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专题：绿色轮胎与先进材料 评 述

绿色轮胎用高性能丁二烯基橡胶合成技术进展

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摘要 绿色轮胎在节能、环保、安全方面的优势使其成为当今世界轮胎的发展趋势. 稀土(钕系)顺丁橡胶(Nd-BR)和溶聚丁苯橡胶(SSBR)是制造绿色轮胎胎面重要的合成橡胶原材料. 本文主要介绍绿色轮胎发展现状、Nd-BR合成技术进展、工业化产品及新型丁二烯基共聚橡胶合成技术进展, 着重介绍微观结构、拓扑结构及共聚组成对其加工性能、物理机械性能及动态力学性能的重要贡献, 为制造绿色轮胎用高性能合成橡胶原材料提供参考. 顺式结构含量在98%以上的Nd-BR具有更加优异的物理机械性能及动态力学性能, 可有效降低轮胎生热、滚动功率损耗、压缩永久变形及终动压缩率, 降低轮胎磨耗并延长轮胎寿命, 更适用于制造绿色轮胎. 长链支化结构Nd-BR可以改善生胶的抗冷流性能、加工性能及与填料的混合性能, 进一步提高硫化胶的物理机械性能和动态力学性能. 高顺式含量丁苯无规共聚弹性体及立构规整丁二烯/苯乙烯共聚物集高顺式聚丁二烯橡胶、丁苯橡胶的优异性能于一体, 综合性能提高, 冰雪路面抓着力提高, 滚动阻力下降, 符合高性能绿色轮胎对合成橡胶原材料的要求.

关键词 绿色轮胎, 顺丁橡胶, 稀土催化剂, 配位聚合, 丁苯橡胶

绿色轮胎是指节能、环保、安全的轮胎, 具有低滚动阻力、低燃油消耗、出色的操纵稳定性、更短的制动距离和更好的耐磨性[1]. 自1992年法国米其林公司绿色轮胎成功问世以来, 绿色轮胎迅速发展. 欧盟有关数据表明: 汽车20%~30%的燃油消耗与轮胎相关; 全球18%的二氧化碳排放与道路交通相关; 轮胎滚动阻力每降低20%~30%, 节油可达5%~7%, 每百公里二氧化碳排放量可减少400 g(http://green-mobility.com/en/green-tires/accessed December, 2015). 若全世界车辆都用绿色轮胎, 每年可节省200亿升燃油, 减少5000万吨二氧化碳排放[2].

欧盟标签法从2012年11月起强制执行, 在欧盟销售的轿车轮胎、轻卡车轮胎、卡车轮胎及公共汽车轮胎必须加贴标签, 标示轮胎的滚动阻力(燃油效率)、湿滑路面抓着力和滚动噪声的等级, 目标是到2020年欧洲能源消耗减少20%. 其中, 滚动阻力共分为7级, 即由优级A至劣级G; 湿滑路面抓着力分为优级A至劣级F共6个等级, 道路噪声分为3个等级[3~5]. 日本、韩国和美国等国家也实施了类似的轮胎分级制. 2014年3月1日, 中国橡胶工业协会发布的《绿色轮胎技术规范》开始试行[6], 这是我国首部绿色轮胎行业自律标准, 将为我国实现轮胎分级打下基础. 2015年全国整体轮胎市场绿色化率有望突破20%, 绿色轮胎在乘用车方面将达到15%; 2020年绿色轮胎将占全国轮胎市场的60%以上, 绿色轮胎在乘用车方面将达到100%左右[7]. 目前国内轮胎大多为中低端产品, 且产能严重过剩, 大部分仅可达到欧盟第1阶段标准, 轮胎产品急需升级[7,8].

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要满足绿色轮胎要求，作为绿色轮胎胎面材料，需要具有低滚动阻力、高耐磨和高抗湿滑性能，对橡胶原材料提出更高要求．稀土(钕系)顺丁橡胶(Nd-BR)分子链具有高度立构规整结构，易发生应变结晶，因而赋予其更加优异的抗拉伸/撕裂性能、耐磨性、耐屈挠性、低生热性、低滚动阻力等，可减少轮胎滞后损失和内生热、降低滚动阻力，降低燃油消耗，提高轮胎的耐磨性、耐久性能和高速性能，综合性能优于镍系、钛系及钴系等传统型顺丁橡胶．采用特定化学组成、结构、分子量及其分布指数的溶聚丁苯橡胶(SSBR)制造轮胎胎面，可提升轮胎的抗湿滑性、耐磨性能，降低生热及滚动阻力，满足绿色轮胎的需要[9,10]．将Nd-BR与SSBR 2种橡胶结合并与白炭黑复合，可制备性能优越的绿色轮胎，与采用传统配方的轮胎相比，滚动阻力可降低25%~30%[11~13]．国内大型轮胎公司如中策橡胶集团、三角轮胎、青岛双星轮胎等公司将Nd-BR应用于乘用胎、全钢子午胎及工程胎的胎面或胎侧中，体现出比传统镍系顺丁橡胶更加优异的回弹性、耐磨性及动态力学性能，而且成品轮胎速度性能明显提高[14~16]．因此，本文着重介绍Nd-BR和新型丁二烯基共聚橡胶的合成技术进展及其性能特点．

1 稀土顺丁橡胶的合成技术进展

1.1 稀土顺丁橡胶用催化剂进展

在稀土顺丁橡胶合成中，催化剂对单体聚合转化率以及聚合产物的分子量、分子量分布、立构规整性及宏观性能等有着重要影响，因此，采用不同催化剂制备的稀土顺丁橡胶的性能也有差异．用于制备稀土顺丁橡胶的催化剂包括: 齐格勒-纳塔(Ziegler-Natta)型稀土催化剂、茂金属稀土催化剂和非茂稀土配合物催化剂[17,18]，其中Ziegler-Natta型稀土催化剂发展较为成熟，已用于工业化生产，其余2种稀土催化剂还处于研究阶段．

我国是世界上最早开展稀土催化烯烃聚合研究的国家之一．1962年，沈之荃研究组[19]首次研究了由钇(Y)、镧(La)、铈(Ce)、镨(Pr)、钕(Nd)、钐(Sm)等稀土元素的无水氯化物与三烷基铝或氯化烷基铝组成的稀土催化体系，并考察了其在丁二烯(Bd)定向聚合中的应用及聚合活性．美国联合碳化物公司[20]公开了由三价稀土有机螯合物-含有卤素离子的化合物-烷基铝组成的催化体系催化双烯烃聚合技术．1969年，美国Goodyear公司发表了采用辛酸铈-烷基卤化铝-烷基铝组成的催化体系进行Bd聚合的研究结果，聚合活性提高，但残留的Ce易导致橡胶老化，因而放弃了继续发展这种催化剂[21]．沈之荃研究组[22~24]又进一步研究了五九酸稀土盐/氢化二异丁基铝-三氯化铝催化体系、环烷酸稀土盐-氢化二异丁基铝-氯化二异丁基铝催化体系及Nd, Pr, Y, La的苯(甲)酰丙酮、苯(甲)酰三氟丙酮或噻吩甲酰三氟丙酮的螯合物与三乙基铝组成的均相催化体系用于Bd聚合的影响规律，轻稀土化合物的催化活性顺序为: Nd>Pr>Ce>La~Y>>Sm，所得聚丁二烯(PB)几乎不含凝胶或凝胶含量很少，1,2-结构含量不大于1%，加工性能及硫化胶物理机械性能良好．20世纪90年代，发展了异辛酸钕-三乙基铝-氯化二乙基铝、异辛酸钕-三异丁基铝-倍半铝、三氯乙酸钕-三异丁基铝-氯化二乙基铝、双三甲氧基硅胺基钕-三异丁基铝-氯化二乙基铝、新癸酸钕-氢化二异丁基铝-倍半铝等多种钕系三元催化剂体系，应用于Bd聚合，产物中顺-1,4含量约为96%，但通常分子量分布较宽[25~29]．对于基于羧酸钕的三元体系，若在催化剂中加入少量共轭二烯烃单体(如: Bd、异戊二烯)，有利于形成均相催化体系，可得到顺-1,4结构含量约为98%的PB，分子量分布变窄[30~33]．基于膦酸稀土盐的三元催化体系通常为非均相体系，催化剂活性和立构选择性相对较低，但聚合产物的分子量分布相对窄[34,35]．

在三元钕系催化剂体系中，若用卤代烃作为卤化试剂，可提高催化活性，提高PB产物的顺-1,4结构含量，并使其分子量分布变窄[34]；若加入醇类、羧酸、含硫或含磷化合物等给电子体来参与活性中心形成，可进一步提高催化活性、稳定催化剂相态、提高顺-1,4选择性(可达99%以上)及降低聚合物分子量分布指数[18,36~45]．

除了Ziegler-Natta型稀土催化剂外，近年来报道了一系列茂稀土催化剂以及非茂稀土配合物催化剂，这两类催化剂具有单一活性中心、配体结构可调控性好等特点．1999年, Hou研究组[44]首次报道了在MMAO作用下茂稀土化合物$(C_5H_5)_2Sm(THF)_2$用于Bd聚合(50℃)，制备出顺式-1,4-含量>98%和分子量分布<1.9的PB．在$AlR_3/[Ph_3C][B(C_6F_5)_4]$作用下，得到的PB具有较高分子量($M_w$=120000~420000)和窄分子量分布(<1.8)，但顺式-1,4-选择性最高仅达95%，降低温度可

提高顺式含量．采用$(C_5Me_5)_2Sm(THF)_2/Al(^iBu)_3/[Ph_3C][B(C_6F_5)_4]$催化体系在50℃下还可实现Bd活性聚合，制备分子量可控的高顺式PB．在上述茂稀土主催化剂的环戊二烯基上引入烷基取代基，可提高催化活性，但是对聚合产物的分子量、分子量分布及顺式-1,4选择性影响不大[47]．稀土金属的种类和烷基铝的种类对聚合物的顺式1,4-选择性也有较大影响[48,49]，在$Cp^*{}_2Ln[(\mu\text{-}Me)AlMe_2(\mu\text{-}Me)]_2LnCp^*{}_2/AlR_3/[Ph_3C][B(C_6F_5)_4]$催化体系中，钆(Gd)、铽(Tb)、镝(Dy)和钬(Ho)与其他稀土金属相比具有更高的顺式1,4-选择性和较高的催化活性．其中选择Gd作为活性中心，三异丁基铝为烷基化试剂，在低温下(−40℃)催化Bd聚合得到顺式-1,4含量>99.9%的PB．采用含有茚基的茂稀土催化剂**a**(图1)可在20℃下催化Bd聚合，并得到顺式-1,4含量>99%的PB，分子量较高(M_n=120000~397000)，分子量分布窄(1.1~1.4)[50]．与双茂催化剂相比，单茂催化剂**b**(图1)催化Bd聚合得到的PB分子量低，顺式1,4-选择性低[51]．非茂稀土配合物在$AlR_3/[Ph_3C][B(C_6F_5)_4]$作用下也能够制备出适合绿色轮胎的PB．含有P^N^P配体的Y配合物**c**(图1)能够在室温下催化Bd活性聚合，得到顺式-1,4含量为99%的PB[52]．含有钳形三齿配体的稀土配合物**d**因其配体的空间结构，能够促进单体定向插入增长，具有较好的立体选择性(图1)，含有N^C^N配体的Nd，Gd，Tb，Dy，Ho，Y配合物与$AlR_3/[Ph_3C][B(C_6F_5)_4]$配合，催化活性高，催化Bd聚合，10 min内转化率达100%，并得到顺式-1,4含量>99%，低温下聚合，顺式含量甚至达到100%的PB，分子量可通过改变单体与催化剂的比例调节，数均分子量为100000~1330000[53]．然而，同为钳形三齿配体的稀土配合物，含有N^N^N配体的Nd配合物**e**(图1)催化Bd聚合顺式1,4-选择性仅能达到97%[54]．虽然茂稀土催化剂及非茂稀土配合物催化剂具有高选择性．PB产物分子量分布更窄，但是这两类催化剂对空气敏感，且需要使用价格昂贵且量大的甲基铝氧烷(MAO)或有机硼化合物作助催化剂．

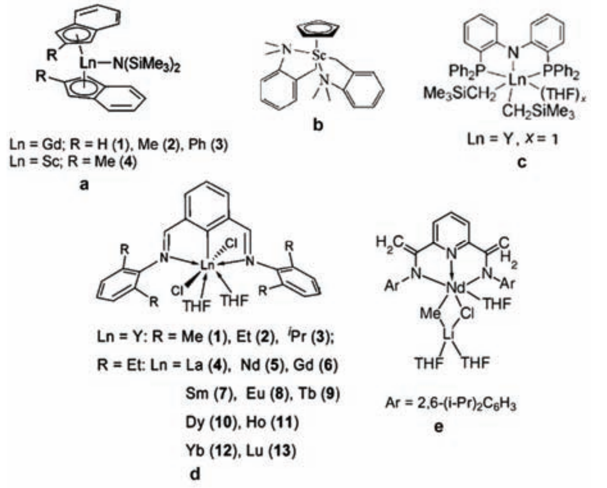

图 1　可用于制备高顺式PB的茂稀土配合物及非茂稀土配合物[46~54]

Figure 1　Lanthanide metallocene and nonmetallocene rare-earth-metal complexes used as precatalyst in the preparation of high *cis*-1,4-polybutadiene[46~54]

随着Ziegler-Natta型稀土催化剂的不断改进，所制备的PB性能逐步提高，使得Ziegler-Natta型钕系催化剂能够成功应用于Nd-BR工业化生产中．德国Lanxess公司和意大利Versalis公司于20世纪80年代率先实现Nd-BR工业化生产，后续美国Goodyear公司、日本JSR及Firestone公司、韩国Kumho公司、俄罗斯NKNH及Sibur公司、捷克Synthos公司、南非Karbochem公司、中国台湾奇美公司、中国石化集团公司、中国石油天然气集团公司等也开始生产Nd-BR．目前世界上有10多个国家/地区的公司可以生产不同牌号的Nd-BR．

Nd-BR生产商、生产能力、产品牌号如下[13,55~62]：德国Lanxess公司生产能力为24万吨/年，主要牌号为Buna CB21, 22, 23, 24, 25和29MES(充油)，门尼黏度分别为73，63，51，44，44和37(http://tsr.lanxess.com)；意大利Versalis公司生产能力为8万吨/年，主要牌号为Europrene Neocis BR40, BR60和BR OE(充油)，门尼黏度分别是43，63和32(http://www.eni.com)；日本JSR公司生产能力为8万吨/年，主要牌号为BR730, CNB700及BR51，门尼黏度分别为55，43及35.5(http://www.jsr.co.jp)；韩国Kumho公司生产能力为5万吨/年，主要牌号为NdBR-40和NdBR-60，门尼黏度分别为43和63 (http://www.kkpc.co.kr)；俄罗斯NKNH公司生产能力为3万吨/年，牌号为PBR-Nd group1, PBR-Nd group2和PBR-Nd group3，门尼黏度为40~49、50~59和60~70(http://www.nknh.ru)；俄罗斯Sibur公司生产能力为3万吨/年，牌号为BR-1243Nd GroupB，门尼黏度为44(http://sibur.com)；美国Goodyear公司生产3个牌号Nd-BR，分别为Budene 1222, 1223和1224，门尼黏度分别为63, 55和44(http://goodyearchemical.com)；捷克Synthos公司生产Synteca 44和Synteca 63 2个牌号的产品，门尼黏度分

别为44和63(http://synthosgroup.com); 日本Firestone公司生产牌号为Diene 140ND, 门尼黏度为40(http://www.firesyn.com); 南非Karbochem公司生产2个牌号产品, 分别为Neodene 40和Neodene 45, 门尼黏度分别为35~45和40~50(http://www.karbochem. co.za); 中国台湾奇美生产能力为6万吨/年, 牌号为PR040G, 门尼黏度为44(http://www.chimeicorp.com); 中国石油天然气集团公司Nd-BR生产能力为1.5万吨/年, 牌号为BR9100, 门尼黏度为39, 44和49[59]; 中国石化集团公司Nd-BR生产能力为3万吨/年, 牌号为BR Nd40, BR Nd50和BR Nd60, 门尼黏度分别为45, 50和63[55].

2012年, 中国石化集团公司采用北京化工大学开发的钕系催化剂技术、聚合工艺技术及分离技术, 建成了中国石化首套Nd-BR装置, 实现了工业化生产, 产品牌号为BR Nd40, BR Nd50及BR Nd60[55]. 2015年, 全世界Nd-BR的总生产能力约为80万吨[13,63]. 世界Nd-BR的生产能力在不断大规模扩能, 有可能在未来20年内成为顺丁橡胶市场的主导产品[13,63,64].

1.2 绿色轮胎对Nd-BR微观结构的要求

对于高顺式的聚共轭二烯烃弹性体, 当顺-1,4结构含量>96%时, 顺-1,4结构含量每增加1%, 对物理机械性能和动态力学性能均有明显影响[17,65~68]. 本课题组[55]研究了Nd-BR顺式结构含量对其加工性能、物理机械性能及动态力学性能的影响. 顺式结构含量对生胶的应力松弛时间及混炼胶Payne效应如图2所示, 随着顺式结构含量由96.3%升高至98.7%, 应力松弛时间由4.95 s逐渐降低至3.00 s, 表明随着顺式结构含量的增加, 生胶加工性能逐渐变佳[69,70]; 储能模量随应变的变化值$\Delta G'$由536 kPa逐渐降低至434 kPa, 说明顺式含量的提升有利于改善无机填料在橡胶基体中的分散, 减弱了填料与填料之间的作用, 增强了填料与橡胶之间的作用.

拉伸强度、定伸应力及断裂伸长率是绿色轮胎原材料硫化胶物理机械性能的重要指标, 与橡胶分子量及其分布指数、分子间作用力、微观结构、结晶和取向均有关系, 在分子量、分子量分布相近的前提下, Nd-BR顺式结构含量对物理机械性能的影响如图3所示. 随着顺式结构含量由95.6%逐渐增加至99.1%时, Nd-BR硫化胶拉伸强度、300%定伸应力及断裂伸长率均呈逐渐升高的趋势, 特别是顺式结构含量增加至98%以上时, 在受到应力作用时产生应变诱导结晶, 起到自增强的作用, 物理机械性能显著提升.

轮胎的安全性(抗湿滑性)、节油性(滚动阻力)可通过材料的动态力学性能(0和60℃下的损耗因子($\tan\delta$))来评价, 在0℃下$\tan\delta$值越高表明抗湿滑性越优异, 轮胎安全性能提升; 60℃下$\tan\delta$值越低表明轮胎滚动阻力越低、生热越低, 有利于降低油耗、减少废气排放. 通过研究不同顺式结构含量的Nd-BR硫化胶动态力学性能(图4), 发现随着顺式结构含量的提高, 0℃下$\tan\delta$值明显提高, 表明抗湿滑性能改善, 而60℃下$\tan\delta$值明显降低, 表明滚动阻力降低、生热降低. 此外, 可采用0和60℃下$\tan\delta$的差值($\Delta\tan\delta$)来表征对于魔三角的调节能力. $\Delta\tan\delta$值越大, 表明对于魔三角的调节能力越强. 对于顺式结构含量在98%以上的Nd-BR, 其$\Delta\tan\delta$值明显高, 表明顺式结构含量高于98%的Nd-BR有利于同时改善抗湿滑性并降低滚动阻力, 达到二者的平衡, 更适宜于制备绿色轮胎.

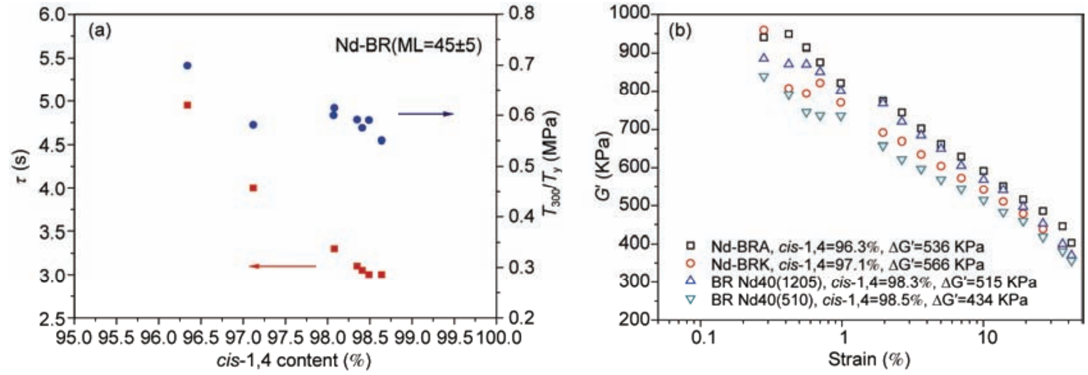

图 2 (网络版彩色)顺式结构含量对Nd-BR生胶应力松弛时间τ(a)及混炼胶payne效应(b)的影响[55]

Figure 2 (Color online) Effect of *cis*-1,4 content on the characteristic relaxation time (τ) (a) and Payne effect (b) of Nd-BR[55]

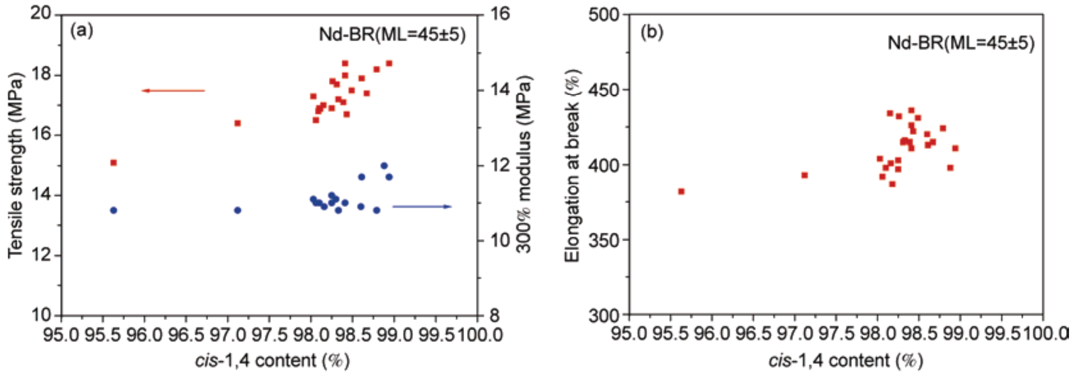

图 3 (网络版彩色)顺式结构含量对Nd-BR硫化胶拉伸强度、300%定伸应力(a)及断裂伸长率(b)的影响[55]

Figure 3 (Color online) Effect of *cis*-1,4 content on tensile strength, 300% modulus (a) and elongation at break (b) of Nd-BR vulcanizates[55]

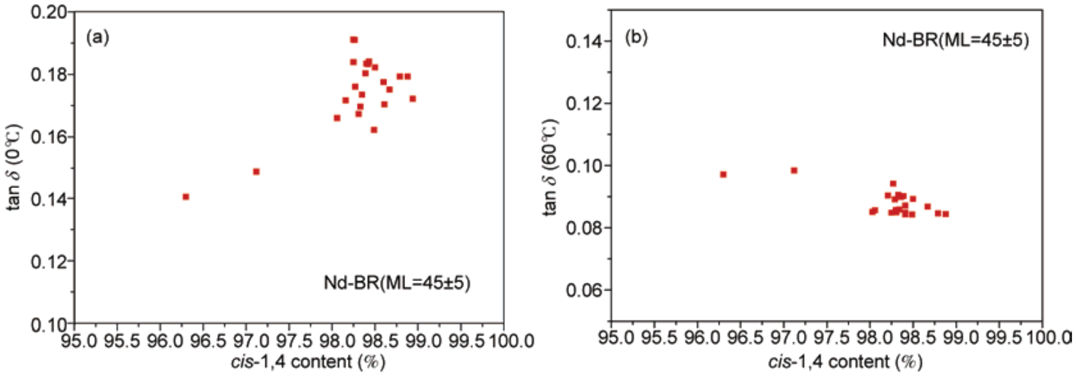

图 4 (网络版彩色)顺式结构含量对Nd-BR硫化胶动态力学性能的影响. (a) 0℃; (b) 60℃[55]

Figure 4 (Color online) Effect of *cis*-1,4 content on dynamic mechanical properties of Nd-BR vulcanizates. (a) 0℃; (b) 60℃[55]

轮胎在滚动过程中受到交变应力作用时，生热、功率损耗、压缩变形及磨耗是评价轮胎性能的重要指标，可分别使用压缩生热温升、滚动温升、滚动功率损耗、压缩永久变形、终动压缩率及阿克隆磨耗来衡量，降低压缩温升、滚动温升、滚动功率损耗、压缩永久变形、终动压缩率及磨耗可以延长轮胎寿命．顺式结构含量对Nd-BR的滚动温升、压缩温升、滚动功率损耗、压缩永久变形、终动压缩率及阿克隆磨耗也有较大的影响，如图5所示．当顺式结构含量由95.2%升高至98.5%时，滚动温升及压缩温升分别下降3.8℃及2.8℃；滚动功率损耗可降低19.4%；压缩永久变形及终动压缩率分别下降37.2℃及29.8%，当顺式结构含量由96.3%升高至98.5%时，阿克隆磨耗值可降低21.4%．因此，提高Nd-BR顺式结构含量至98%以上，可有效降低轮胎生热、滚动功率损耗、压缩永久变形及终动压缩率，降低轮胎磨耗并延长轮胎寿命．

顺丁橡胶中高的顺式-1,4结构含量赋予其高断裂强度、高撕裂强度、耐磨、耐屈挠、低生热、低滚动阻力、低滞后损失等一系列优点，还具有拉伸结晶和自增强的特点，可减少轮胎滞后损失和内生热，降低滚动阻力、燃油消耗，提高轮胎耐磨性和抗湿滑性，提高轮胎耐久性能和高速性能，适合于制造高耐磨性胎面胶．

高顺式结构含量对提高橡胶性能具有重要意义，提高聚共轭二烯烃橡胶中顺式结构含量已成为学术界和工业界的研究发展趋势[33,37~45,55,65~68,71]．除了高顺式结构含量有利于提高Nd-BR的性能外，长链支化结构Nd-BR可以改善生胶的抗冷流性能、加工性能及与填料的混合性能，进一步提高硫化胶的物理机械性能和动态力学性能．与相应线形Nd-BR相比，长链支化Nd-BR具有以下优势[72~76]: (1) 改善生胶的抗冷流性能; (2) 改善生胶与无机填料的分散性; (3) 拉伸强度提高; (4) 滞后损失减小，生热低; (5) 抗湿滑性能提高，滚动阻力下降，有利于节能降耗及提高安

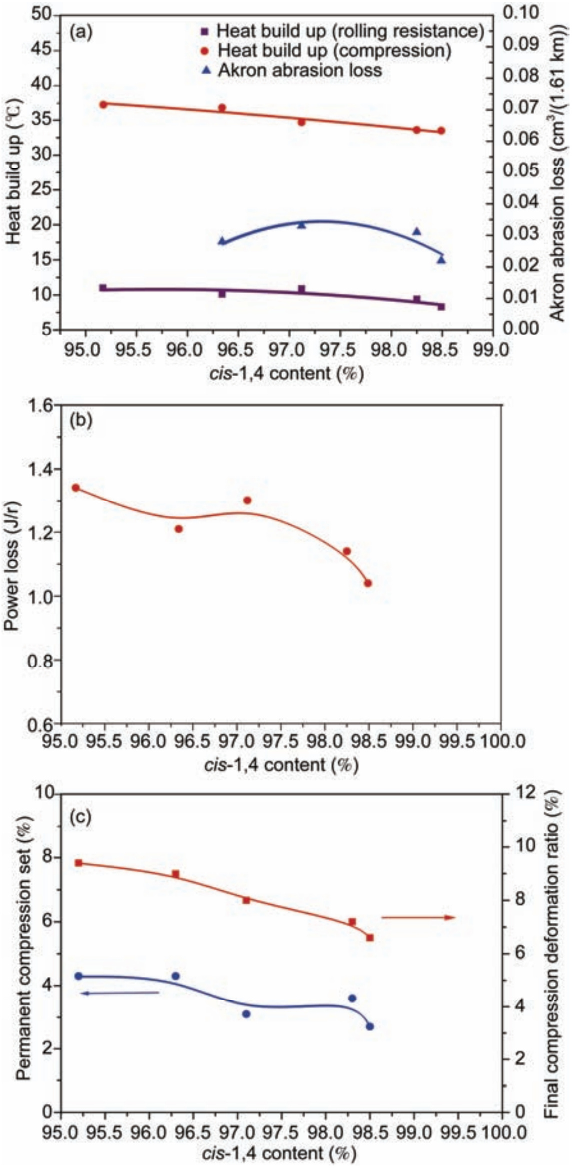

图 5 (网络版彩色)顺式结构含量对Nd-BR硫化胶滚动温升、压缩温升及Akron磨耗(a), 功率损耗(b), 压缩永久变形及终动压缩率(c)的影响[55]

Figure 5 (Color online) Effect of *cis*-1,4 content on rolling heat build-up, compression heat build-up and Akron abrasion loss (a), power loss (b), compression set and the final compression ratio (c) of Nd-BR vulcanizates[55]

全性，实现滚动阻力、抗湿滑性和耐磨性的综合平衡. 目前制备长链支化Nd-BR的方法主要有链端支化及链中支化2种方式. 链端支化时，支化剂在聚合体系未终止的情况下加入，支化剂的官能团与线形分子活性链端偶联反应，支化剂采用有机卤化物、含环氧基团的胺类化合物、含氨基的醛类或硫醛类化合物、环氧或酸酐功能化的不饱和天然油、四氯化锡、苯基三氯化锡、四氯化硅等，形成3臂或4臂的星形支化聚合物，但偶联效率相对低[77~79]. 链中反应制备长链支化Nd-BR，可采用线形Nd-BR与S_2Cl_2等双官能试剂发生加成反应，交联剂利用S_2Cl_2与PB分子链上双键发生加成反应，通过–S–S–键的交联产生长链支化结构，但易在局部发生交联产生凝胶，且–S–S–键在生胶塑炼时易产生断链[73,74]. 用高效的巯基-烯烃“点击化学”的方法，采用双巯基烷烃类化合物、多巯基烷烃类化合物、多巯基酯类化合物及引发剂对高顺式PB进行改性，在PB主链间产生交联结构[72,75,76]. 德国Lanxess公司于2013年12月正式推出2款长链支化结构Nd-BR新产品，其牌号分别为Buna Nd 22 EZ和Buna Nd 24 EZ，改善了填料与橡胶的快速混合，提高了加工性能[80].

2 高顺式丁二烯/苯乙烯共聚弹性体

溶聚丁苯橡胶(SSBR)是制备绿色轮胎的另一种合成橡胶，具有优良的物理机械性能、抗湿滑性和加工性能，但因阴离子聚合缺乏立体化学特性，导致分子链上Bd结构单元中顺式结构含量较低(~35%). SSBR需与高顺式的Nd-BR并用才能制造高性能绿色轮胎. 若将Bd结构单元的顺式-1,4结构含量提高至95%以上，将高顺式PB链段、Bd/苯乙烯(St)共聚结构通过化学键连接在同一大分子链中，达到分子水平的混合，是目前在制造轮胎时物理机械共混顺丁橡胶、丁苯橡胶无法比拟的，有望将丁苯橡胶、顺丁橡胶的优异性能有机结合起来，降低丁苯橡胶的滚动阻力和滞后损失，提高回弹性、耐磨性及耐低温性能，形成新型高顺式Bd/St共聚弹性体. 这需要采用具有立体选择性优异的配位聚合方法来实现. 采用过渡金属(钛、镍及钨)催化剂体系，催化Bd/St共聚合时，共聚物分子量低($[\eta]<0.8$ dL/g)，钴催化剂体系虽然可以提高共聚物分子量($[\eta]=2.67$ dL/g)，但是St含量仅为4.3%，难以合成兼具高顺式、高苯乙烯结合量及高分子量的Bd/St共聚物[81~83]. 采用茂稀土催化剂也难以解决Bd与St无规共聚的问题，只能制备Bd与St的嵌段共聚物，且存在共聚合反应的转化率偏低、共聚物分子量偏低等问题[84~86].

采用钕系催化剂，可以制备Bd/St无规共聚物，但前期研究结果中存在共性问题：即共聚物分子量相对低，顺式结构含量随着St结合量的上升而明显下降，难以合成兼具高顺式、高苯乙烯结合量及高分

子量的Bd/St共聚物[87~96]．采用改进的稀土金属羧酸盐/烷基铝/含卤素的烃类化合物/含卤素的羧酸酯类化合物/羧酸/醇类的复合体系催化St和共轭二烯烃进行配位共聚合，催化剂具有较高的催化活性和立构选择性，单体转化率可达80%以上，且所得共轭二烯烃结构单元顺式结构含量高达95%以上，甚至可达98%以上，重均分子量为7.0×10^4~1.5×10^6，St结合量(质量)在4%~60%．在提高St含量的情况下仍可获得高分子量、高顺式含量的丁苯无规共聚弹性体，提高共轭二烯烃结构单元顺式结构含量可赋予材料优异的回弹性、耐磨性、低滚动阻力及耐低温性能[97]．

通过可控/活性配位聚合，制备了一种在高顺式丁苯无规共聚链段上键接富含间规立构聚苯乙烯链段的新型弹性体，聚合物重均分子量为1.0×10^5~1.1×10^6，聚共轭二烯烃链段的顺-1,4含量为92%~98.7%，高顺式丁苯无规共聚链段St结合量(质量)为5%~38%．顺式结构含量的提高可赋予材料优异的弹性、耐寒性、耐磨性、滞后损失和低生热特点，St含量提高可改善材料抗湿滑性及冰雪路面抓着力．当高顺式丁苯无规共聚链段顺式结构含量为95.4%．St质量含量为16.5%时，与普通SSBR相比，冰雪路面抓着力可提高82%，滚动阻力可下降30%．因此，将高顺式丁苯橡胶优异的抗湿滑性、弹性、耐寒性、耐磨性、滞后损失和低生热以及富含间规立构聚苯乙烯的高结晶性、高弹性模量、低损耗因子以及耐热耐溶剂等性能集于一身，硫化胶具有以下优势：(1) 在不失去丁苯橡胶特有性能的同时还有抵抗变形能力强、耐磨性优异的特点；(2) 损耗模量低，滞后损失减小，生热低；(3) 硫化胶的玻璃化转变温度低，改善其耐寒性；(4) 实现低滚动阻力、抗湿滑性和耐磨性的综合平衡[98]．

3 结论

随着我国《绿色轮胎技术规范》开始试行，绿色轮胎将成为未来的发展趋势，开发适用于制造绿色轮胎的Nd-BR和丁苯橡胶具有重要意义．Ziegler-Natta型稀土催化剂、茂稀土催化剂、非茂稀土配合物催化剂已成功应用于合成高性能顺丁橡胶．顺式结构含量是影响Nd-BR物理机械性能及动态力学性能的重要指标之一，顺式结构含量在98%以上的Nd-BR具有更加优异的物理机械性能及动态力学性能，更适用于制造绿色轮胎．长链支化Nd-BR可以进一步改善生胶的抗冷流性能、加工性能及其与填料的混合性能，进一步提高硫化胶的物理机械性能和动态力学性能．高分子量、高顺式含量丁苯无规共聚弹性体及立构规整Bd/St共聚物作为两种新型弹性体材料，具有优异的弹性、耐低温性、低生热、低滚动阻力、高抗湿滑性、耐磨性及自增强特性，有望为绿色轮胎提供新一代高性能合成橡胶原材料．

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Progress in the synthesis of high performance butadiene-based elastomer for green tires

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The advantages of green tires in energy saving, environmental protection and safety make it become the trend of the tire. Neodymium-based high *cis*-polybutadiene rubber (Nd-BR) and solution styrene-butadiene rubber (SSBR) are two important raw materials for manufacturing green tire. Situation of green tire, progress in the synthesis of Nd-BR and butadiene-based copolymer, current status of some industrialized Nd-BR and development of rare earth catalysts have been reviewed, which is helpful for the production of high-performance synthetic rubber for green tire. The main Nd-BR producers are Lanxess, Versalis, ChiMei, Kumho, Japan Synthetic Rubber, Nizhnekamskneftekhim, Goodyear, Firestone, Sibur, Synthos and Karbochem. The commercial Nd-BR products are normally divided into three grades according to the various Mooney viscosity ($ML_{1+4}^{100℃}$) of around 45, 55 and 63. Furthermore, the effect of microstructure, composition and topology on processing property, mechanical properties and dynamic mechanical properties of Nd-BR and butadiene-based copolymer were introduced. Stereo-specificity is a key factor for the performance of Nd-BR product. The results of the characteristic relaxation time (τ), yield stress (T_y), 300% modulus (T_{300}), and T_{300}/T_y for various Nd-BR indicated that the increase of *cis*-1,4 content was benefit for the improvement of processing properties. The decrease of $\Delta G'$ with an increase in *cis*-1,4 content indicated that Nd-BR with high *cis*-1,4 content of around 98.5% behaved low Payne effect, which was mainly attributed to the strong interaction between polymer and filler. Excellent processing performance means that the addition of fillers to rubber compounds are easy to scatter. These can short the mixing time and produce the highest quality product with the lowest possible cost. Nd-BR products with higher *cis*-1,4 content possess the superior mechanical properties and dynamic mechanical properties of BR vulcanizates, such as modulus at 300%, tensile strength, abrasion resistance, heat build-up, compression properties and rolling resistance and wet-skid resistance. Nd-BR which possesses *cis*-1,4 content of more than 98% has more excellent mechanical properties, dynamic mechanical properties, and is suitable for green tire as raw materials for the excellent properties such as low heat build-up, rolling power loss, compression deformation, compression ratio and abrasion loss. Long chain branched Nd-BR possesses an improved cold flow resistance, processing performance and mixing performance with the filler. High *cis*-1,4 butadiene/styrene elastomer and stereospecfic butadiene/styrene copolymer combine excellent performance of Nd-BR and SBR. Both mechanical performance and skid resistance ability on ice road were increased, while rolling resistance was decreased for the vulcanizates. These excellent properties of the synthetic rubbers are beneficial for manufacture of high-performance green tires.

green tire, *cis*-polybutadiene rubber, rare-earth catalyst, coordination polymerization, butadiene/styrene rubber

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