High aspect ratio nanofillers for rubber composites

M Galimberti[1], V Barbera[1], A Bernardi[1], D Locatelli[1], G Prioglio[1], L Giannini[2]

[1] Politecnico di Milano, CMIC "G. Natta" Department, Via Mancinelli 7, 20131 Milano (I)

[2] Pirelli Tyre, Via Piero e Alberto Pirelli 25, 20126 Milano

Abstract. This work is focused on high aspect ratio nanometric fillers for rubber compounds. Their ability to establish stable interaction with the rubber matrix is discussed. An sp^2 carbon allotrope such as a high surface area graphite and a clay, such as sepiolite, are then in particular considered. It is shown how their chemical functionalization can promote the interaction with the polymer chains and positively affect the compounds' properties.

Introduction

Reinforcing fillers are essential components of rubber composites, as they allow to achieve the mechanical properties required by the composites' applications [1-2].

Many sp^2 carbon allotropes are efficient reinforcing fillers for rubber materials. Carbon black has been used since the beginning of the last century [1-2]. After the discovery of fullerenes [3], many other carbon allotropes have become available: single [4-5] and multi-walled [6-7] carbon nanotubes (CNT), graphene (G) [8-11] or graphitic nanofillers made by few layers of graphene [12-15]. Many scientific papers have been published, focused on rubber composites based on carbon nanotubes [16-22] and graphitic materials [20, 22-33]. Studies are available on hybrid carbon filler systems [34-40].

Silica in the precipitated form, combined with a sulphurated coupling agent [41-42], is acknowledged as the best filler for composites with low dissipation of energy and fuel consumption [1-2, 43-45]. Other efficient fillers for rubber composites are also inorganic oxides and hydroxides, such as clays [20, 46-52]. Studies on hybrid filler systems between silica and clays have been reported [53-54]. Hybrid filler systems between carbon allotropes, inorganic oxides and hydroxides have been studied [55-58].

Carbon allotropes and inorganic oxides and hydroxides, used as fillers for rubber composites, are classified as nanometric or nanostructured fillers [1-2]. A material is defined as a nanomaterial when it has an external dimension in the nanoscale or it has internal structures or surface structures in the nanoscale, ranging approximately between 1 nm and 100 nm [59]. Carbon black and silica are nanostructured fillers: their primary particles have at least one dimension below one hundred nanometers and are joined together to form aggregates with a length of at least 200 nm. Clays, carbon nanotubes, graphene and related materials are nanometric fillers: they are made by nanosized primary particles which can be separated and individually dispersed in the rubber matrix.

Nanometric fillers (CNT, GRM, clays) have high aspect ratio, that means high ratio between the largest and the lowest dimension. The nanosize and the high aspect ratio lead to a very large surface area. Nanometric fillers can thus establish a large interfacial area with the polymer matrix. Indeed, the interfacial area i.a. is defined by Equation 1 as follows:

$$i.a. = s.a. * \rho * \phi \qquad [1]$$

where s.a. is the surface area, ρ is the filler density and ϕ is the filler volume fraction.

The high interest and the large amount of research dedicated to nanometric fillers is thus clear. However, is the interaction between the high aspect ratio nanometric filler and the rubber matrix stable? The polymer chains occluded in the voids of nanostructured carbon black and silica are responsible for the stable rubber-filler interaction and for the high mechanical reinforcement at large deformation. Nanometric fillers are not considered as structured fillers, that means having voids able to accommodate polymer chains.

A way to have a stable interaction between filler and rubber chains would be to establish chemical bond. As mentioned above, chemical bonds are formed between silica and unsaturated polymer chains thanks to the use of sulphur based silanes. However, nanometric fillers such as clays (e.g.: bentonites and sepiolite) have low reactivity with silanes. sp^2 carbon allotropes do not have functional groups able to establish chemical bonds with the rubber chains or with coupling agents either. Such lack of reactivity transforms the opportunity of having a large interfacial area (presented by the nanometric high aspect ratio fillers) available for the polymer chains into a problem of dissipative supramolecular interactions.

This contribution is focused on high aspect ratio nanometric fillers: multiwalled carbon nanotubes (CNT), high surface area nanosized graphite (HSAG), organically modified montmorillonite (OC) and sepiolite (S). Their interaction with the rubber matrix is in particular discussed. A brief overview of data available in the scientific literature is reported. Chemical modification is proposed as a successful tool to promote a chemical bond with the rubber chains and, hence, stable interactions.

1. Mechanical reinforcement of rubber composites with high aspect ratio nanofillers

Rubber nanocomposites based on high aspect ratio nanometric fillers are characterized by high values of elastic modulus at low strain. Some of the authors prepared nanocomposites based on synthetic poly(1,4-cis-isoprene) (IR) and different amounts of CNT [34, 36], HSAG [35, 36] and OC [56], as well as on carbon black (CB) (CB N326) [36]. Some features of the sp^2 carbon allotropes are reported in **Table 1**.

Table 1. Main features of sp^2 carbon allotropes used for the preparation of rubber nanocomposites.

Carbon filler	BET surface area (m²/g)	DBP absorption number (ml/100g)	Number of stacked layers	pH
CB N326	77	85	5	5.7 – 9.7
CNT – 1[a]	200	316	10	n.d.
CNT - 2 [a]	300	n.d.	8	n.d.
HSAG	330	162	35	4.6

[a]CNT: 1 - Baytubes® C150 P from Bayer Material Science, 2 – Nanocyl 7000 from Nanocyl

The used filler volume fraction was up to about 10% and vulcanization was performed with a traditional sulphur based system (sulphur, sulphenamide). In **Figure 1**, the elastic modulus E, normalized with respect to the matrix modulus E_m, is reported as a function of the vol% of the filler.
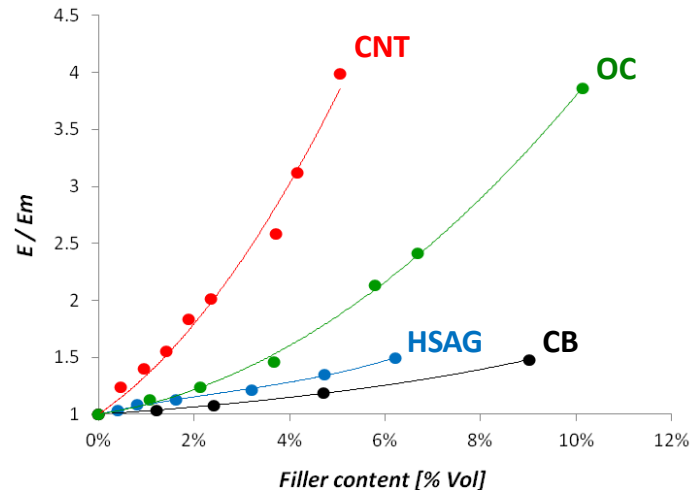
Figure 1. E/E_m vs vol% of filler for composites with CNT, OC, HSAG and CB as the fillers (for refs, see text)

It is thus evident that high aspect ratio nanofillers give rise to a larger elastic modulus than carbon black. Such behaviour was rationalized thanks to a correlation between the elastic modulus and the specific interfacial area [38]. This correlation is shown in **Figure 2** for CB and CNT as sp[2] carbon allotropes.
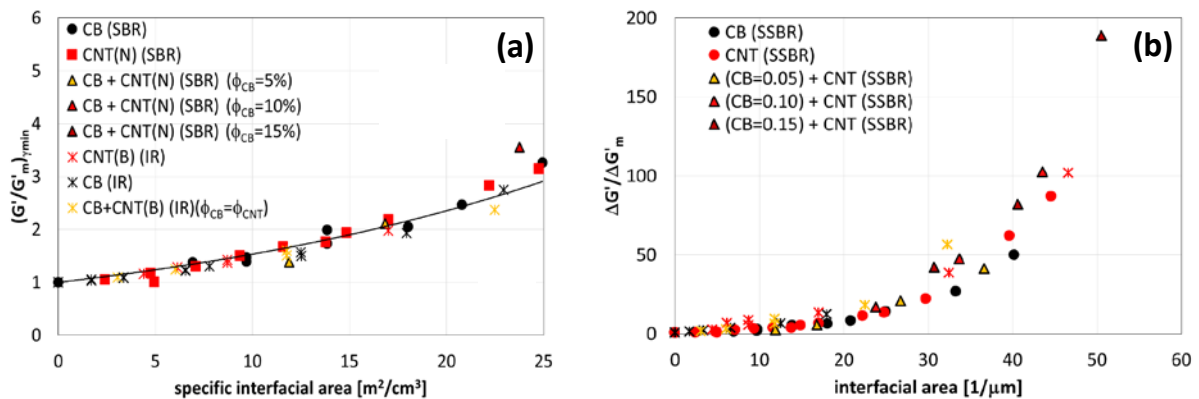

Figure 2. $(G'/G'_m)_{\gamma min}$ (a) and $(\Delta G'/\Delta G'_m)$ (b) vs specific interfacial area for composites of ref. 38, with exponential fitting curves

Experimental points were fitted with a common line, a sort of master curve, up to about 30.2 and 9.8 mass % as CB and CNT content, respectively. The lower modulus values obtained with HSAG were attributed to the actual HSAG surface area, much lower than the nominal one, measured by means of nitrogen absorption.
The key role played by the interfacial area in affecting values of elastic modulus is thus evident. However, such extended filler-matrix interaction is based on supramolecular forces and faints with the extent of the strain. Figure 3 shows the values of shear G' modulus vs strain amplitude for the same composites [34-36, 56].
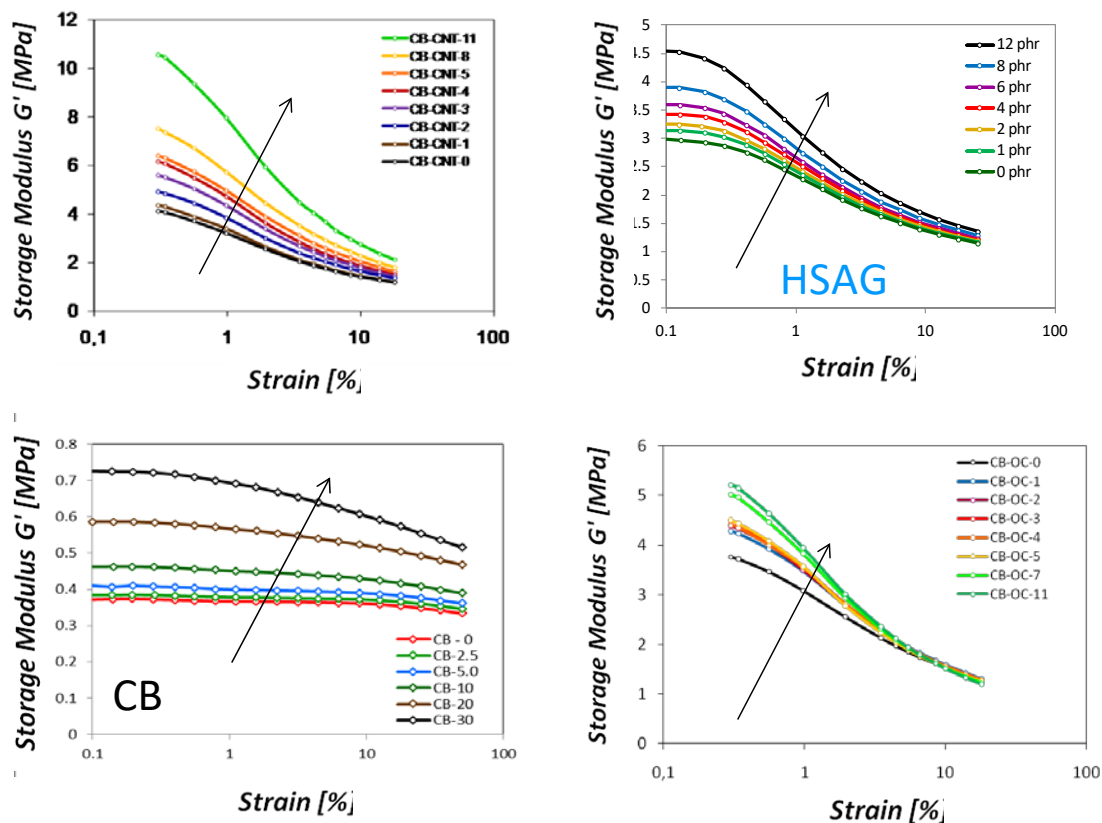
Figure 3. G' storage modulus vs strain % for composites with different fillers (refs: 34-36, 56)

Graphs in **Figure 3** show that, at the same filler content, composites with high aspect ratio nanofillers have large non linearity of the shear G' modulus, that means larger Payne effect [60]. This is due to the larger surface area of nanofillers. In fact, reporting the values of ΔG' of the filled composites normalized with respect to ΔG' of the matrix (ΔG'/ΔG'$_m$) vs the interfacuial area, as in the graph in Figure 2b, points can be fitted with the same exponential curve, for composites based on CNT and CB.

To properly understand the behaviour of OC based composites, it is worth examining the results reported in the following. IR based composites were prepared, with the following recipe (parts per hundred rubber, phr): IR 100, filler 12, dicumyl peroxide 2.0. In Figure 4(a) are shown curves of shear G' modulus vs strain % for uncured composites and in Figure 4(b) are shown stress strain curves for the cured composites.

The same relative effect on mechanical reinforcement can be observed for the sp[2] carbon allotropes, whereas OC does not give rise to any appreciable reinforcement and appears to act as a plasticizer.

Results reported so far show that the increase of surface area for sp[2] carbon allotropes is not translated in mechanical reinforcement at large deformation, in the absence of chemical bonds between the filler and the rubber matrix and of a structure in the filler, that means if the filler is not able to occlude the rubber chains. Moreover they confirm that pristine clays [61] and OC are not able to intercalate and thus to occlude polymer chains [48-50] and that a large part of the mechanical reinforcement arises from the effect of the ammonium cation on vulcanization and then on the crosslinking network.
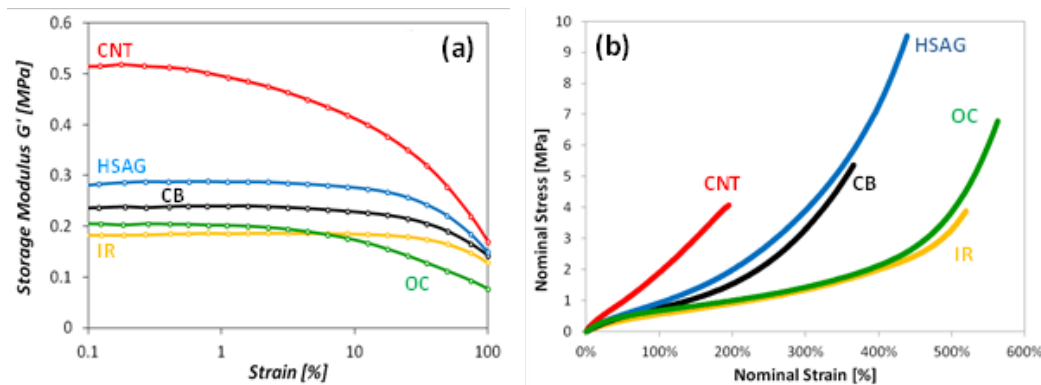
Figure 4. G' vs strain % for uncured composites (a) and stress strain curves for peroxide cured (b) IR based composites with 12 phr of filler

2. Chemical modification of high aspect ratio nanofillers

The most promising way to promote a stable interaction between a high aspect ratio filler and the rubber matrix appears to be the chemical modification of the filler, with the aim of establishing a chemical bond with the rubber chains.

2.1 The strategy

A strategy was defined. Aim was to prepare chemically reactive high aspect ratio nanofiller, moving from a "white" and a "black" building block. Sepiolite and high surface area nanosized graphite (HSAG) were selected as the building block, an inorganic oxide-hydroxide and an sp² carbon allotrope. Part of the strategy was to develop innovative strategies for the chemical modification. Main objective was also to develop sustainable functionalization methods.

2.2 Chemical modification of high aspect ratio oxide-hydroxide

Sepiolite was selected as the high aspect ratio oxide-hydroxide. Sepiolite was treated with HCl, with the aim to remove an amount of magnesium suitable to promote the chemical reactivity of the clay with silane coupling agent, preserving the high aspect ratio of the clay. Details have been already reported elsewhere [62-63].

Here are shown data of a composite based on 1,4-cis isoprene and butadiene rubbers and the silica/sepiolite hybrid filler system. Acid treated sepiolite had 80% of residual magnesium and maintained its fibrillary structure, after the acid treatment. The recipe of the reference composite (phr) was: BR 60 IR 40 ZnO 4, silica 30, silane TESPT 5, stearic acid 1, 6-PPD 1.5, TMQ 1, Sulphur 2.3, TBBS 80 4. In the composite with the hybrid filler system, 7 phr of sepiolite were used in place of 10 phr of silica. Data from dynamic mechanical measurements in the axial mode and from stress strain tests are in Table 2.

Data in **Table 2** show that the composite with the acid treated sepiolite achieves the best compromise between dynamic rigidity, low hysteresis and tensile properties. In particular, it is worth underlining that acide treated sepiolite allows to improve the mechanical reinforcement reducing the hysteresis of the composite.

Table 2. Data from dynamic-mechanical and quasi static measurements on composites based on silica and silica/sepiolite (see text)[a]

Property	Filler in the composite		
	Silica	Silica + Sepiolite	Silica + Sepiolite/HCl (Mg 80%)
σ_{50} (MPa)	100	106	111
σ_{100} (MPa)	100	112	115
σ_B (MPa)	100	127	104
ε_B (%)	100	122	109
E' (23°C) 100 Hz	100	103	113
E' (70°C) 100 Hz	100	102	113
Tan delta (23°C) 100 Hz	100	107	87
Tan delta (70°C) 100 Hz	100	106	85

[a] Relative index is reported: 100 for reference composite. For sepiolite based composites: the higher the better, except for Tan delta

2.3 Chemical modification of high aspect ratio nanosized graphite.

The high surface area graphite HSAG, whose main features are in Table 1, was functionalized with 2-(2,5-dimethyl-1*H*-pyrrol-1-yl)-1,3-propanediol (Serinol Pyrrole, SP), whose chemical structure is in **Figure 5**.
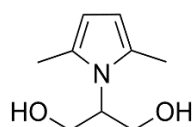

Figure 5. 2-(2,5-dimethyl-1*H*-pyrrol-1-yl)-1,3-propanediol (Serinol Pyrrole, SP)

Details about the functionalization of HSAG with SP have been reported elsewhere [64, 65]. Nanocomposites were prepared, based on natural rubber (NR) and high surface area graphite (HSAG), either pristine or functionalized with SP (HSAG-SP). The functionalization allowed to prepare the nanocomposite via latex blending, whereas melt blending was used for HSAG based compounds. Functionalization of HSAG with SP allowed to obtain a better filler dispersion, to reduce the composite's viscosity and to obtain a comparable vulcanization kinetics and a lower Payne effect from shear strain sweep tests, giving better tensile ultimate properties and an improved fracture behavior.

References

[1] Medalia A I and Kraus G 1994 *The Science and Technology of Rubber 2nd ed Mark JE, Erman B, Eirich FR Eds. Elsevier Academic Press* **8** pp 387-418

[2] Donnet J B and Custodero E 2005 *The Science and Technology of Rubber 2nd ed Mark JE, Erman B, Eirich FR Eds. Elsevier Academic Press* **8** pp 367-400

[3] Kroto H W 1987 *Nature* **329**

[4] Iijima S and Ichihashi 1993 T *Nature* pp 363-603

[5] Bethune D S, Kiang C H, de Vries M S, Gorman G, Savoy R, Vazquez J et al 1993 *Nature* pp 363-605

[6] Iijima S, *Nature*, 1991, 354-356.

[7] Monthioux M and Kuznetsov VL 2006 *Carbon* **44** pp 1621-1623

[8] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V, Firsov A A 2004 *Science* **306** pp 666–669

[9] Geim A K and Novoselov K S 2007 *Nat. Mater* **6** pp 183–191

[10] Allen M J, Tung V C and Kaner R B, *Chem. Rev.*, **2010**, 110, 132–145

[11] Zhu Y W et al 2010 *Adv. Mater* **22** pp 3906–3924

[12] Geng Y, Wang S J and Kim J K 2009 *J. Colloid Interface Sci* **336** pp 592–598

[13] Kavan L, Yum J H and Gratzel M 2011 *ACS Nano* 2011 **5** pp 165–172

[14] Nieto A, Lahiri D and Agarwal A 2012 *Carbon* **50** pp 4068–4070

[15] Paton K R, Varrla E, Backes C, Smith R J, Khan U, O'Neill A, and Higgins T 2014 *Nature materials* **13** pp 624-630

[16] Bokobza L 2007 *Polymer* **48** 4907

[17] Maiti M, Bhattacharya M, Bhowmick A K 2008 *Rubber Chemistry and Technology* **81**, 384

[18] Ciselli P, Lu L, Busfield J J, and Peijs T 2010 *e-Polymers* **10**

[19] Nah C, Lim J Y, Cho B H, Hong C K, and Gent A N 2010 *Journal of applied polymer science* **118** pp 1574-1581

[20] Galimberti M, Cipolletti V, Musto S, Cioppa S, Peli G, Mauro M, Guerra G, Agnelli S, Riccò T, Kumar V 2014 *Rubber Chemistry and Technology* **87** pp 417-442

[21] Tang Y, Ma L, He Y, Chen H, Jiang Y, and Xu J 2019 *Polymer Science* **A** pp 1-9

[22] Bokobza, Liliane 2019 *Nanomaterials* **9**

[23] Bhattacharya M, Maiti M, Bhowmick A K 2009 *Polymer Engineering & Science* **49**

[24] Bhowmick A K, Bhattacharya M, Mitra S 2010 *Journal of Elastomers and Plastics* **42**

[25] Al-Solamya FR, Al-Ghamdib A A, Mahmou W E 2012 *Polymer for Advanced Technology* 23, 478

[26] Kumar V, Giese U, Hanel T, Galimberti M, Giannini L 2014 *Kautschuk Gummi Kunstoffe* **67** pp 38-46

[27] Kumar V, Giese U, Hanel T, Galimberti M, Giannini L 2014 *Kautschuk Gummi Kunstoffe* **67** pp 29-36

[28] Yang Z, Guo B and Zhang L 2017 *Rubber Chemistry and Technology* **90** pp 225-237

[29] Fan Y, and Cho U R 2019 *Polymer Composites* **40**(S2) E1426-E1433

[30] Liu Y, Zhang H, Porwal H, Tu W, Wan K, Evans J, Bilotti E 2018 *Journal of Materials Chemistry C* **6** pp 2760-2768

[31] Zhou X, Wang L, Cao X, Yin Q, Weng G *Applied Polymer Science* 2019 **136** 47278

[32] Seo J G, Lee C K, Lee D, Song S H 2018 Journal of Industrial and Engineering Chemistry **66** 78-85

[33] Yang Z, Liu J, Liao R, Yang G, Wu X, Tang Z, Guo B, Zhang L, Ma Y, Nie Q, Wang F *Composites Science and Technology* **132** 68-75

[34] Galimberti M, Coombs M, Riccio P, Riccò T, Passera S, Pandini S, Conzatti L, Ravasio A, Tritto I 2012 *Macromol Mater. Eng*, C **298**, pp 241-251

[35] Galimberti M, Kumar V, Coombs M, Cipolletti V, Agnelli S, Pandini S, Conzatti L 2014 Rubber Chemistry and *Technology*, C **87(2)**, pp 197-218

[36] Agnelli S, Cipolletti V, Musto S, Coombs M, Conzatti L, Pandini S, Riccò T, Galimberti M, 2014, *Express Polymer Letters*, C **8(6)**, pp 436-449

[37] Galimberti M, Cipolletti V, Agnelli S, Pandini S, 2017, *Rubber World,* pp 28-37

[38] Galimberti M, Infortuna G, Guerra S, Barbera V, Agnelli S, Pandini S 2018 *Express Polymer Letters* **12** pp 265–283

[39] Galimberti M, Infortuna G, Barbera V, Guerra S, Bernardi A, Agnelli S, Pandini S 2018 *Rubber World* **257** pp 24-30

[40] Wang J, Zhang K, Cheng Z, Lavorgna M, Xia H 2018 *Plastics Rubber and Composites* **47** pp 398-412

[41] Voet A, Morawski J C, Donnet J B 1977 *Rubber Chem. Technol.* pp 50-342

[42] Rauline R 1991 *Compagnie Generale des Establissements Michelin*

[43] Leblanc J L 2002 *Progress in Polymer Science* C **4** pp 627-687

[44] Scwaiger B, Blume A 2000 *Rubber World* C **222** pp 32-38

[45] Sato M, Dierkes W K, Blume A 2017 *Tire Technology International* pp 66-70

[46] Wang Y et al 2000 *Journal of Applied Polymer Science* C **78** pp 1879-1883

[47] Galimberti M, Lostritto A, Spatola A, Guerra G 2007 *Chemistry of Materials* C **19** pp 2495-2499

[48] Galimberti M, Senatore S, Conzatti L, Costa G, Giuliano G, Guerra G 2009 *Polymer Advanced Technology* C **20** pp 135-142

[49] Galimberti M, Giudice S, Cipolletti V, Guerra G 2010 *Polymers for Advanced Technologies* C **21** pp 679-684

[50] Cipolletti V, Galimberti M, Mauro M, Guerra G 2014 *Applied Clay Science* C **87** pp 179-188

[51] Galimberti M, Coombs M, Cipolletti V, Spatola A, Guerra G, Lostritto A, Giannini L, Pandini S, Riccò T 2014 *Applied Clay Science* **97** pp 8-16

[52] Bergaya F, Jaber M, Lambert JF, Natural and synthetic layered clays sepiolite, Chapter 1 in Galimberti M. Rubber-Clay Nanocomposites. Wiley. 2011

[53] Galimberti M, Cipolletti V, Cioppa S, Lostritto A, Conzatti L 2017 *Applied Clay Science* C **135** pp 168-175

[54] Nordmeer J Proceedings of 194th Technical Meeting of the Rubber Division of the American Chemical Society, Inc., October 9 - 11, 2018, Louisville (KY)

[55] Galimberti M, Coombs M, Cipolletti V, Riccio P, Riccò T, Pandini S, Conzatti L 2012 *Applied Clay Science* pp 57-66

[56] Galimberti M, Coombs M, Cipolletti V, Giannini L, Conzatti L 2013 *Applied Clay Science* C **83-84** pp 449-456

[57] Lin Y, Liu S, Peng J, Liu L 2016 *Composites: Part* **86** pp 19-30

[58] Cao L, Sinha T K, Tao L, Li H, Zong C, Kim J K 2019 *Composites: Part B* **161** pp 667-676

[59] ISO/TS 80004-1:2015(en)

[60] Payne A R, Whittaker R E 1971 *Rubber Chemistry and Technology* **44** pp 440-478

[61] Wu Y P, Wang Y Q, Zhang H F, Wang Y Z, Yu D S, Zhang L Q, Yang J 2005 *Compos. Sci. Technol.* **65** pp 1195-1202

[62] Giannini L, Tadiello L, Hanel T, Galimberti M, Cipolletti V, Peli G, Morazzoni F, Scotti R, Di Credico B WO 2016/174629 Al

[63] Galimberti M, Cipolletti V, Peli G, Barbera V, Bernardi A, Locatelli D, Giannini L Presented at the 194th Technical Meeting of the Rubber Division of the American Chemical Society, Inc. Louisville (KY), October 9 - 11, 2018

[64] Galimberti M, Barbera V, Guerra S, Conzatti L, Castiglioni C, Brambilla L, Serafini A 2015 *RSC Adv.* C **5** pp 81142-81152

[65] Barbera V, Brambilla L, Milani A, Palazzolo A, Castiglioni C, Vitale A, Bongiovanni R, Galimberti M 2019 *Nanomaterials* pp 9-44