Chapter 8
Reinforcement of Recycled Rubber Based Composite with Nano-Silica and Graphene Hybrid Fillers

A. B. Irez, E. Bayraktar, and I. Miskioglu

Abstract Nano-silica and Graphene have been used as the main reinforcing fillers that increase the usefulness of recycled rubber composite. As each filler retains its specific advantages, the use of nano-silica/graphene combinations should improve the mechanical and dynamic properties of recycled rubber composite. But, the optimum nano-silica/graphene ratio giving rise to the optimum properties requests to be explained. In this work, reinforcement of recycled rubber composite with nano-silica/graphene hybrid filler at various ratios was studied in order to determine the optimum nano-silica/graphene combinations. The toughness properties and tribological behaviour indicating the reinforcement of recycled rubber based composite were evaluated. Microstructural and fractural analyses were made by Scanning Electron Microscopy (SEM).

Keywords Epoxy · Recycled rubber · Wear resistance · SEM · Fracture toughness

8.1 Introduction

Elastomers are very well classified in the polymer family that exhibit rubber-like elasticity [1–8]. Their general characteristics involve viscoelastic behaviour, a low modulus of elasticity, a high failure strain along with very weak inter-molecular forces. Among other properties, rubber provide good heat resistance, ease of deformation at ambient temperatures and exceptional elongation and flexibility before breaking. These properties have established rubber as excellent and relatively cheap materials for various applications in many sectors including automotive, industrial, packaging, healthcare and many others. Currently the rubber industry is vast developing because of the wide commercial penetration of specific materials accompanied by an increased industrial and academic interest, resulting in a steady rise in global annual revenues, predicted to be US56$ billion by 2020 [1, 3, 4, 8]. However, utilization of the recycled rubber for the manufacturing of the new composites is a very economical way for cost effective composite design. Last decades, the usage of the recycled rubber obtained from fresh and clean scrap rubber for different industrial applications such as automotive and aeronautical engineering has been very well developed as very useful material for the composites either as a matrix or as a reinforcement. Extensively, this rubber powder come directly manufacturing of sportive affaires, shoes etc., For this reason, it is feasible to use it after chemical (silanization) and devulcanization treatments for cost effective composite design [3, 5, 8, 9].

Reinforcement of the rubber based composites with nano graphene and/or graphene nano plates (GnPs) are very extensive applications in composite design for mainly aeronautic and aerospace applications. Graphene are known and used widely used as multi- functional reinforcement materials that can improve the electrical, piezo-resistive, dielectric, thermal, mechanical and gas barrier properties of elastomer based composites even at extremely lower loadings. Because of the exceptionally high surface area, as compared to other graphite derivatives, an enormous improvement in properties is observed for graphene composites. Correspondingly, they exhibit unique advantages, as compared with all other organic and inorganic fillers, and are thus useful in many applications. Finally it may be concluded that graphene can be applied to improve the gas permeability (like layered silicates), electrical and thermal conductivity (like carbon nanotubes) of rubber based hybrid composites.

A. B. Irez
CentraleSupélec, Université Paris-Saclay, Gif-sur-Yvette, France

E. Bayraktar (✉)
Supmeca-Paris, School of Mechanical and Manufacturing Engineering, Saint-Ouen, Paris, France
e-mail: bayraktar@supmeca.fr

I. Miskioglu
Michigan Technology University, Engineering Mechanics Department, Houghton, MI, USA

P. R. Thakre et al. (eds.), *Mechanics of Composite, Hybrid and Multifunctional Materials, Volume 5*, Conference Proceedings of the Society for Experimental Mechanics Series, https://doi.org/10.1007/978-3-319-95510-0_8

The interactions between the various elements of a complex multicomponent system, such as the ones found in graphene/elastomer nanocomposites, play a major role on the final physico-chemical properties of the material. For this reason, in much of the literature, surface chemistry is applied to the different components of the system, in order to ensure chemical compatibility between them. In addition, it can lead to the formation of chemical bonds focused towards the improvement of the properties of the initial material and a satisfactory dispersion of the filler.

As for the reinforcement of the rubber based composites with nano silica (SiO_2 d < 15–30 nm) particles [10–12] can increase toughening of the rubber based composites and its distribution in matrix is very easily managed that give a multiphase hybrid-toughened composite structure. The rubber based composites reinforced with nano silica and graphene nano plates (GnPs) show higher thermal conductivity of rubber based composites containing of nano silica and GnPs in a certain ratio. According to the former experience obtained in the same research project, these composites have shown higher thermal conductivities (variable between 25–30 ± 5.5 W/m K) at a fixed ratio of the reinforcement as considered in this work (nano Silica/GnPs = 2.5) [3].

In the frame of the common research project that is going on, a hybrid rubber based composite reinforced with nano silica+ graphene nano-plates (GnPs) has been designed for electronic applications, mainly in the manufacturing of the electronic devices for the control panels in aerospace, defense industry due to the high capacity of thermal conduction, etc. We believe that this new composite design by using nano silica and graphene nano plates may exposed a novel interface design approach for developing multifunctional rubber based composites.

8.2 Experimental Conditions

8.2.1 Materials Processing

In this study, at the beginning recycled rubber particles were blended with solid bisphenol-A type epoxy powders in pre-defined mass rates. However, because of the insufficient free chains of rubber particles, formation of a robust and durable bonding between epoxy and recycled rubber is quite challenging. For this reason, fresh scrap rubber should be devulcanized. In fact, devulcanization is known to be an operative practice for manufacture of recycled rubbers to increase flowing capacity and also to be remoulded during manufacturing of new designed composites. During this process, formerly created sulphur links are tried to be broken and also new other links are generated, it means that the structure of the material is modified entirely as renewable process. Thanks to this process, newly created free chains make possible have chemical bonding between rubber and epoxy [3–5, 13, 14].

A new design of devulcanized rubber based composite, reinforced with nano silica and graphene nano platelets (GnPs) are prepared in several steps:

1. Chemical treatment was applied on rubber. The principal of the chemical treatment consists in a short silanization process followed by acrylic acid followed by silanization in order to activate the surface of the rubber particles.
2. After drying of the chemically treated rubber powders, they are exposed to short microwave heating in two stages during 4 min under 900 W of power in order to avoid degradation of the main chains called devulcanization.
3. At the final stage, devulcanized rubber were mixed with a little amount of epoxy resin powders for binding of rubber matrix and reinforcements. This mixture used as a matrix after that the new designed composites are manufactured by using classical powder metallurgy methods.
4. After the mixture of the reinforcements (here nano silica and GnPs) in the matrix, a fast-rotating toothed-wheel milling process was carried out during 4 h to obtain fine rubber powder.
5. After having a homogeneous powder compound, the composite specimens were manufactured by using double uniaxial action press at a temperature of 180 °C under a pressure of 70 MPa during the heating of 30 min.
6. All of the specimens (30/50 mm in diameter) were cooled slowly in the press. All of the specimens were post-cured isothermally at 80 °C for 24 h.

The compositions of silica and GnPs reinforced epoxy-recycled rubber based composites (called as SG I-II-III hereafter) were given in Table 8.1.

As seen the reinforcement percentage in the rubber matrix, the ratio SiO_2/GnPs = 2.5 was kept as constant to calculate molar ratio in the mixture for adding to the rubber matrix. By this way, adhesion of nano silica and GnPs to the rubber 90 wt% + Epoxy 10 wt% are carried out at very high levels.

Table 8.1 Composition of the epoxy-rubber based composites

Rubber based composition Epoxy – SBR rubber (10 wt% Epoxy – 90 wt% Rubber)	SG I	SG II	SG III
Reinforcements (wt %)	5 nano $SiO_2$2 GnPs	7,5 nano $SiO_2$3 GnPs	10 nano $SiO_2$4 GnPs

Table 8.2 Hardness values of SG specimens

Hardness measurement	
Specimen	Shore D
SG I	77.2
SG II	78.3
SG III	79

Table 8.3 Density values of SG specimens

Hardness measurement	
Specimen	Density (g/cm^3)
SG I	1438
SG II	1455
SG III	1467

8.2.2 *Microstructure: Fracture Surface Analyses and Shore-D Hardness Measurements*

Fracture surface damage analyses and microstructural observation have been realized by means of optical (OM) and scanning electron microscopy (SEM). SEM observation was realized on fracture surface of the tested specimens with Scope/JSM-6010LA Jeol® electron microscope.

Surface hardness measurements of the specimens were performed after post curing. Shore D hardness test measurements on the polished flat surfaces of the specimens were carried out according to ASTM D 2240 using Shore D hardness tester, (type HBD-100-0). Hardness results were given in Table 8.2.

Three-point bending tests (3 PB) have been carried out according to the ASTM D790 standards. Tests were realized with the machine Zwick Proline Z050TN and during the tests crosshead speed was selected as 1 mm/min. Flexural strength and strain were obtained from the test results. At least three specimens for each composition were used and standard deviation and average values were given in results chapter with standard deviation values. In addition, fractural properties such as plain strain fracture toughness (K_{Ic}) and critical strain energy release rate (G_{Ic}) were investigated with SENB specimens and the tests were realized according to ASTM D5045 standard. Notches were introduced by tapping a fresh razor blade.

Charpy impact tests have been carried out by means of Zwick 5102 pendulum impact tester with a 1 J pendulum configuration for measuring the resilience behaviour of the composites. Relative density for each composition was also measured and they were summarized in Table 8.3.

8.2.3 *Wear Resistance (Scratch Test) and Damage Analysis via 3D Optical Roughness Meter*

In the current research basic idea on the tribological behaviour of the epoxy and recycled elastomer based composites was evaluated performing scratch tests. A 3D optical surface scanner was utilized to assess damage zone after the scratch test in terms of scratch depth and average scratch roughness.

The contact between the sliding diamond indenter and the surface of the composite material during scratch test was analyzed. The normal and tangential forces on indenter were recorded. However, main focus was given to the damage area and volume. In the frame of the current research, the resistance to scratch deformation was evaluated in terms of scratch depth, worn surface and volume subsequent to scratching only under dry conditions and 50,000 and 100,000 number of cycles of wear.

8.3 Results and Discussions

8.3.1 Microstructure of the Composites

In Fig. 8.1 two different specimens were shown in different diameters for different characterizations. They were manufactured by means of hot compaction technics.

After hot compaction, transversal sectioning was made then mounted specimens were polished. Then, general microstructures in the transversal direction of three compositions were observed by means of OM and they were shown in Fig. 8.2. From the figures, it is said that all of the compositions have shown a considerably homogenous distribution of the reinforcements in the structure. White circular particles in different dimensions were considered as rubber. In addition, homogeneously distributed amorphous media are thought as epoxy matrix. However, more precise identification requires EDS analysis. On the other hand, silica and GnPs cannot be detected via OM due to their nano-scale dimensions.

8.3.2 Three Point Bending Tests and Fracture Surface Observation

Three-Point Bending (3 PB) tests have been carried out for each type of compositions. These tests have been repeated with 4–5 specimens to optimize the results for the all of three composition.

8.3.2.1 Flexural Testing and Fracture Toughness Determination

Flexural stress is calculated during three-point bending test according to the Eq. 8.1:

$$\boldsymbol{\sigma} = \frac{\mathbf{3}\boldsymbol{x}\boldsymbol{P}\boldsymbol{x}\boldsymbol{l}}{\mathbf{2}\boldsymbol{x}\boldsymbol{b}\boldsymbol{x}\boldsymbol{h}^{\mathbf{2}}} \tag{8.1}$$

In this formula, l is the span length, P is the maximal bending load, b and h are the sample width and thickness, respectively.

Flexural strain, ε_{f}, was determined according to the Eq. 8.2:

$$\varepsilon_f = \frac{6Dh}{l^2} \tag{8.2}$$

where, D is the maximum deflection at the center of the specimen.

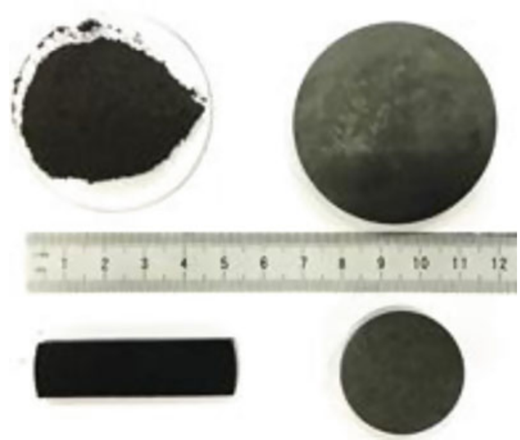

Fig. 8.1 Macrograph of the specimens after compacting and post curing d = 30–50 mm

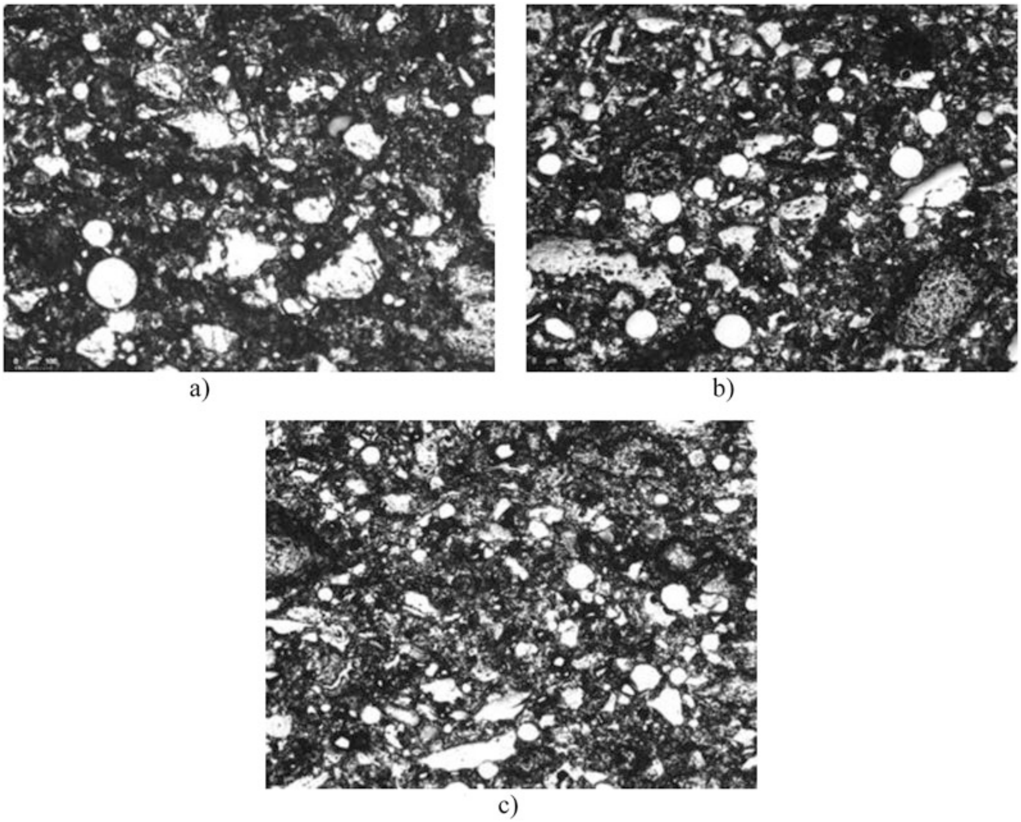

Fig. 8.2 Microstructure of the composites called here as (**a**) SGI, (**b**) SGII and (**c**) SGIII respectively

Therefore, E_B is the modulus of elasticity in bending and it is expressed with the Eq. 8.3 as follows:

$$E_B = \frac{l^3 m}{4bh^3} \tag{8.3}$$

where, m is the tangent of the initial straight portion of the stress-strain curve.

The mode I fracture toughness, K_{Ic}, was determined by testing of the SENB specimens and K_{Ic} was calculated according to the Eq. 8.2:

$$K_{Ic} = \frac{F}{B\ w^{1/2}} f(x); \quad x = \frac{a}{W} \quad ,0 < \frac{a}{W} < 1 \tag{8.4}$$

where F is the maximum force from the load-elongation plot; B is the thickness of the specimen; W is the width and "a" is the total notch length.

f(x) is the geometry correction factor and is expressed with the Eq. 8.3 as follows:

$$f(x) = 6(x)^{0.5} \left\{ \frac{\left[1.99 - x(1-x)\left(2.15 - 3.93x + 2.7x^2\right]\right.}{(1+2x)(1-x)^{1.5}} \right\} \tag{8.5}$$

Critical strain energy release rate (fracture energy) G_{Ic} was calculated using the expression Eq.8.4:

$$G_{Ic} = \frac{{K_{Ic}}^2}{E} \tag{8.6}$$

Table 8.4 Comparison of mechanical properties of SG specimens

	Flexural stress (MPa)	Flexural modulus (MPa)	Strain in break (ε %)	K_{Ic} (MPa $m^{1/2}$)	G_{Ic} (kJ/m^2)
SG I	10.41 ± 7.9	929.1 ± 696	0.,63 ± 0.16	0.66 ± 0.12	0.48 ± 0.18
SG II	14.53 ± 4.8	884.9 ± 380	0.40 ± 0.05	0.62 ± 0.02	0.43 ± 0.03
SG III	17.84 ± 0.3	1092.2 ± 304	0.38 ± 0.06	0.90 ± 0.09	0.75 ± 0.15

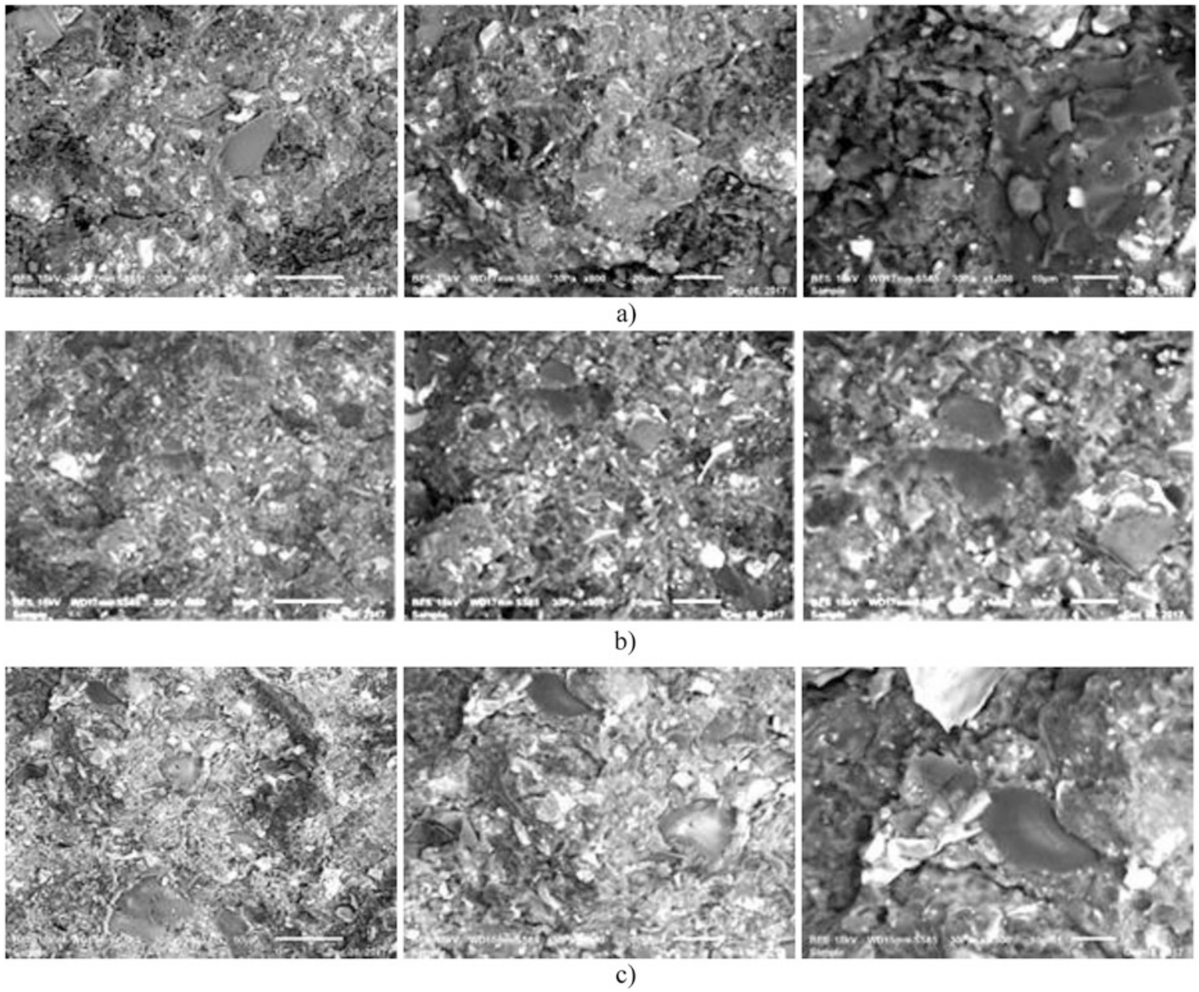

Fig. 8.3 (**a**) Fracture surfaces after 3 PB testing SG I (b) SG II (**c**) SG III

where *E* is the elasticity modulus for plane stress approach examined for thin specimens.

Table 8.4 indicates the mechanical properties in bending mode. Fracture toughness values were also presented in the table.

Table 8.4 indicates that The hybrid rubber based composites reinforced with nano silica and graphene nano plates (GnPs) with a certain ratio have shown enhancements in the mechanical properties, and more significantly, fracture toughness (K_{IC}), which can be explained by synergistic impact coming from the intrinsic physical characteristics of the reinforcements it means that nano silica and graphene nano plates (GnPs). In this study, the highest K_{IC} can be obtained with addition of small amounts of nano-silica particles (5, 7.5 and 10 wt %) with a constant ratio of 2.5 with graphene nano plates (GnPs).

Fracture surfaces obtained from 3 PB tests have been analyzed by means of Scanning Electron Microscopy (SEM). It noticed that good adhesion of the both of the reinforcements in the rubber based matrix by creating an ideal interface for each composition, as presented in Fig. 8.3 with different fracture surfaces taken by SEM.

Cavitation and void formation in the rubber matrix with matrix expansion and locally, debonding of nano particles with consequent void growth have been observed in the structure as the improved toughening mechanisms. For this evolution, the mixture of devulcanized rubber (90 wt %) with epoxy (10 wt %) plays an important role. Some of the specimens with homogenous distribution of the nanoparticles have shown a typical debonding of the silica nanoparticles with GnPs that

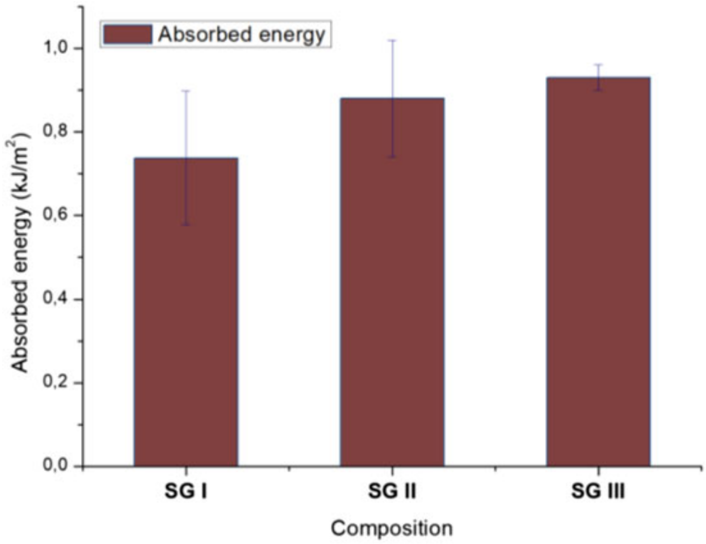

Fig. 8.4 Absorbed energy during charpy impact tests for SG specimens

should be origins of the weakening of the matrix–particle interface. The toughness improvement in hybrid rubber based composites should be direct related to the increment of the debonding phenomena that can increase the size of the plastic zone in the structure. This case facilitate the devulcanized rubber based composites to dissipate additional fracture energy.

8.3.3 *Charpy Impact Testing*

Last mechanical characterization was realized to see the impact resistance and energy absorbance capability of the manufactured composites. Each composition group was tested with at least three specimens. Absorbed energies during impact testing of the composites were presented in Fig. 8.4. It seems that the absorbed energy for each specimen during the impact tests is related to the increment of the plastic zone in the structure due to the debonding of the nano particles. Higher dispersion of the values is also related to the test specimens prepared under laboratory conditions; hot compaction, cutting notch effect, etc.

8.3.4 *Damage Analysis by Means of Scratch Test and 3d Optical Roughness Meter*

After completing mechanical tests, tribological characterization of the composites were done by macro scratch tests. Surface damages were observed three dimensionally by an optical surface scanner. The results are presented in the Fig. 8.5.

In Fig. 8.6 the volume and surface of the damage trace after scratch calculated from roughness test results are given. It can be said that, by the increase of the reinforcement content, composites become more resistant to wear.

In reality, because of the high shear stress at the interfaces the interfacial shear stress should probably be the main reason for damage of the matrix and reinforced filler interfaces. When the indenter is slipping, tangential tensile stress is caused on the surface behind the indenter, while in front of the indenter the tangential stress is compressive.

8.4 Conclusion

The hybrid rubber based composites reinforced with nano silica and graphene nano plates (GnPs) have shown enhancements in the mechanical properties, and more significantly, fracture toughness (K_{IC}), which can be explained by synergistic impact coming from the intrinsic physical characteristics of the reinforcements; it means that nano silica and graphene nano plates

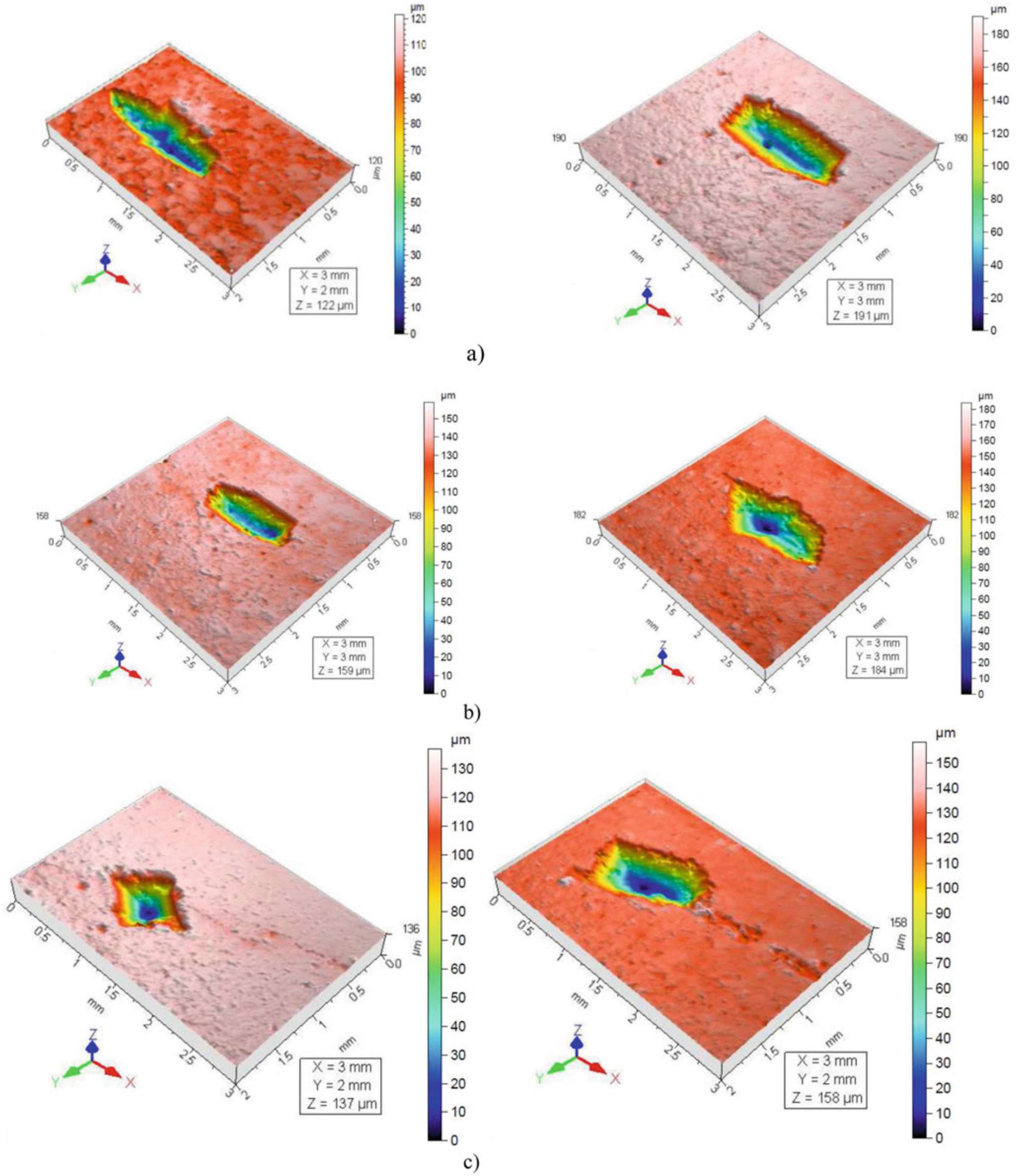

Fig. 8.5 Three dimensional damage traces obtained in the direction of width and length for (**a**) SG I (**b**) SG II (**c**) SG III for 50 k cycles and for 100 k cycles

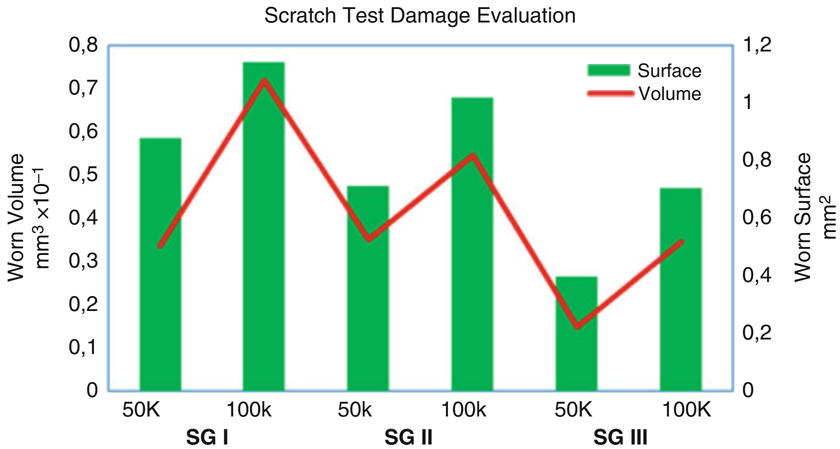

Fig. 8.6 Comparison of scratch damage traces presented as volume lost and damage surfaces obtained by wear-software for the specimens SG I-II-III for 50 and 100 k cycles, respectively

(GnPs) with certain ratio. In this study, the highest K_{IC} can be obtained with addition of small amounts of nano-silica particles (5, 7.5 and 10 wt %) with a constant ratio of 2.5 with graphene nano plates (GnPs).

Cavitation and void formation in the rubber matrix with matrix expansion and locally, debonding of nano particles with consequent void growth have been observed in the structure as the improved toughening mechanisms. For this evolution, the mixture of devulcanized rubber (90 wt %) with epoxy (10 wt %) plays an important role. Some of the specimens with homogenous distribution of the nanoparticles have shown a typical debonding of the silica nanoparticles with GnPs that should be origins of the weakening of the matrix–particle interface. The toughness improvement in hybrid rubber based composites should be direct related to the increment of the debonding phenomena that can increase the size of the plastic zone in the structure. This case facilitate the devulcanized rubber based composites to dissipate additional fracture energy.

In another aspect of these composites is related to the higher thermal conductivity of rubber based composites containing of GnPs graphene in varying ratios. According to the former experience obtained in the same research project, these composites have shown higher thermal conductivities (variable between 25–30 ± 5.5 W/m K) at a fixed ratio of the reinforcement as considered in this work (nano Silica/GnPs = 2.5).

Acknowledgments The authors thank Dr. H-A. Alhas from Airbus-Space, London/UK for general support and also for his valuable discussion in certain stages of this project. Also they would wish to acknowledge research foundation of Supmeca/Paris.

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