科学通报 2016 年 第 61 卷 第 31 期：3371 ~ 3378
专题：绿色轮胎与先进材料 评 述
《中国科学》杂志社
SCIENCE CHINA PRESS

高性能轮胎用橡胶纳米复合材料的制备与性能

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2015-07-27 收稿, 2015-09-30 修回, 2015-10-05 接受, 2015-10-27 网络版发表
国家自然科学基金(51333004, 51073009)资助

摘要 “节油、安全”的高性能轮胎已成为世界汽车轮胎的发展趋势. 构成轮胎的橡胶复合材料中，胎面胶、钢丝圈垫胶和气密内衬层胶等高性能纳米复合材料是发展节油轮胎的关键材料. 胎面胶是轮胎与路面直接接触的部分，要求具有低滚动阻力、高抗湿滑性能和优异的耐磨性；钢丝圈垫胶位于钢丝圈上端，起到填充和加强胎圈的作用；气密内衬层胶贴覆在轮胎内表面，起到保持轮胎气压的作用. 本文主要介绍了近年来胎面胶用白炭黑/橡胶纳米复合材料、钢丝圈垫胶用针状硅酸盐/橡胶纳米复合材料、气密内衬层胶用黏土/橡胶纳米复合材料，以及含碳纳米管和石墨烯增强的新型橡胶纳米复合材料的制备方法、性能特点及应用状况，并对将来的发展进行了展望.

关键词 橡胶纳米复合材料，原位改性分散，乳液复合，滚动阻力，气密性

橡胶材料由于分子间作用力小，自由体积大，常温下处于无定形的高弹态，自身强度低，必须经过增强才能被应用. 2000年, Hamed[1]和本课题组[2]提出了橡胶的高效增强必须使用纳米粒子增强的观点，至今已被大量引用. 事实上，橡胶工业从1904年开始应用的炭黑就是纳米粉体，至今仍然是橡胶工业最广泛使用的传统增强剂. 汽车轮胎是橡胶消耗量最大、炭黑用量最大的橡胶制品领域，也是应用新型高性能弹性体纳米复合材料最多的领域. 轮胎是由很多不同的半部件经专门的成型机制成胎坯，然后硫化而制备的，不同部位如胎面、钢丝圈垫胶(三角胶)、气密内衬层等对弹性体复合材料性能要求各不相同. 新型弹性体纳米复合材料的应用为轮胎的高性能化提供了保证，而轮胎也为高性能弹性体纳米复合材料的规模化应用提供了巨大空间. 轮胎行驶时，胎面胶、三角胶和气密内衬层胶用橡胶纳米复合材料由黏性损耗所导致的油耗占轮胎油耗的比例分别为39%, 13%和8%，合计60%. 因此，本文主要对胎面、三角胶、气密内衬层等轮胎部件用新型弹性体纳米复合材料的制备及性能特点等进行综述，并对其今后的发展做出展望.

1 胎面用白炭黑/橡胶纳米复合材料

胎面是轮胎与路面直接接触的部分，不仅影响轮胎的干、湿及冰雪路面的抓着性，而且影响轮胎的滚动阻力，直接关系到轮胎行驶时的安全性能与油耗. 高性能胎面胶的要求是：低滚动阻力(节油)、高抗湿滑性能(安全)和优异的耐磨性(寿命). 实际上三者很难平衡，往往顾此失彼，因此三者的关系被人们称为“魔三角”. 其原因分析如下：纯橡胶的强度低，必须加入大量的纳米填料增强(用量大于40 g/100 g橡胶，即用量大于40 phr. Phr，对每100份(以质量计)橡胶添加的份数)，以提高其强度和耐磨性；轮胎滚动时，胎面会产生周期性的形变，由于大量纳米填料的加入，胎面橡胶纳米复合材料在周期性的变形过程中，填料与填料间的摩擦、填料与橡胶间的摩擦将

引用格式：吴友平，张立群. 高性能轮胎用橡胶纳米复合材料的制备与性能. 科学通报, 2016, 61: 3371–3378
Wu Y P, Zhang L Q. Preparation and properties of rubber nanocomposites applied to high performance tires (in Chinese). Chin Sci Bull, 2016, 61: 3371–3378, doi: 10.1360/N972015-00867

导致材料内部的滞后生热急剧增加，从而使轮胎的滚动阻力增加；橡胶材料经纳米增强后，复合材料的模量和硬度增加，与湿路面的接触面积减小，抗湿滑性能下降．突破滚动阻力、抗湿滑性能和耐磨性之间的“魔三角”关系[3,4]，一直是高性能胎面材料设计者追求的目标．研究证实，大量填料在橡胶基体中的分散状态、填料与橡胶间的界面作用是平衡优化胎面材料“魔三角”性能的关键[5]．

炭黑是橡胶增强的传统纳米填料，应用近150年．自20世纪90年代初，粒径仅为10~20 nm，表面含有可反应硅羟基的纳米二氧化硅(即白炭黑)开始应用于胎面胶．目前，白炭黑增强橡胶纳米复合材料应用于制备低滚阻的“绿色轮胎”胎面胶料已成为轮胎行业的共识[5]．但是，如何实现极性白炭黑在非极性橡胶如丁苯橡胶、天然橡胶、顺丁橡胶等橡胶基体中均匀分散，并取得良好的界面结合，仍然是胎面材料设计者和研究者关注的问题．

为了提高白炭黑在橡胶中的分散，大量研究表明[6~11]，在制备橡胶混炼胶的过程中，将白炭黑与硅烷偶联剂同时加入橡胶基体中实现对白炭黑的原位改性分散，与使用预先改性白炭黑的方式相比，更经济、更被工业界所接受．1992年，米其林公司申请了一种低滚动阻力胎面材料制备方法的专利[12]．溶聚丁苯橡胶(SSBR)和顺丁橡胶(BR)并用作基体橡胶，以白炭黑为填料，硅烷偶联剂为双(3-三乙氧基硅烷基丙基)四硫化物(TESPT)，强调了混炼过程的温度控制，温度范围最好在145~165℃，以保证白炭黑与偶联剂的充分反应，通过两步混炼法可制备高性能胎面胶料．与传统炭黑增强的胎面胶料相比，白炭黑增强的SSBR/BR胶料不仅具有较低的滚动阻力，而且在湿路面和雪地路面有较好黏附性能．

原位改性分散技术可用于各种纳米粉体，其基本原理已经被阐明：利用橡胶材料特有的高加工黏度所传递的高剪切力，以及填料与改性剂的亲合作用，对纳米粉体聚集体实现边表面改性、边剪切分散，示意图如图1所示．对白炭黑原位改性分散的过程是：在橡胶混炼过程中同时加入硅烷偶联剂和白炭黑，利用橡胶基体传递的高剪切力破碎白炭黑的聚集体，同时在较高的混炼温度下，白炭黑表面的羟基与偶联剂的烷氧基之间发生化学反应，从而实现白炭黑表面的有机化改性，阻止了白炭黑的再聚集[13]；因此白炭黑的有机改性和分散同时进行，互相促进．原位改性反应是一种在高黏度橡胶熔体中发生的固相化学反应，其关键在于偶联剂的类型与用量，以及与之相匹配的原位改性反应温度和时间的准确控制．国内外在此方面开展了大量的研究工作[6~11]，为工业化制备性能稳定的白炭黑胎面胶料提供了基础．尽管如此，橡胶的高黏度以及纳米分散时产生的极高界面面积(10000 m^2/100 g橡胶)，导致原位改性分散时黏性耗能很大，进而导致混炼温度升至很高、难以控制，特别是大容量密炼机作为混炼装备时，这一状况更加恶化．各大轮胎企业和橡塑加工装备企业进行了很多的研究工作，力图解决这一问题；国际轮胎巨头在混炼装备和混炼工艺上都有自己的专有技术(know-how)，高度保密．

为保证白炭黑的均匀分散，除了对原位改性工艺和装备方面的研究外，国内外研究者还对新型橡胶、偶联剂以及白炭黑的品种等开展了大量研究，制备出了新型带功能基团的SSBR，新型偶联剂Si75，高分散白炭黑等，期望将原材料研发和工艺实施相结合，为工业化制备高性能的白炭黑增强的胎面胶料提供保障．

为了深入探讨白炭黑增强SSBR/BR胶料优异的性能，Wang[13,14]和本课题组[15~19]对白炭黑胶料的微观结构与性能间的关系进行了研究．与炭黑胶料中的炭黑填料网络相比，在白炭黑-硅烷偶联剂胶料中白炭黑填料网络明显降低[13,15]，表明白炭黑通过原位改性分散技术可在橡胶基体中达到优异分散；而

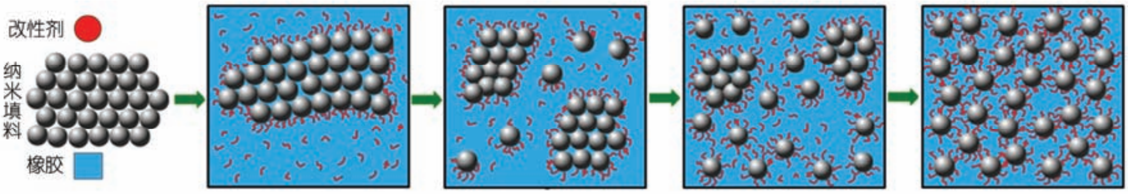

图 1 (网络版彩色)纳米粉体的原位改性分散过程示意图

Figure 1 (Color online) The diagram of *in situ* modification and dispersion of nanopowder

且白炭黑与橡胶界面间通过偶联剂形成了化学键，界面滑移大大减少，而炭黑与橡胶间的界面相互作用以物理吸附和表面的拓扑限制为主，容易产生界面滑移[15]. 因此，材料受到周期外力作用时，白炭黑-硅烷偶联剂胶料中填料-填料间的摩擦、填料-橡胶间的摩擦较小，材料内部的生热较低，将其作为胎面胶料制备的轮胎的滚动阻力明显降低. 白炭黑和橡胶界面间的化学作用也使白炭黑胶料的耐磨性能明显提高，可与炭黑胶料相媲美[14]. 另外，白炭黑的硬度明显高于炭黑，在湿滑路面上具有穿透水膜的作用，增加了轮胎和路面间的有效接触，是白炭黑胶料具有优异抗湿滑性能的原因之一[18,19].

虽然将原位改性分散技术制备的白炭黑胶料用于低滚动阻力胎面胶料已被工业界应用，但是在工业实施过程中，要准确控制原位改性的温度并不容易. 湿法混合技术已受到学术界和产业界的高度关注. 卡博特公司基于天然橡胶胶乳，采用独特的连续液相混合凝固工艺制备天然橡胶/炭黑母胶，称为卡博特弹性体复合材料(CEC)[20,21]. 与密炼机机械混炼相比，CEC胶料中炭黑分散效果很好，综合性能明显提升[20]. 但如何在溶液合成的SSBR和BR中液相(湿法)混合白炭黑，虽有不少专利[22~26]，但未见商品出售. 湿法混炼技术在成本、母胶的稳定性和性能等方面仍需下大力气，加强研究.

2 轮胎气密内衬层用黏土/橡胶纳米复合材料

轮胎气密内衬层贴覆在轮胎内表面，起到保持轮胎气压的作用，其主要性能要求是：优异的气密性，与外胎良好黏合，并有一定的耐疲劳性能，不开裂. 1950年，无内胎轮胎问世，卤化丁基橡胶因其优异的气密性，长期以来在轮胎内衬层胶料中占主导地位，其组分和形式未发生明显变化. 随着纳米复合材料科学与技术的发展，层状硅酸盐矿物如黏土、累托石等，以纳米片层分散在橡胶中制备的黏土/橡胶纳米复合材料具有强度高和气密性好等优点[27~31]，可满足气密内衬层胶料的性能要求.

制备黏土/聚合物纳米复合材料的方法有原位聚合纳米复合方法、有机改性黏土-聚合物熔体共混插层方法、有机改性黏土-聚合物溶液混合方法等，这些方法虽然能使黏土在聚合物基体中达到纳米级分散，但存在成本高、工艺复杂、难工业化等问题. 本课题组[32]发明了乳液复合法(latex compounding method，LCM)，该方法巧妙利用了黏土层间阳离子(如钠离子)强烈水化作用的特点，在快速搅拌作用下，使矿物自有的片层结构以纳米尺度解离分散于水中，形成硅酸盐纳米片层的水分散体，结合大多数橡胶均有自己的乳液形式(乳胶粒子直径一般为50~200 μm)的优势，先使它们在水相中混合，然后通过共凝聚固定分散结构，脱水后得到纳米复合材料，LCM的混合和凝聚的过程如图2所示[29]. 由于在水相混合，LCM混合过程的黏度低、易操作、成本低，易工业化.

采用LCM制备的黏土/橡胶纳米复合材料(20 phr黏土)的氮气透过性能比相应的纯胶可降低约50%，其优异的气体阻隔性主要源于纳米分散黏土片层大大地延长了气体扩散的路径[29]. 黏土/橡胶间的界面作用可通过在水相中加入改性剂进行调节，以进一步提高黏土/橡胶纳米复合材料的强度[33,34]. 填料用量为10 phr时，经偶联剂改性的黏土/丁苯橡胶纳米复合材料的定伸、拉伸强度明显高于白炭黑、高耐磨

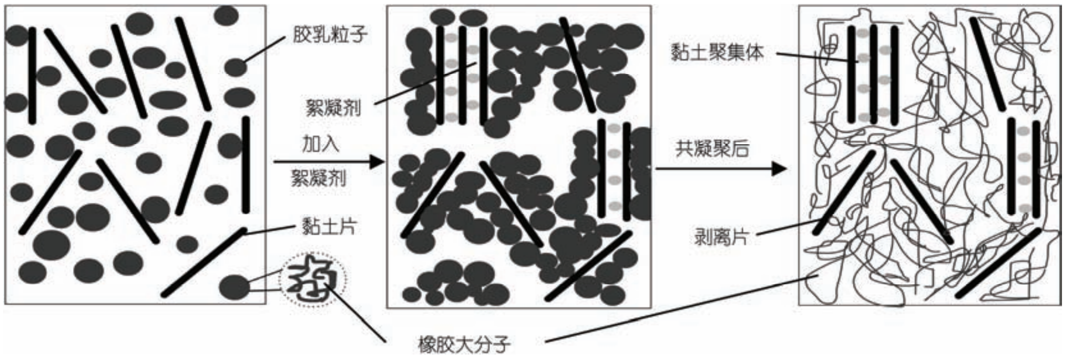

图 2 LCM的混合和凝聚过程示意图[29]

Figure 2 The process of the mixing and co-coagulating in LCM[29]

炭黑N330增强丁苯橡胶[33]. 另外, 纳米黏土片层具有优异的阻断裂纹扩展的能力, 少量的黏土片层还可以大幅度地提高橡胶材料的抗疲劳破坏和抗切割性能[35,36]. LCM与喷雾干燥相结合, 还可制备出剥离型的黏土/橡胶纳米复合材料[37].

基于LCM制备了一系列橡胶基纳米复合材料, 包括天然橡胶[29,31]、丁苯橡胶[27~30]、丁腈橡胶[29,38]等. 目前已规模化制备出黏土/丁苯橡胶母胶和黏土/天然橡胶母胶, 并应用在轮胎气密内衬层和抗切割工程胎面[39,40].

3 三角胶用针状硅酸盐/橡胶纳米复合材料

轮胎钢丝圈部位垫胶为高硬度的三角形芯胶, 也称三角胶, 位于钢丝圈上端, 起到填充和加强胎圈的作用, 能够改善子午胎侧向刚性分布, 同时与胎侧区形成均匀的刚柔过渡. 三角胶的性能要求是: 良好的刚性(高硬度、高模量)、优异的表面黏附性能等. 三角胶的硬度高, 为邵尔A85以上. 传统三角胶通常以天然橡胶为基体, 通过配合高用量炭黑, 同时加入大量硫黄提高橡胶的交联密度, 以达到提高硬度和模量的目的. 坡缕石, 又名凹凸棒土(FS), 是一种由纳米单晶短纤维组成的针状硅酸盐矿物. 纳米单晶纤维直径为20~30 nm, 长度为0.5~2 μm, 表面富含活泼羟基. 通过偶联剂对FS预先改性[41~43]或者采用原位改性分散技术[44]将FS解离成纳米短纤维分散在SBR, 天然橡胶(NR)等橡胶基体中, 可制备出一种具有高硬度、高模量的橡胶/FS纳米纤维复合材料, 满足三角胶的性能要求.

与传统增强填料——颗粒状炭黑相比, FS的纳米纤维具有较高的长径比, 所获得的复合材料表现出短纤维增强橡胶复合材料的力学特性, 如低应变下高定伸、高硬度、高撕裂强度和明显的各向异性, 尤其是在相同填料用量下, FS/橡胶复合材料的定伸应力、硬度显著高于炭黑/橡胶复合材料[43]. 另外, 传统炭黑和橡胶界面主要以物理作用为主, FS表面富含活泼羟基, 通过硅烷偶联剂改性, FS与橡胶间可形成强的化学作用, 提高弹性模量, 降低动态生热[44]. 由于不再需要添加高用量的硫黄和炭黑, 无喷霜现象, 明显改善了材料的表面黏着性能. 而且, 纳米短纤维的绝对长度小, 最长不超过2 μm, 因此, FS/橡胶复合材料的加工黏度明显低于短纤维增强的橡胶复合材料, 加工性能良好[44]. 轮胎公司的轮胎成品实验结果表明, FS/橡胶复合材料在三角胶上具有良好的应用前景.

4 新型填料增强的橡胶纳米复合材料

碳纳米管(carbon nanotube, CNT)和石墨烯自身具有极高模量, 优异的导电、导热特性, 对橡胶起增强作用的同时, 还能赋予橡胶复合材料导电和导热性能. 下面主要介绍这两类复合材料制备及性能特点.

4.1 CNT/橡胶复合材料

CNT/橡胶复合材料的制备方法主要有机械共混法[45,46]和乳液混合法[47]. 尽管CNT在机械混合过程中有不同程度的断裂, 会削弱其增强效果, 但机械共混法的工艺简单、CNT分散好, 更易工业化实施. 为提高CNT与橡胶基体的相容性, 目前普遍采用酸处理来实现CNT的表面官能化, 并通过添加偶联剂强化CNT与橡胶间的界面结合. 对CNT/橡胶复合材料的性能研究主要集中在强度、导电、导热等方面[48,49].

CNT在被高压压扁或弯折后, 除去外力可像弹簧一样回复原状. 基于此特性, 本课题组[50]提出了“纳米弹簧”增强轮胎橡胶材料的概念, 在保证弹性纳米粒子(如CNT)与橡胶强界面结合的情况下, 利用其弹性变形性, 储存可回复的弹性势能, 从而起到一个纳米弹簧的作用, 既保证了增强作用, 又通过回复弹性的提高降低了动态滞后损失和生热. 利用CNT的导电性, 本课题组[51]申请了将CNT应用于节油轮胎胎面材料, 降低静电积累、提高轮胎安全性的专利. 并在北京首创轮胎公司批量制备了系列高性能绿色轮胎, 滚动阻力达到了欧盟标签法的B级水平.

基于CNT的高导热性能, 还在风神轮胎有限公司成功试制了大尺寸的工程轮胎, 力图解决工程轮胎胎肩生热高、散热差、易肩空的普遍性难题.

4.2 石墨烯/橡胶纳米复合材料

人们对石墨烯/橡胶纳米复合材料也进行了大量的研究, 其制备方法主要有乳液混合法[52~56]、溶液混合法和机械共混法. 其中, 乳液混合法充分利用了橡胶的乳液形式, 与石墨烯的水分散液进行水相混合, 该方法环境友好、工艺简单, 而且石墨烯在橡胶基体中的分散效果好. 与炭黑、CNT相比, 石墨烯片层对橡胶具有更好的增强效果. 石墨烯/橡胶纳米复合材料具有优异的力学性能、气体阻隔性能[52,53]、导电性

能以及导热性能. 通过油酸胺强化氧化石墨烯和橡胶间的界面, 3 phr氧化石墨烯增强的丁苯橡胶纳米复合材料的拉伸强度可达到11.5 MPa[55]. 石墨烯用量为1.9%(体积百分比)时, 石墨烯/羧基丁腈橡胶纳米复合材料的空气透过率可降低55%[52]. 1 phr石墨烯还可明显提高NR抵抗裂纹引发和扩展的能力[56]. 石墨烯/橡胶纳米复合材料优异的综合性能使其在轮胎材料方面的具有潜在的应用价值, 我们和华南理工大学、玲珑轮胎股份有限公司合作制造出了世界第1条石墨烯橡胶纳米复合材料绿色轮胎, 测试结果表明滚动阻力接近A级.

5 展望

采用原位改性技术制备白炭黑橡胶纳米复合材料的原理及影响因素已被人们认识, 基于此, 研发加工安全性更好的偶联剂品种、高分散的白炭黑、新型的带功能基团的橡胶品种将是今后研究的重要方向. 湿法混合技术制备白炭黑、炭黑橡胶母胶在成本、稳定性和性能等方面需要加强研究, 以期获得分散好、性能优、能耗低的混合方法.

除炭黑、白炭黑等零维填料外, 纤维状的一维填料如CNT, FS, 以及片状的二维填料如黏土、石墨烯等新型填料也广受关注, 新型的一维和二维填料增强的橡胶纳米复合材料的优异性能正在被人们所揭示和认识. 新型的纳米复合材料在轮胎上的应用关键取决于CNT和石墨烯的低成本制备, 及其相应的易工业化实施的橡胶纳米复合材料制备方法. 采用乳液混合法制备层状填料(黏土、石墨烯)/橡胶纳米复合材料, 以及采用原位改性分散法制备纤维状填料(FS, CNT)/橡胶复合材料更易工业化实施. CNT和石墨烯的低成本制备技术, 仍需一段时间研究和培育.

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Preparation and properties of rubber nanocomposites applied to high performance tires

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The high performance tire with low fuel consumption and high wet skid resistance is the developing trend of tires in the world. Among the varied rubber composites comprising of tires, the rubber composites applied to tire tread, bead filler and inner liner are the keys to develop high performance tires. This review mainly introduces the preparation methods and properties of novel rubber nanocomposites for tires, and the future development trend is also suggested.

Tire tread, which directly contacts the road, should meet the demands of low rolling resistance, high wet skid resistance and excellent abrasion resistance. The filler type, filler dispersion level and the filler-rubber interaction are important affecting factors for tire tread rubber composites. Now, silane-silica filled rubber nanocomposites are usually used as tire tread materials for high performance tires. This is due to the facts that silane-silica filled rubber nanocomposites exhibit lower rolling resistance and higher wet skid resistance than carbon black filled rubber nancomposites. The underlying mechanism was also discussed. To ensure the fine silica dispersion, *in situ* modification dispersion method is often applied during the industrial preparation process, and exact controlling *in situ* modification temperature is the key. In addition, liquid compounding method has attracted increasing attention. Further, new types of filler, such as carbon nanotube (CNT) and grapheme, can also be used in tire tread rubber nanocomposites, and the latest advances are mentioned.

Bead filler, applied on the top of bead bundles, gives filling and reinforcing performance. Rubber nanocomposites used for bead filler should exhibit high modulus, high hardness, and excellent adhesion. Fibrillar silicate (FS) is composed of many fibrillar nanosized single crystals. Similar to silane-silica filled rubber composites, FS filled rubber composites can also be prepared by in-situ modification dispersion method to improve FS dispersion and interfacial interaction. Similar to the conventional short microfiber reinforced rubber, FS/rubber composites also exhibited high modulus, high tear strength, and anisotropy. It is worthy to note that FS filled rubber composites show better flow characteristics than short microfiber reinforced rubber. The potential of FS filled rubber nanocomposites used for bead filler was discussed.

Innerliner, placed on the inner surface of tubeless tires, is to maintain the air pressure, and it requires that the rubber nanocomposite should have excellent gas barrier property. Clay, different from CB and silica, is of layered structure, and it can greatly improve the gas barrier property of rubber materials by its nanolayers. Clay can be dispersed on a nanometer level in rubber matrix by latex compounding method (LCM). LCM combines and fully makes good use of the two facts: (1) Many rubbers have their own latex form and latex can be considered as nanopolymer spheres dispersed in a water medium; (2) layered structural clay can be totally exfoliated by water. Further, for LCM, the organic modifier can also be added into the clay/water suspension to *in situ* modify the clay layers to improve interaction between clay and rubber matrix. And so, LCM is a low cost and easily controlled process. The clay/rubber nanocomposites prepared by LCM exhibit excellent mechanical and gas barrier properties, and they can be a good alternative for innerliner materials. Industrialized clay/rubber nanocomposites have been applied in tire inner liner, off the road tire tread and etc.

For spherical and fibrillar types of filler, such as silica, FS and CNT, the fine dispersion and interfacial interaction can be achieved by *in situ* modification dispersion method; for layered fillers, such as clay and graphene, LCM is an effective method to obtain the fine dispersion and interfacial interaction. In the future, the applications of CNT and graphene filled rubber nanocomposites will largely depend on their preparation costs.

rubber nanocomposite, *in-situ* modification and dispersion, latex compounding, rolling resistanc, gas permeability

doi: 10.1360/N972015-00867