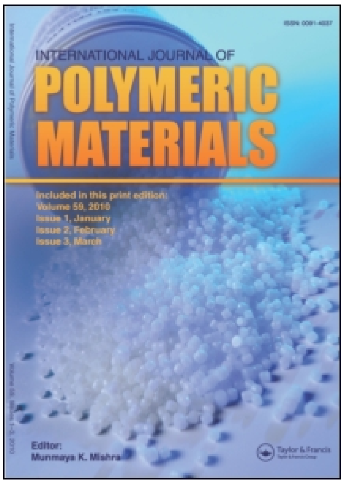

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Effects of γ-Radiation Treatment on the Reinforcing Properties of Carbon Black in Rubber Compound

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Commercial graphite flakes and carbon black grade N234 have been subjected to γ-radiation treatment to a total dose of 1MGy. The resulting radiation-damaged materials were studied by Raman spectroscopy. Raman spectra have revealed that graphite underwent substantial changes in its structure with formation of hexagonal diamond sites as well as onion-like and amorphous carbon domains. Changes also in the Raman spectra of irradiated carbon black have been observed which could be interpreted in the light of the results on irradiated graphite.

A compound evaluation of γ-treated carbon black has been performed in comparison to a pristine sample. The results show a spectacular increase in the reinforcing effect as measured by the 200% and 300% modulus, hence an increase of the filler-to-polymer interaction, a reduction of the Payne effect and of the hysteresis (measured by tand at 70°C).

Keywords: Carbon black; Graphite; γ-radiation; Raman spectroscopy; Rubber compounding

INTRODUCTION

Since the beginning of the nineties, there was a sudden and rapid increase in the use of silica, especially in passenger car tire tread compounds. Previously, carbon black was almost the sole reinforcing agent in tire compounds. This increase was due to the discovery that silica-based tread compounds are able to improve simultaneously the winter and wet performance of a tire with the additional benefit of reducing the rolling resistance in comparison to an analogous tread compound filled with carbon black. The consequence of the development of silica-based technology is that today almost all the most known tire-makers (in Europe) are able to offer passenger tires with silica filled tread compound which are able to save at least 5% of fuel consumption in comparison to a conventional tire with a carbon black reinforced tread. The fuel saving is due to the improved low rolling resistance offered by silica technology. This situation has stimulated new research approach in the field of carbon black due to the strong demand of black fillers which are able to give low hysteresis without affecting traction and wear performances and which could be a valid alternative or which could be complementary to silica. The typical guideline followed by researchers is based on the key idea that by linking by chemical bonds as much as polymer chain fraction on the black surface, the desired reduction of the hysteresis can be achieved. This key idea follows the analogy with silica which has a surface rich in silanol groups which are ideal sites for chemical reactions and hence for linking rubber chains with silica surface, leading to unbeatable general results.

The most interesting research results which have reached the commercial (or semi-commercial) availability were the development of a completely new hybrid filler made by domains of silica and carbon black present on the same aggregates [1, 2]. This hybrid filler was prepared by a unique co-fuming process in a furnace [1, 2] by burning simultaneously hydrocarbon oil and an organosilicon compound (as in the case of pyrogenic silica). An alternative approach involved the production of carbon black having a highly disordered surface structure [3, 4] (high surface roughness). This new carbon black family is produced by physical surface modification directly in a furnace reactor [4]. Studies with atomic force microscopy [4] has confirmed the increased level of surface disorder, while transversal ^{1}H-NMR relaxation spectroscopy has confirmed that the fully immobilized and the partially immobilized polymer chain segments on carbon black surface increases at the expenses of mobile and loosely bound chain segments in the blacks having higher surface disorder in comparison to conventional blacks [4]. One feature of the carbon black having an higher surface roughness is the reduced size of the graphite-like crystallites which for the 300 series of black passes from 1.6 nm of conventional black down to 1.1 nm for the black having high surface disorder. Similarly for the 200 black series the crystallites are reduced from the original 1.2 nm to 0.7 nm [4].

Thus the high surface roughness can lead to chemisorb a larger polymer fraction than the conventional blacks because the larger number of reactive sites present as carbon dangling bonds. This fact has been confirmed by studying the gas absorption properties of different carbon blacks [5] and is shown in Figure 1, where we can see that the blacks having high surface disorder (called N220inv and N234inv in Fig. 1) show from 4% to 10% increased absorption capacity. Carbon black graphitization implies the annealing of the surface defects with consequent increase of the surface order. Consequently the graphitization leads to a reduction of the surface area and to a more ordered and crystallized surface. Therefore, as shown in Figure 1, the differences in gas absorption properties between an original black with high surface disorder and the graphitized black is simply spectacular while it is significant but less remarkable in the case of a conventional black.

It has already been reported that carbon black has a concentration of about 10^{20} free spins per gram [6], not all of these free radicals are available to react with the rubber polymer but it is obvious to think that by increasing the surface disorder of carbon black a larger number of these sites will became available to react with rubber and form chemical links with it. Additionally it should be mentioned that during mixing also the mechanochemical degradation of rubber creates additional free radicals which react with black surface [6–8]. Elsewhere we have already discussed in detail the interaction between carbon black surface and diene polymers both theoretically, from the chemical standpoint [7], in the light of the recent discovery of Prof. Donnet and co-workers [8] that fullerene-like structures are present on carbon black surface, and from the experimental standpoint using model compounds [9].

As part of our research program on carbon allotropes synthesis, characterization and functionalization (carbyne, fullerenes, diamond-like carbon and carbon black) [10–20], recently we have shown that by using oxidized carbon black [21] or carbon black modified by nitrosation and nitration [22] in rubber compounds it is possible to achieve an hysteresis reduction without looses in other key physical and dynamical properties.

In the present work, we will show that another simple method to achieve high surface disorder in carbon black involves the high energy radiation treatment.

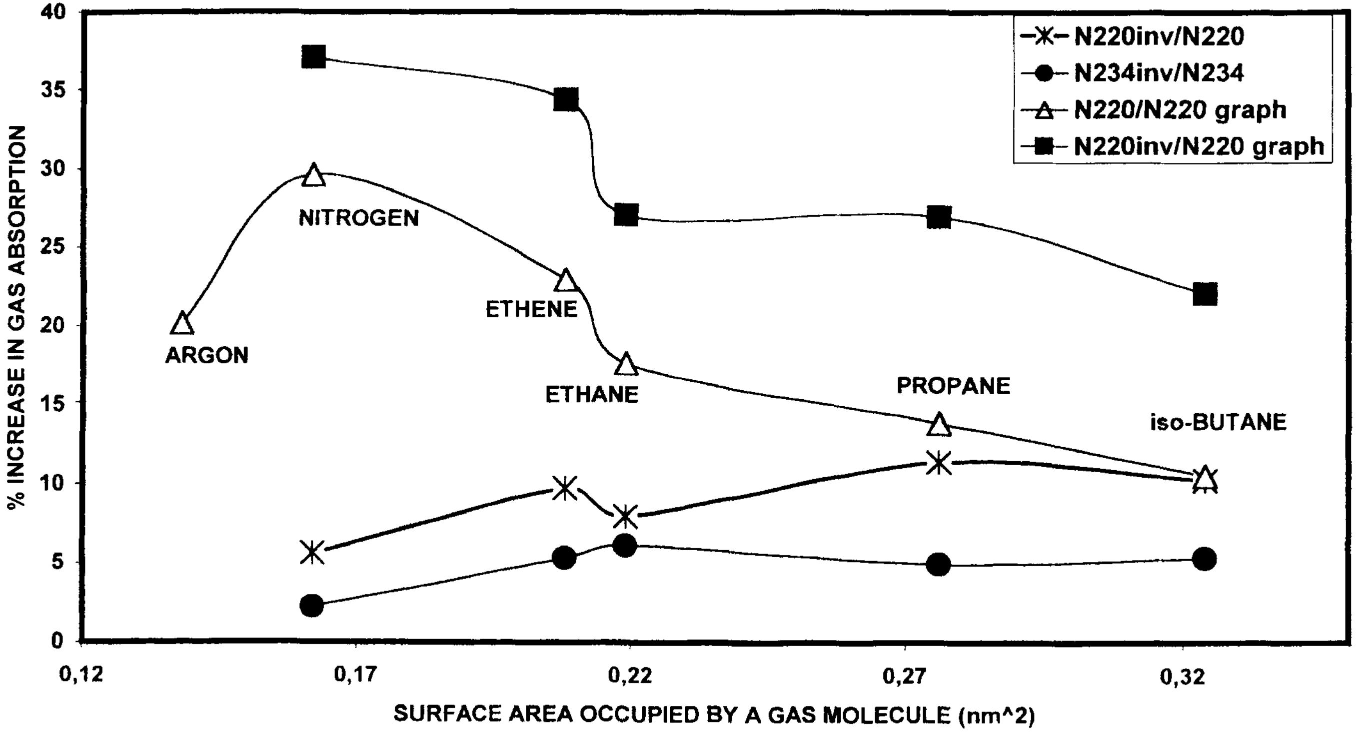

FIGURE 1 Gas absorption on carbon black. From: A. Schroder *et al.*, KGK, 52, 814 (1999), elaborated by the author of the present work.

EXPERIMENTAL

γ-radiation Treatment

A 2 kg sample of commercially available N234 carbon black (Vulcan 7H from Cabot Ravenna) was divided into two portions 1 kg each. One of the two portions of carbon black was placed into an open glass pot inside the chamber of a γ radiation source from ^{60}Co. The irradiation was conducted at a rate of 5.7 kGy/h for a total dose of 1 MGy. In the same irradiation chamber 10 g of graphite (Aldrich) was placed into an evacuated and sealed glass flask to use it as a reference material.

Raman Spectroscopy

Raman spectra of γ-irradiated and pristine samples were recorded on a Renishaw System 2000 spectrometer equipped with an integral microscope (Olympus BH2) and two excitation lasers at 514 nm (ion Ar^+ laser from Spectraphysics model 236 C) and 782 nm (lased diode from Renishaw). The detector was a double Peltier-cooled CCD (385 × 578 pixel) working at – 70°C.

Compound Evaluation

The carbon black samples were tested in a Brabender – Plasticorder laboratory mixer using the following formulation: SBR (BUNA VSL5525-1) 96.25 phr, high-*cis*-BR 30.0 phr, filler 70 phr, liquid silane Si-69 (Degussa – Huls) 2.5 phr or 0 phr, stearic acid 1 phr, zinc oxide 3.5 phr, antioxidant/antiozonant (6PPD) 1.0 phr, TBBS 1.7 phr, sulfur 1.0 phr. Each evaluation was run in duplicate as follows:

COMPOUND 1 (cpd 1): untreated N234 without silane
COMPOUND 2 (cpd 2): untreated N234 with silane
COMPOUND 3 (cpd 3): γ-treated N234 with silane

All evaluations were run according to ISO standards. The dynamic properties were measured on a mechanical spectrometer The data are summarized in Tables I and II.

TABLE I Processing

Compound		*MDR* 30′ @ 160°*C*				
		Torque			*ts*-2	*ts*-90
Comp. ID	*Filler*	*Min*	*Max*	*D Torq.*	(*min*)	(*min*)
CPD-1	N234	7,8	26,9	19,1	4,57	9,11
CPD-1	N234	7,7	26,3	18,6	4,92	9,92
CPD-2	N234+Si69	8,4	28,3	19,9	3,65	13,9
CPD-2	N234+Si69	8,5	28,1	19,6	3,7	13,86
CPD-3	Gamma N234+Si69	8,4	29,9	21,5	3,28	11,78
CPD-3	Gamma N234+Si69	8,3	29,7	21,4	3,21	12,01
Average of the above data						
CPD-1	N234	7,8	26,6	18,9	4,75	9,52
CPD-2	N234+Si69	8,5	28,2	19,8	3,68	13,88
CPD-3	Gamma N234+Si69	8,4	29,8	21,5	3,25	11,90

TABLE II Physical/

Compound		25*M*	50*M*	100*M*	200*M*	300*M*	*TS*	*EB*	*M ratio*	*Hardness*
Comp. ID	*Filler*	*Mpa*	*MPa*	*MPa*	*MPa*	*MPa*	*MPa*	(%)	300/100	*ShoreA*
CPD-1	N234	1,00	1,32	1,80	4,05	7,39	17,37	618	4,11	65
CPD-1	N234	1,05	1,34	1,88	4,22	7,62	17,62	618	4,05	65
CPD-2	N234+Si69	1,13	1,45	2,17	4,90	8,75	19,09	598	4,03	67
CPD-2	N234+Si69	1,11	1,46	2,21	5,12	9,14	18,37	548	4,14	67
CPD-3	Gamma N234+Si69	1,13	1,53	2,53	6,21	10,71	18,93	470	4,23	66
CPD-3	Gamma N234+Si69	1,20	1,60	2,63	6,39	11,02	19,43	522	4,19	67
Average of the above data										
CPD-1	N234	1,03	1,33	1,84	4,14	7,51	17,50	618	4,08	65
CPD-2	N234+Si69	1,12	1,46	2,19	5,01	8,95	18,73	573	4,08	67
CPD-3	Gamma N234+Si69	1,17	1,57	2,58	6,30	10,87	19,18	496	4,21	67
Index values										
CPD-3/CPD-2		104	108	**118**	**126**	**121**	102	**87**	103	100
CPD-3/CPD-1		**114**	**118**	**140**	**152**	**145**	**110**	**80**	103	103
CPD-2/CPD-1		109	109	**119**	**121**	**119**	107	93	100	103

characteristics

Viscosity	*Dispersion*		
ML(1 + 4)100°*C*	*Visual analysis*	*Kontron analysis*	
24 *hrs*	*Visual rating*	% *Undisp. CB#*	*Counts* > 40*um*
69	Good/very good	1,66	85
68	Very good	2,12	114
73	Good/very good	1,72	103
72	Good/very good	1,35	106
71	Good	1,74	110
70	Good/very good	1,67	120
69	Good/very good	1,9	100
73	Good/very good	1,5	105
71	Good/very good	1,7	115

Dynamic properties

Strain sweep at 10 *MHz*						*Strain sweep*		*Bound*	*Abrasion resist all*	
G'o	*G'oo*	*dG'*	*G'o*	*G'oo*	*dG'*	*Tan delta max*		*rubber*	14% *index*	21% *index*
0°*C*			70°*C*			(0°*C*)	(70°*C*)	%	%	%
30,900	1,900	29,000	5,120	0,912	4,208	0,585	0,296	35	100	100
31,400	1,850	29,550	5,770	0,894	4,876	0,581	0,318	36	93	112
32,500	2,050	30,450	4,790	0,999	3,791	0,572	0,273	45	95	140
26,600	1,950	24,650	4,700	1,020	3,680	0,573	0,265	45	104	118
27,300	1,980	25,320	4,720	1,060	3,660	0,576	0,260	41	96	119
27,100	1,980	25,120	4,330	1,030	3,300	0,575	0,254	47	93	115
31,150	1,875	29,275	5,445	0,903	4,542	0,583	0,307	36	97	106
29,550	2,000	27,550	4,745	1,010	3,736	0,573	0,269	45	100	129
27,200	1,980	25,220	4,525	1,045	3,480	0,576	0,257	44	95	117
92	99	92	95	104	93	101	96	98	95	91
87	106	**86**	**83**	**116**	**77**	99	**84**	**124**	98	**110**
95	107	94	87	**112**	82	98	**88**	**127**	103	**122**

RESULTS AND DISCUSSION

Raman Spectroscopy

The approach to increase the surface roughness or, which is the same, the surface disorder of carbon black has already given good results in terms of hysteresis reduction as discussed in the introduction of the present work. This result was achieved by physical surface modification directly in a furnace reactor [4]. However in our opinion, it is possible to modify freely the surface and the bulk chemical structure of carbon black after its production. This can be done by radiation damage of carbon black.

It is in fact well known that radiation damage is accumulated by graphite leading to changes in its dimension, strength, thermal conductivity *etc.* [23, 24]. Some defects can be annealed by heating the irradiated sample. Heating is accompanied by an evolution of an excess of enthalpy known as "Wigner energy" [23, 24]. Long studies on radiation-damaged graphite have clarified that there is little difference in principle between the type of damage ultimately resulting from neutrons, fast heavy particles or even fast electrons, except as regards to the distribution of defects [24] and the displacement threshold dose per atom [25].

It is particularly remarkable that the electron irradiation of carbon soot produces onion-like structures which have been interpreted as superior homologues of Buckminsterfullerene [26, 27]. Electron irradiation and annealing, causes the carbon onions collapse to form ultradisperse diamonds [28–30]. This transformation is not irreversible and it is possible to transform ultradisperse diamond back to onion-like carbon [31]. Since in carbon black have been already identified both onion-like and fullerene-like structures [8], it is reasonable to think that a radiation treatment could increase the concentration of these sites. An increase of the concentration of these sites should lead to an improved filler-polymer interaction as we have discussed elsewhere [7, 9]. This concept is supported by the classic studies of Wolkenstein and his school [32] who have studied the effect of radiation damage on the activity and the absorption properties of surface catalysts.

Among the studies on the radiation damage of graphite, limited attention has been devoted to the radiation damage caused by high energy electromagnetic radiation like γ radiation. Only very recently some results on this subject appeared in literature [33] and were very interesting because show that γ radiation induces graphite plane rotation of 10° according to X-ray diffraction. This prompted us to repeat that study by irradiating graphite at 1 MGy radiation dose and to study the resulting radiation damage by Raman spectroscopy [34, 35]. Here we would like to report only the conclusions of our works on this matter, while for more detailed discussion we remand to the Refs. [34, 35]. First of all we would like to show the Raman spectra of pristine graphite (Fig. 2) and radiation damaged graphite at 1 Mgy radiation dose (Fig. 3). What we can immediately observe from these spectra is that the I_D Raman band associated to the structural defects is significantly increased in intensity (compare Fig. 3 with Fig. 2) and is shifted from the original 1350 cm^{-1} down to 1305 cm^{-1}. This fact together with certain features of the I_G band of the irradiated graphite sample leads us to conclude [34, 35] that γ treatment of graphite causes the formation of

- Domains of glassy carbon (amorphous carbon)
- Domains of hexagonal diamond (lonsdaelite)
- Domains of onion-like particles.

The interpretation of the Raman spectra of γ treated carbon black is not as clear as in the case of graphite. The reason of this is due to the fact that carbon black is already a disordered material and the radiation damage cannot be detected as in the case of graphite. Anyway, spectra deconvolution has given the following interesting results:

	I_D *cm*$^{-1}$ *(intensity)*	I_G *cm*$^{-1}$ *(intensity)*	I_D/I_G	L_a*(nm)*
N234 PRISTINE	1376 (352.8)	1598 (337.9)	1.044	4.17
N234 1MGy	1370 (91.2)	1596 (77.1)	1.18	3.68

Showing that radiation treatment has modestly shifted to shorter wavenumber the I_D band, hence in the same direction observed more neatly in the case of graphite. Additionally radiation treatment has modified the I_D/I_G band ratio, which, by adopting the formula of Tuinstra [36], has led to a reduction in crystallite size as expected in the case of a more disordered material.

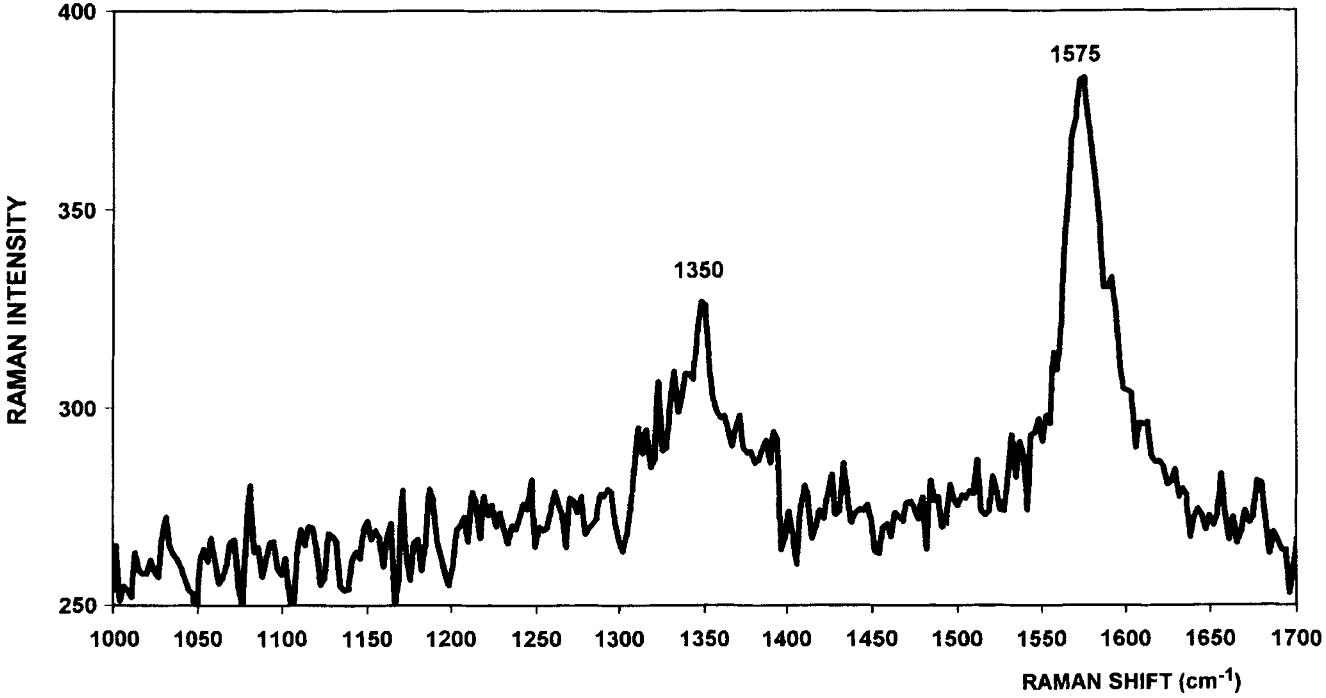

FIGURE 2 Graphite, pure untreated graphite flakes.

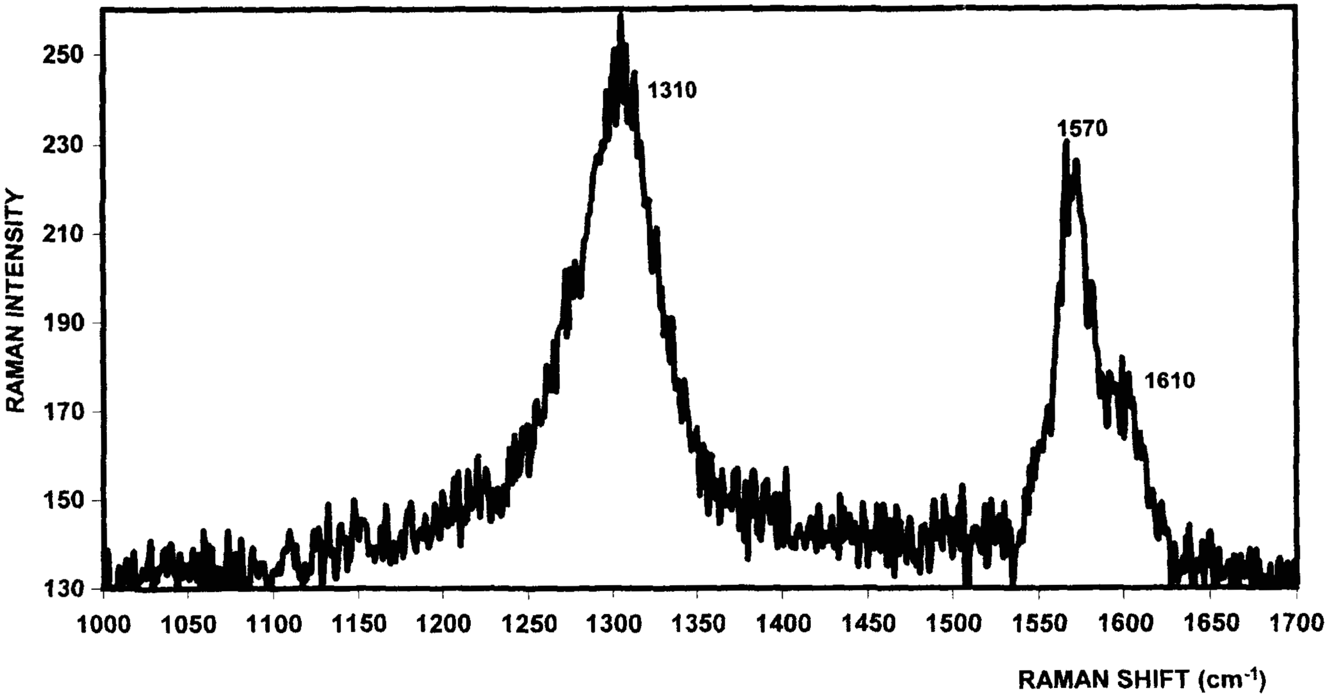

FIGURE 3 Graphite, 1Mgy gamma radiation dose, recorded at 782 nm Raman laser (10 s, 1.25 mW).

All the above data in conjunction with the model study on graphite irradiation strongly suggest that γ radiation treatment of N234 induces the formation of bulk and surface defects which are expected to improve the chemisorption properties and the rubber-to-filler interaction.

Compound Evaluation

As reported in the experimental section, three compounds have been evaluated. The first one filled with untreated carbon black N234, the second filled with untreated black and silane and finally the third filled with radiation-treated N234 plus silane.

In Table I are reported the processing characteristics of the three compounds tested in duplicate and the averages. The MDR rheometer shows that γ-treated N234 (plus silane) has an higher torque max, slightly higher delta torque which is related to an higher crosslinking density and it is faster curing in comparison to untreated N234 plus silane. The compound viscosity and the degree of dispersion are somewhat comparable to the control. In Table II are reported the physical and dynamical compound properties with the averages and the indexes. For a more direct reading, we have reported these data as indexes in Figures 4, 5.

The data on physical properties (Fig. 4) show a significant increase in modulus especially at high elongation where γ-treated N234 (with silane) is 26% higher in modulus than control (untreated N234 plus silane) at 200% elongation and above 20% higher in modulus at 300% elongation. At low elongation (25% and 50%) the modulus increase is not so high as at high elongation. This experimental fact strongly suggests that the filler-to-polymer interaction have been enhanced by γ-radiation treatment while the filler-to-filler interaction (as indicated by moduli at low elongation) is not affected so dramatically. Similar results, but in a more dramatic form are observed when comparing γ-treated N234 plus silane with untreated N234 (without silane). In this case the increase in the reinforcing effect is generalized and involves also the modulus at low elongation, but again the most spectacular results are obtained for the 200% modulus which is increased by more than 50%. As blank reference

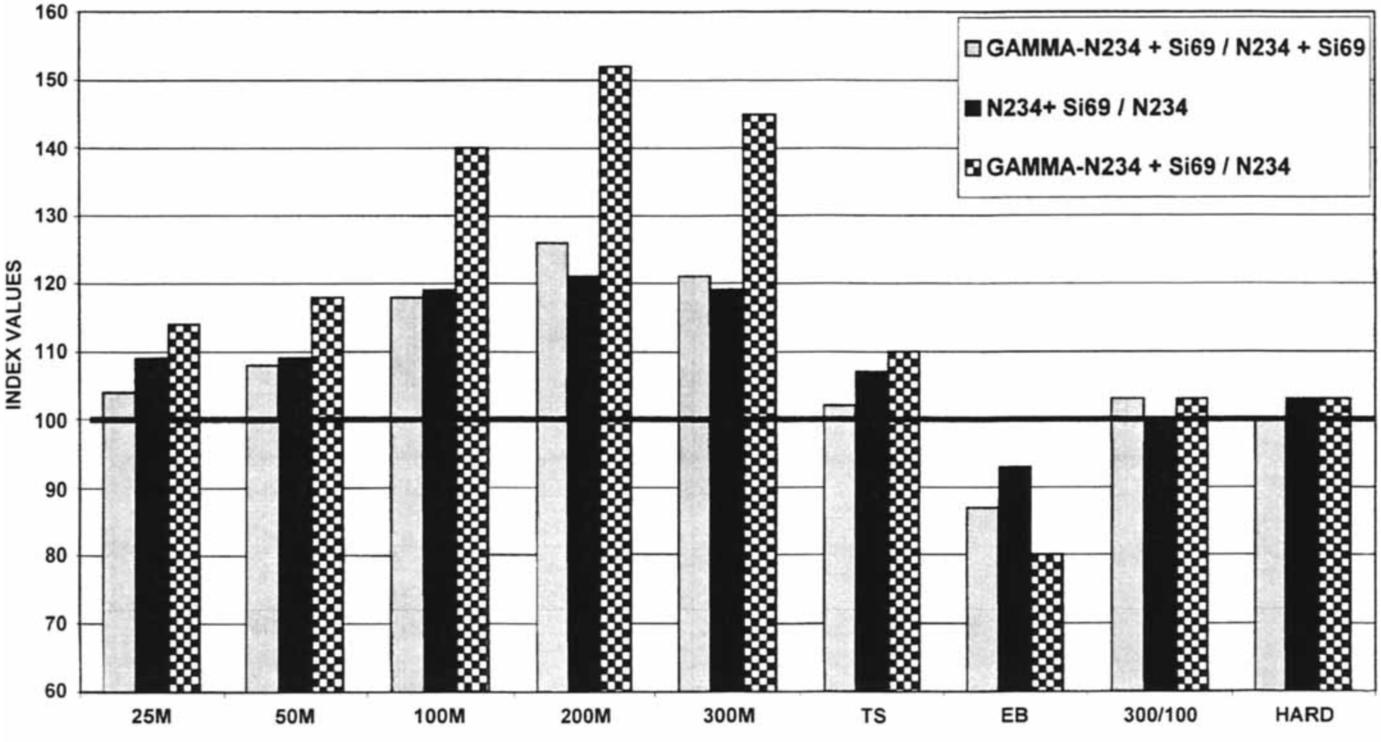

FIGURE 4 Effects of gamma radiation on compound properties of N234.

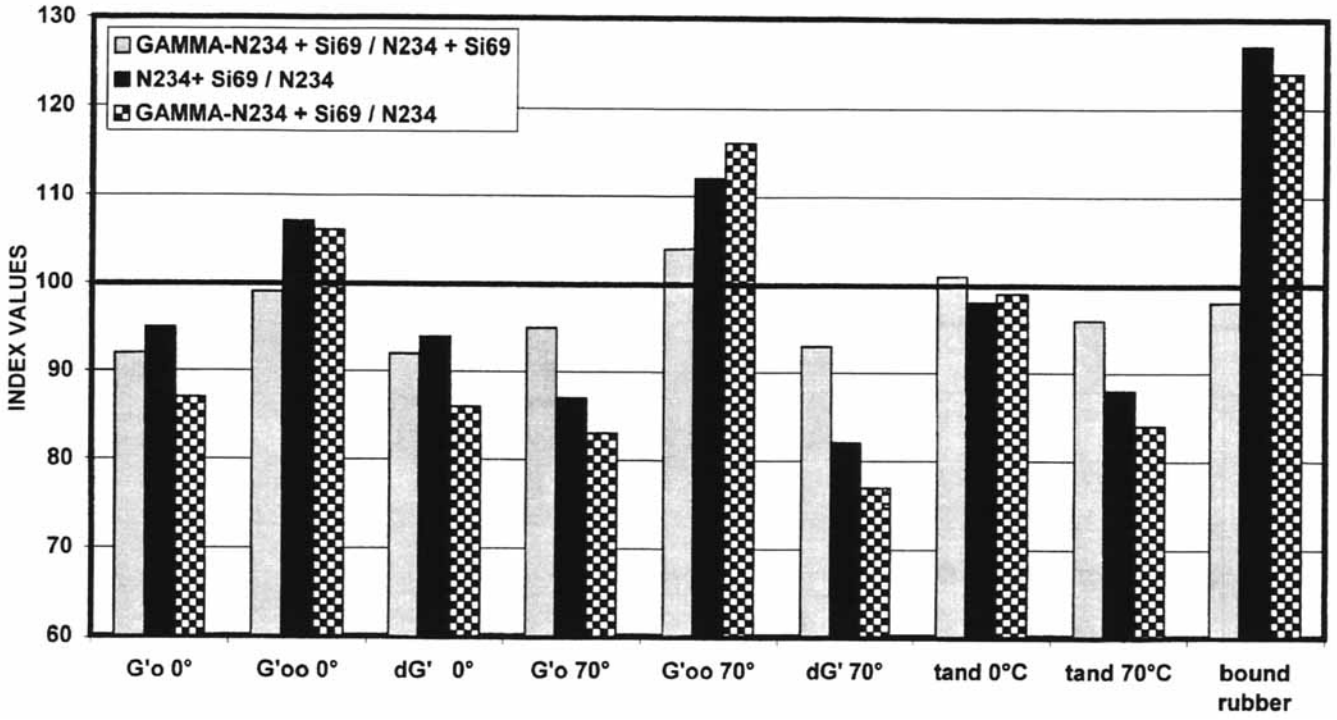

FIGURE 5 Effects of gamma radiation on compound properties of N234.

we have reported also the ratio between untreated N234 plus silane on pure untreated N234. In this case we can observe the reinforcing effect due to the presence of silane only. By subtracting the silane effect in the case of γ-N234 + Si69/N234, it is clear and evident that the radiation treatment of N234 leads to an additional increase in modulus of more than 20% at 200% elongation (as total it was +52%).

If we compare these results with commercial blacks called inversion blacks [3] or nano-structure blacks [4] having unusually high surface roughness obtained by physical surface modification directly in a furnace reactor, we can see that the 300% modulus increase is limited to only 10–12% maximum [3]. Thus, γ-radiation treatment causes a more neat and significant increase in modulus than the physical treatment in a furnace reactor.

Figure 5 shows that the hysteresis at low temperature (which correlates with tire tread wet traction) is not affected by radiation treatment and similar results are achieved among the three samples. However, the hysteresis measured by tanδ at 70°C (which correlates with tire tread rolling resistance) show a reduction of about 5% in the case of γ-radiation treated N234. Silane is able by itself to reduce the hysteresis and again by subtracting the silane effect we can confirm that the effect of γ-radiation at 1MGy dose leads to a reduction of hysteresis of about 5%. These results should be compared again with the new carbon black family (called inversion blacks or nano-structure blacks) produced by furnace process and having high surface roughness [3,4]. In this case the hysteresis reduction is more pronounced for the inversion blacks and is of the order of magnitude of 10%.

However, radiation treatment gives a larger degree of freedom because we have tested only 1MGy of radiation dose, but at significantly higher radiation dose we believe that it is possible to introduce an additional higher number of defects and reaction sites so that the hysteresis should be improved even more. Additional comments from Figure 5 is a trend to low elastic modulus at very low elongation G_0' and low dynamic stress softening effect with increasing strain amplitudes (lower Payne effect) dG'. This is in line with the results obtained on the inversion blacks [4] and are expected for fillers having an high surface roughness.

CONCLUSIONS

For the first time we have evaluated in a rubber compound N234 furnace carbon black treated with γ-radiation (total radiation dose 1MGy). The results look promising because of:

- The observed spectacular increase in the reinforcing properties as measured by the 200% and 300% modulus. This fact suggests an increase of the filler-to-polymer interaction.
- The hysteresis measured by tanδ at 70°C (which is a predictor of tire tread rolling resistance) is reduced of 5% in the case of γ-treated N234 while it is not affected at 0°C (a predictor of tire tread wet traction).
- The Payne effect as measured by the variation of G' as function of strain is reduced as expected for carbon blacks with high surface disorder.

All these experimental results in compound are in agreement with the Raman spectroscopic data which, in graphite irradiated with γ-radiation suggest the formation [34, 35] of:

- Hexagonal diamond sites
- Onion-like domains
- Amorphous carbon domains.

The same or similar sites are induced by radiation-treatment of carbon black which is by itself a partially amorphous object. These sites created by radiation treatment are again onion-like sites and, it may be also fullerene-like sites. Some of these sites are already present in conventional carbon black [8] and they play a key role in bound rubber formation [7, 9], in the reinforcing effect [7, 9] and in the hysteresis reduction if there will be a significant slowing down of the dynamic of the chains which are close or attached to the disordered and rough surface of carbon black. The consequence of this last fact will be a reduction of the glass transition temperature of the bound rubber layer with the consequent reduction in hysteresis.

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