).

The elongation at break decreases, as it is expected, with the increase of RS diblock-copolymer content as a filler effect result.

The increase of styrene-butadiene diblock-copolymer molecular weight (table 2) in the order RS1 < RS 2 < RS 3 is conducive to simultaneous entlargement of polybutadiene block length improving the extending

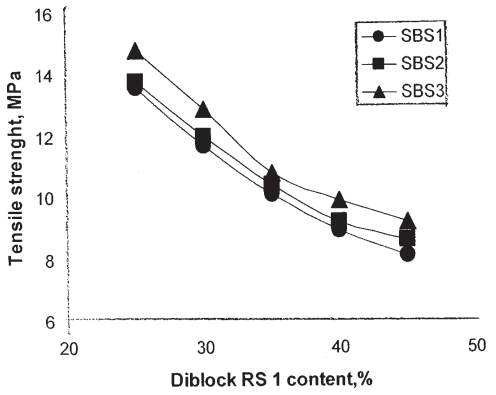


Fig. 4. Tensile strength dependence on SBS molecular weight and RS 1 content.

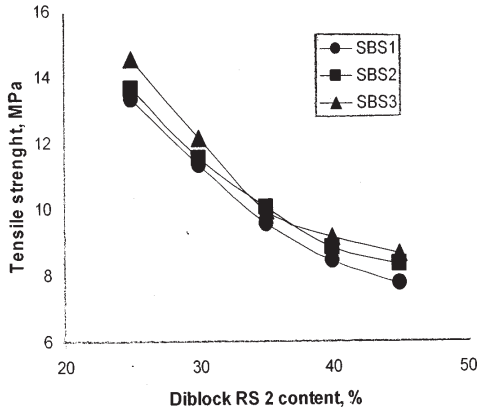


Fig. 5. Tensile strength dependence on SBS molecular weight and RS 2 content.

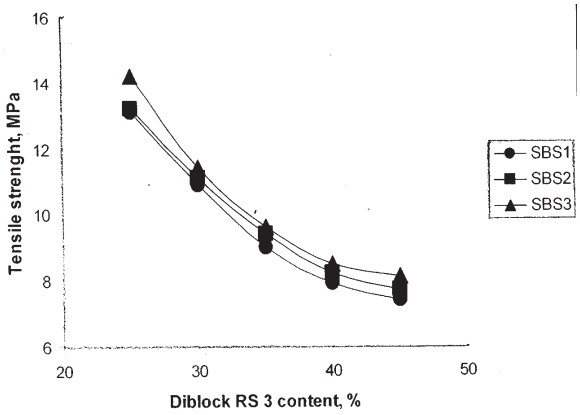


Fig. 6. Tensile strength dependence on SBS molecular weight and RS 3 content

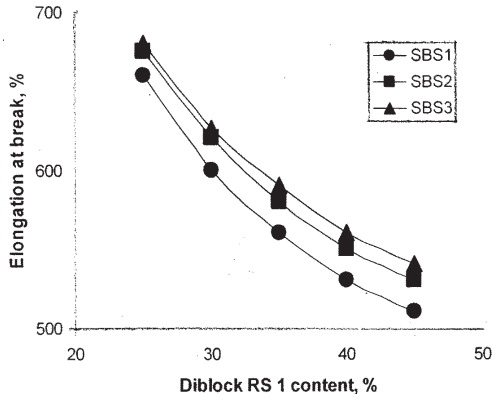


Fig. 7. Elongation at break dependence on SBS molecular weight and RS 1 content.

effect, explaining thus the increase of elongation at break in the same order.

It must be remarked that all films present values of elongation at break higher than the imposed limit of 500 %.

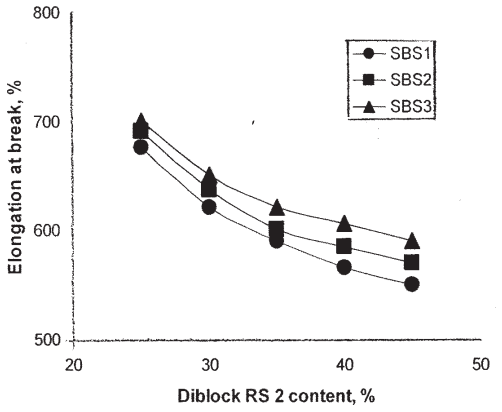


Fig. 8. Elongation at break dependence on SBS molecular weight and RS 2 content.

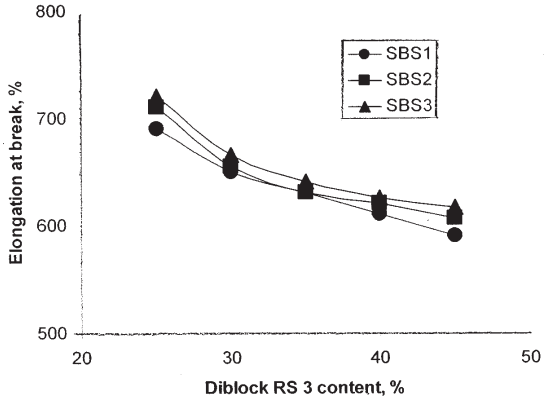
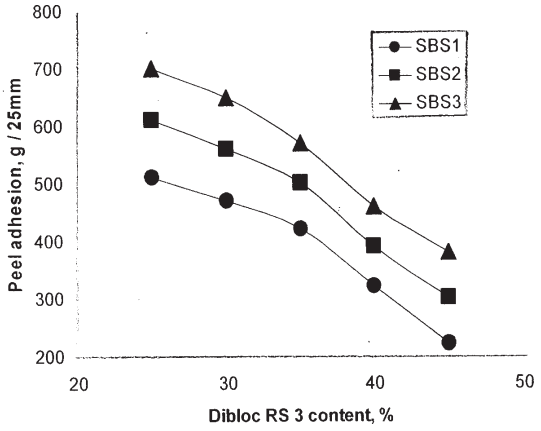


Fig. 9. Elongation at break dependence on SBS molecular weight and RS 3 content



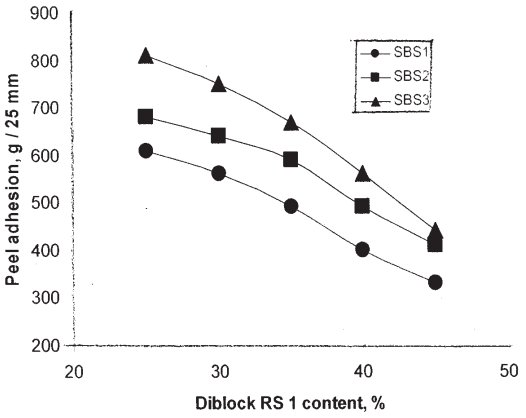


Fig. 10. Peel adhesion dependence on SBS molecular weight and RS 1 content

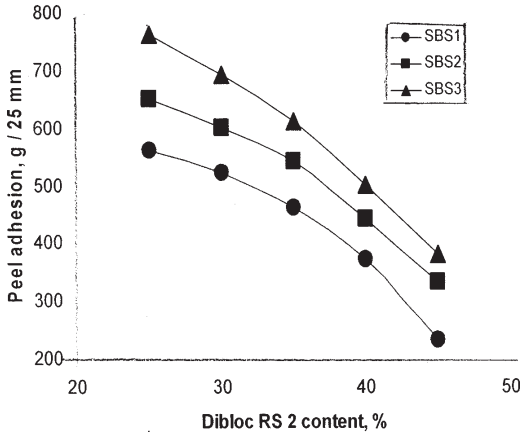


Fig. 11. Peel adhesion dependence on SBS molecular weight and RS 2 content

Fig. 12. Peel adhesion dependence on SBS molecular weight and RS 3 content

SBS	RS 1 content, %	RS 2 content, %	RS 3 content, %
SBS 1	25 - 40	30 - 40	40
SBS 2	25 - 45	25 - 45	40 - 45
SBS 3	25 - 40	25 - 40	35 - 40

Table 4
THE POLYMER COMPOSITION FOR MASKING SOLUTION FORMULAE

The peel adhesion of all films decreases in relationship with the RS content enlargement because the diblock-coplymer acts as a filler, diminishing the SBS matrix contribution which results in a signifiant difference from the value of peel adhesion (fig. 10 - 12).

The molecular weight increase of SBS improves the film peel adhesion as a result of better mechanical properties of unfilled polymers (table 1). All films present pell adhesion values higher than the imposed limit of 300 g / 25 mm excepting two values at maximum filling degree (45 % for SBS 1).

After analyzing the solution and film properties, it were established the composition of formulas which assure the best metal protective coating in the chemical milling process. The values are summarysed in table 4.

Conclusions

By experimental research it was estabilished the influence of polymers composition in relationship with their

molecular weight effect on the masking solution and protective film properties, and finaly the best compositions of masking solution formula were obtained.

The styrene-butadiene dibloc-copolymer using as filler in masking solution composition assures a great longitudinal compositional stability when the solution is long time stored, because the density of RS and SBS bloc-copolymers are very near, and the polymers present a good compatability.

The exclusion of the chemical cure results in large energy and processing time savings.

All the stripped protective coating films, before and after etching process, may be recovered and redissolved in adequate amount of tetrachloroethylene and thus the masking solution is more to be remarked. The total polymers recycling contribute in a natural way to the enviromental protection.

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Manuscript received: 19.07.2010