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Some performance characteristics of plasma surface modified carbon black in the (SBR) matrix

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Abstract

Performance of carbon black reinforced elastomers strongly depend on the adhesion at the filler–matrix interface. Surface characteristics of carbon blacks can be changed by use of a number of different techniques each with certain advantages and disadvantages and as regards to these, plasma surface modification is a novel one. This study aims to check the limits of applicability of plasma surface modification of carbon black to be used in the tire manufacturing industry. For this purpose, RF range cold plasma has been utilized in styrene or butadiene atmospheres. Tensile strengths and percent elongations of vulcanizates are found to respond differently if modified fillers are used as compared with those prepared by the unmodified fillers. Glass transition temperatures of vulcanizates are found to correlate well with the results of mechanical properties. Findings are also supported by the SEM pictures. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Plasma surface modification; Carbon black; SBR vulcanizates

1. Introduction

Filled polymer systems are very popular for the industry for both cost and performance objectives [1].

It is also well established that carbon black (CB) is one of the most important classical reinforcing fillers, especially for the rubber technology [2] although the use of silica in tyres has also been prompted recently [3].

CB as one of the major inputs in tire industry, has some extraordinary features. These are mainly due to the effects of their high porosities, their irregular shapes and structures in general [4]. Surface area of CB is one of the most critical parameters considered for degree of reinforcement, which supply necessary sites to polymer chains for wetting. As some of the polymer chains may also enter into the holes of the particles depending on the rheological (viscosity) properties of the polymers, the so-called physical entrapment and physical crosslinks may also play an important role during reinforcement of elastomeric matrices.

One of the most important parameters for the performance of a composite material is the degree of adhesion at the matrix–filler interface [5–7] which has been explained by several theories, i.e. by diffusion, chemical, electrostatic as well as by mechanical interlocking; each being valid for special cases. In this context, one should remember that; diffusion theory is not successful to explain the diffusion of soft polymer chains into a hard glassy matrix, chemical theory is only valid when there is a chemical reaction between the surfaces and electrostatic theory is insufficient to state the reason for adhesion between neutral surfaces. Finally, mechanical inter-locking theory fails to explain the adhesion between two mechanically perfect surfaces. However, the thermodynamic adsorption and wetting approach is more general where one of the most important factors is the acid–base interaction between the matrix and filler surfaces [8]. This criterion is of our prime interest because most of the CB surfaces are known to be acidic [9] and in the case of rubber matrices with relatively basic components like acrylonitrile or styrene, these interactions should play an important role for the adhesion—however with a strong dependency on the structure of the latter expected in some cases: for conventional SBR 1502, the matrix is relatively neutral due to the high percentage of randomly distributed (neutral) butadiene units [10] where acid–base interactions are supposed to play a minor role. However, for this system, still the high percentage of existing butadienes in the system is expected to wet the filler surfaces to some extent easily, because of flexibilities of chains and high surface areas involved. In the adsorption

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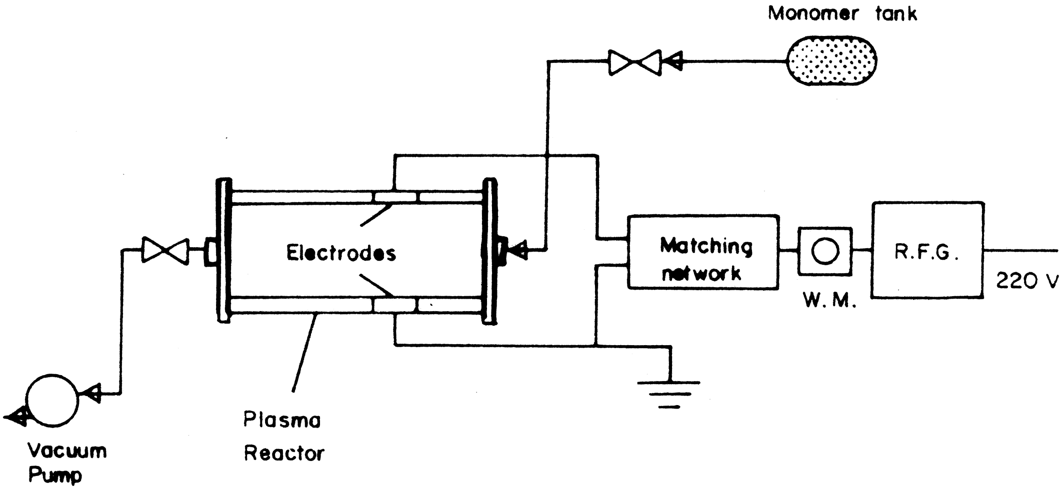

Fig. 1. Schematic representation of the plasma system.

and wetting approach, an another important factor that affects adhesion is the interfacial adhesion tension at interfaces [11] where the work of adhesion is considered. It is a well established fact that, as two surfaces become identical then the interfacial adhesion tension between them becomes zero leading to a maximum in adhesion energy. Obviously, interfaces in any multiphase polymeric system should be modified properly to approach this optimum condition.

In this particular study, it is assumed that

1. high surface areas and structural advantages of CBs can both be preserved after their surface modification and
2. that the acid–base interactions play a minor role for the SBR matrix selected. In fact, it should be possible to achieve the first of these by use of plasma technique, which can produce a very thin polymer film coat on the substrate [12]. One of the most striking results obtained by plasma is that, during the process, the energy is transmitted not only on the "sunshine (direct contact)" part of the substrate but also to the "shade" part [13]; which means production of a thin plasma polymer coat on all surfaces of the substrate [12], certainly distinguishing plasma method from that of others, i.e. UV utilization.

One of the main purposes of this study is to check the applicability of this technique in modifying CB surfaces for their use in the tire manufacturing industry. Another purpose is to see the effect of differences in performances of rubber composites prepared with a series of CBs, each surface modified differently in plasma. In this study, it is also aimed to shed some more light on our understanding of the importance of surface areas and surface selectivity parameters in reinforcing of elastomers. Finally, it is also aimed to stress the importance of plasma polymerization technique in achieving the goal of selective surface modification without affecting the surface areas, which is the continuation of our series of studies; some parts of which were published earlier [12,14].

2. Experimental

2.1. Chemicals

SBR 1502 used was a Petkim (Turkish Petrochem.Ind. Inc.) product; cold-continuously polymerized, non-staining, emulsion type styrene–butadiene rubber with 23.5% of bound styrene. It had $M_w = 320–400$ k and $M_n = 80–110$ k.

CB used was Petkara ISAF N-220 grade product of Petkim with 20–25 nm particle sizes.

Styrene, butadiene, zinc oxide, stearic acid, trimethyl dihydroquinoline (TMQ, used as antioxidant), sulphur and *N*-*t*-butyl-2-benzothiazole sulpenamide (TBBS, used as accelerator) were all reagent grade.

2.2. Surface area determinations

A Micromeritics Model 2280 nitrogen adsorption surface area analyzer was used during surface area determinations in the range of 80–100°C, where ASTM D-3037 is followed. Each test was repeated for at least three times.

2.3. Plasma system and plasma treatment

In this study, a r.f. plasma system with 13.56 MHz frequency was used capacitively. CB sample was loaded into a PMMA tray situated in the tubular Pyrex glass reactor (Fig. 1).

System was purged with styrene vapor at an adjusted flow rate to maintain the pressure at around 1–1.5 mmHg. Then 30 W of power was applied for 30 min at room temperature to produce the plasma polymer of styrene, (PPS). The same procedure was applied with butadiene gas to treat the carbon

Table 1
Recipe

Constituent	phr
SBR 1502 Rubber	100
Filler	35
ZnO	3
Stearic acid	2
Antioxidant	2
Sulfur	2
Accelerator	1.3

black with plasma polymer butadiene, (PPB); in a separate experiment. The power used was 10 W. in the latter case and it was applied for 26 min. Plasma polymerization conditions selected and used for both were those optimized before known to yield to plasma polymerizations with minimum yields mainly, associated with negligible plasma modifications [14,15].

2.4. Coating of substrate from solution

Polystyrene (0.16 and 0.24 g: $M_w = 10\ 000$) was dissolved in ether separately to prepare polymer coats on carbon black mechanically for comparison purposes. Previously weighed amounts of CB were then poured into the beakers. System was mixed well as the ether was let to evaporate slowly. Samples prepared by this way were then dried in a vacuum oven at room temperature to the constant weight.

2.5. Preparation of vulcanizates

The contents of the recipe [13,16] (given in Table 1) were mixed in a Brabender Plasticorder plv 151 mixer head in two steps [17]. The temperature was at 100°C and a 45 rpm of rotor speed for 2.5 min was used during the first stage of mixing the masterbatch. During the second stage of mixing of curatives, the temperature was kept at 90°C for 2 min at the same rotor speed.

Compounds prepared by this way were then compression molded for vulcanization at 160°C under 103 MPa for 25 min.

2.6. Tensile tests

A table model 1183 type Instron tensile machine was used to measure the tensile strength of the samples. Tests were done at 23°C with the crosshead speed of 500 mm/min.

Table 2
Properties of composites prepared by differently modified fillers

Filler	Surface area (m^2/gm)	T_g (°C)	Tensile strength (MPa)
Carbon black	115	−20.0	25.9 + 3.9
pps coated CB	115	−19.5	27.7 + 1.5
ppb coated CB	106	−28.0	17.6 + 4.5

2.7. Thermal analysis

A Dupont model 983 DMA was utilized at resonance mode for determination of dynamic mechanical performance.

2.8. Scanning electron microscopy

A Cambridge Stereoscan S4-10 model electron microscope was used to investigate the fracture surfaces of vulcanizates. Samples used for this purpose were the same that used for tensile tests.

3. Results and discussion

Table 2 presents some data for the plasma treated and untreated CB. As it is seen from the table, PPS coat did not change the original surface area of virgin CB substrate at all; and it decreases the surface area somewhat for ca. 8% coat for the PPB case. As plasma experiments were also followed spectroscopically by following the deposits on optical crystals placed in the same system, there was enough evidence collected for the production of PPS and PPB during plasma treatments. With these in mind, one can easily conclude that in the PPS case, a very thin polymer coat is obtained while for the PPB the coat is denser. In fact, butadiene is known to polymerize much faster in plasma than styrene and hence more polymers is expected for butadiene case filling in some of the pores, where same plasma operational parameters were employed for both.

One of the different ways of initiating polymerizations by plasma is believed to be by creation of the active centers at the surface of substrate. It is speculated that gaseous monomer molecules can diffuse through the bulk of the substrate, most easily if it is already powdery, and polymerize at any location on the surface; randomly. Another argument about plasma polymerization is that both initiation and propagation steps take place in the gas phase and then the polymer precipitate on any surface available in the reactor. Certainly, both events can also happen simultaneously. There have been a critical doubt for all cases about the coat obtained in plasma if filler particles are used as substrates, i.e. the thickness of the coat may not be the same at all locations and even some of the filler particles especially those staying deep in the bulk may be left uncoated. However, after Inagaki [18] and our previous studies for the same filler treated in plasma [12]; at least it is understood that all CB surfaces in the plasma system are expected to be coated with the plasma polymer. One can also conclude that plasma polymer coat obtained on CB is so thin in the case of PPS that there is practically no blockage of the pores and no decrease in the original absorptive capacity of it. In fact, similar results were also reported even for an inorganic non-conducting filler like bauxide in plasma [14] where pore sizes and pore size distributions did not change appreciably after plasma treatment. As a result of the difficulties of

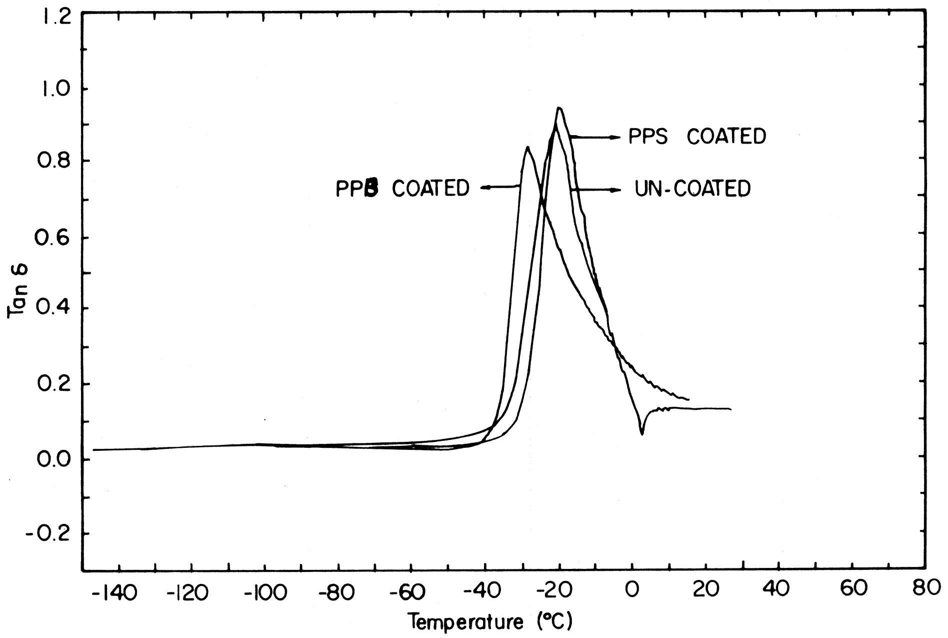

Fig. 2. DMA curves for the uncoated, PPS and PPB carbon black filled SBR vulcanizates (at 35 phr loading).

spectroscopic techniques involved in particular with carbon black, we were unable to justify these results with further evidence; although by use of ESCA it was clearly shown in one of our previous studies [12] that carbon black surfaces are coated by plasma polymer almost homogeneously on all sides for similar conditions.

From the same table, some details of mechanical performances and glass transition temperatures of the rubber samples filled with untreated and treated CB in accordance with the recipe given in Table 1 (at 35 phr loadings) are also presented. Figs. 2 and 3 complement these data. Observation of a similar T_g value for CB loaded samples both untreated and PPS treated simply imply that the number of the effective physical cross links are almost the same in both, probably because of the same level of available surface areas. Therefore, slight increase in the tensile strength is observed for the samples with PPS treated CB and it can be explained by a decrease in the interfacial adhesion tension, as a result of the similarities between treated filler and matrix surfaces at the interface. In other words, most probably surface selectivity becomes dominant in this case. Improved adhesions are also observed from SEM pictures of fracture surfaces for these samples also do confirm this result (Fig. 4(a)–(c)). Further, even a slight

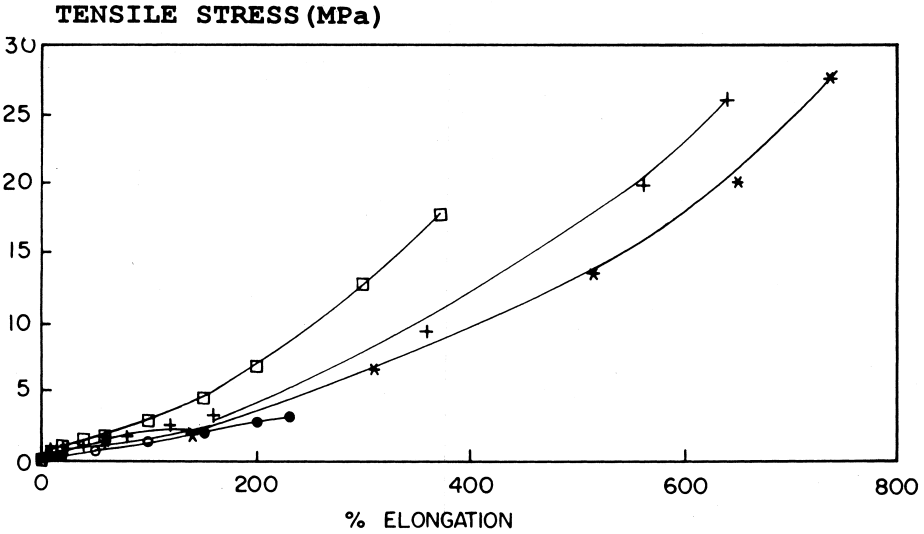

Fig. 3. Unidirectional stress–strain curves of unfilled (●), uncoated (+), PPB coated (□) and PPS coated (∗) carbon black filled SBR vulcanizates.

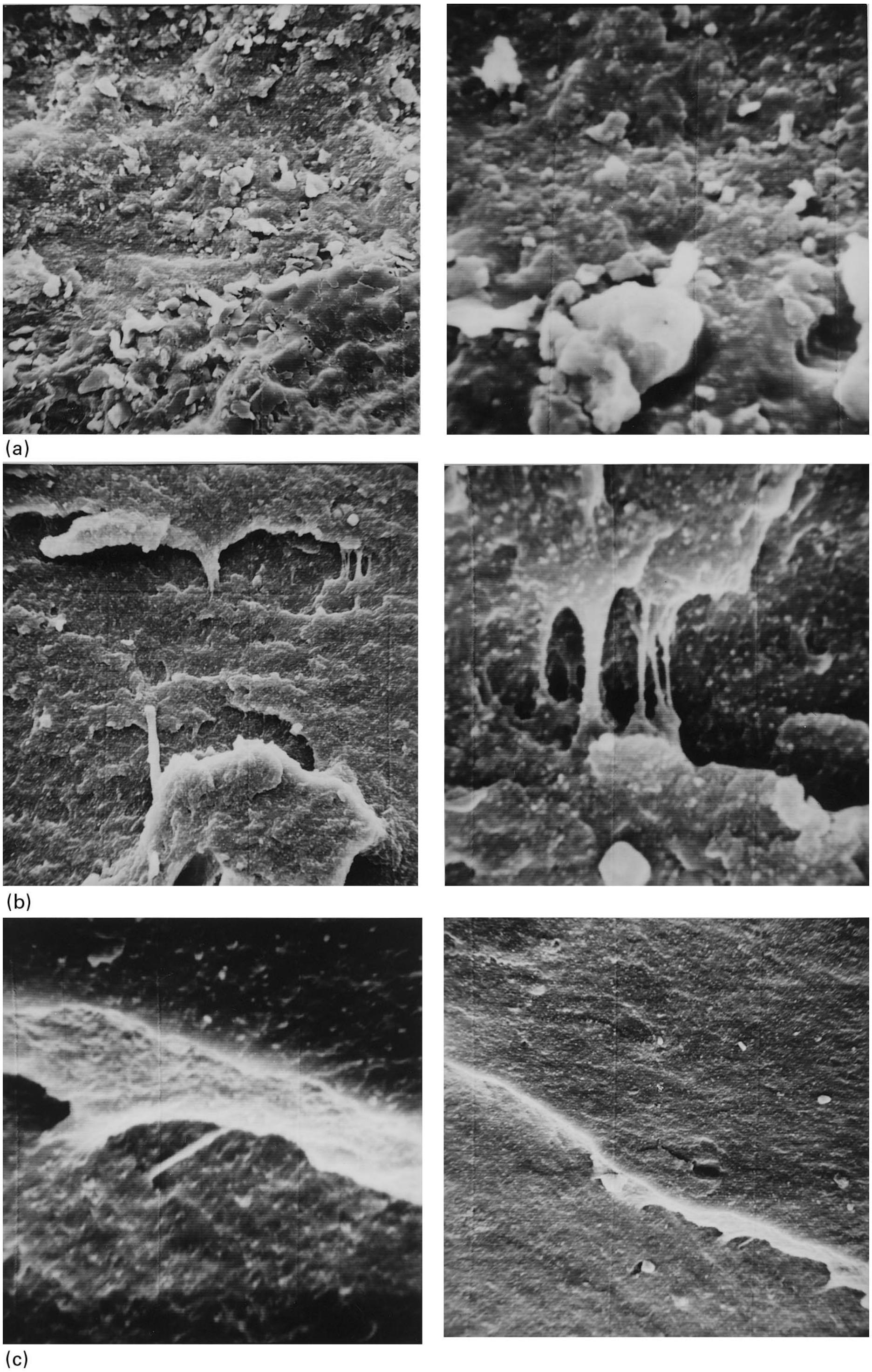

Fig. 4. SEM photographs of virgin/surface plasma modified CB loaded (35 phr) SBR vulcanizates from their fracture surfaces. (All photographs at left are with × 1600 and right with × 8000 magnifications.) (a) uncoated, (b) PPS coated and (c) PPB coated CB.

decrease in surface area of the filler which obviously has a great importance for the reinforcement of elastomers results in the decrease of the number of effective crosslinks and hence appreciable decreases both in the tensile strength (ca. 30%) and T_g values (from -20 to -28°C) for the samples where PPB coated CB were employed. To shed some more light on the subject at this point, rubber composites prepared with CB fillers having thicker coats of polystyrene (all prepared by solution casting method from their polymer solutions) were tested mechanically and the results obtained are presented in Fig. 5 along with that obtained with plasma coated CBs. As seen in the figure, as the coat

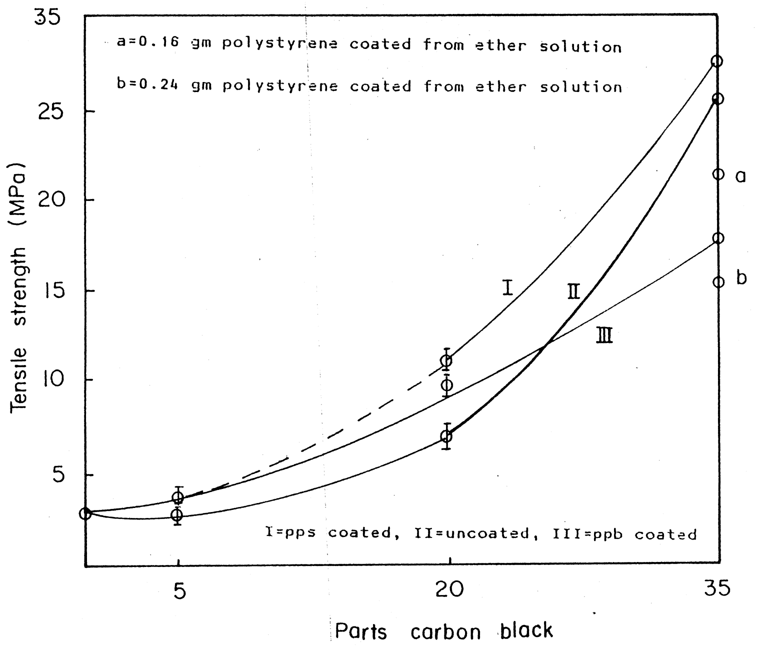

Fig. 5. Tensile strengths vs parts filler for carbon black filled SBR vulcanizates (tensile strengths of solution casted data are also included,details of which are given at the top). I = PPS coated, II = Uncoated, III = PPB coated carbon black filled vulcanizates.

gets thicker; the degree of reinforcement gets weaker as expected as pores of the filler were blocked more and fewer available sites for wetting results.

4. Conclusions

1. By the use of plasma, it is possible to apply surface modifications to carbon black by retaining the original surface areas practically.
2. As a result of its unique features in obtaining modifications within a very limited small region at the surface, plasma technique can offer a very promising method for critical surface modifications, which can result in considerable savings of cost by using a smaller amount of filler for the same mechanical performance, if interfacial adhesion tension of carbon black surfaces can be modified properly by plasma to become identical of the rubbery matrix.

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