

· 专论 ·

## 弹性体材料的高性能和功能性改性\*

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**摘 要** 高性能和功能性改性一直是高分子材料的一个重点发展方向. 基于我们的研究工作, 概述了一些新型纳米颗粒(如硅酸盐纳米短纤维、石墨纳米片层、纳米氢氧化镁)增强的橡胶复合材料, 特别是复合方法(以获得良好的分散与界面)、结构-性能关系, 以深刻理解橡胶材料的纳米增强; 另一方面报告了有关介电性弹性体和抗菌性弹性体超细纤维的制备与功能特性研究的新进展.

**关键词** 高分子材料, 弹性体, 改性, 高性能, 功能性

## HIGH PERFORMANCE AND FUNCTIONALITY MODIFICATION OF ELASTOMER MATERIALS

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**Abstract** High performance and functionality modification is always one of the issues in polymeric materials field. Based on our researches, this paper reviews some new nanoparticles (such as silicate short nanofibers, graphite nanosheets and  $\text{Mg}(\text{OH})_2$  nano-particles) reinforced rubber nanocomposites involving compounding methods to get good dispersion and interface, as well as structure-property relations, which help to understand the nano-reinforcement of rubbers. Meanwhile, the preparation and functionality of dielectric elastomers and anti-bacteria ultrafine elastomeric fibers are also reported.

**Keywords** Polymer materials, Elastomer, Modification, High performance, Functionality

## 1 INTRODUCTION

High performance and functionality modification is always one of the issues in polymer materials field. Particle size of fillers is of first importance besides their structural morphology and surface activity<sup>[1]</sup>. As we know, nanosized carbon black and silica are two kinds of nanofillers that have been widely used to reinforce rubbers. Here some new nanoparticles, such as silicate short nanofibers, graphite nanosheets

and  $\text{Mg}(\text{OH})_2$  nano-particles, were finely dispersed into rubbers showing good reinforcement. Surface modification and the dispersing methods were explored to get good dispersion and rubber-filler interface. The resultant effects on the structure-property relations of the nanocomposites were also discussed. Meanwhile, the preparation and functionality of dielectric elastomers and anti-bacteria ultrafine elastomeric fibers are reported.

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## 2 RUBBER REINFORCEMENT BY NEW NANOPARTICLES

### 2.1 Rubber/Fibrillar Silicate Nanocomposites

Fibrillar silicate (FS) is one type of hydrated magnesium aluminum silicate clay composed of many fibrillar nano-single crystals (short nanofibers), typically as palygorskite or attapulgite, as shown in Fig. 1. We found that the interactions between FS single crystals were extremely weak, and the surface of FS was full of Si—OH or Al—OH<sup>[2]</sup>. Rubber/FS nanocomposites were successfully prepared by traditional mechanical blending method, in which rubber was blended directly with FS *in situ* modified by silane coupling agent in rubber matrix<sup>[3~8]</sup>, and as well as by latex compounding, in which rubber latex was blended with FS aqueous suspension<sup>[9]</sup>.

The first method is simple and as efficient as the second. Numerous nanofibers contained in palygorskite micron powders were released out due to the weak stacking force between nanofibers and under high shear stress associated with high viscosity of rubber matrix<sup>[3]</sup>. *In situ* modification using silane coupling agent can improve the dispersion of FS and strengthen the interfacial bonding between FS and rubber, as indicated in Fig. 2. As a result, modified FS shows visible reinforcement for different rubbers, such as styrene butadiene rubber (SBR), natural rubber (NR), nitrile rubber (NBR), carboxyl terminated nitrile rubber (CNBR), ethylene-propylene terpolymer rubber (EPDM), hydrogenated nitrile butadiene rubber (HNBR) and chloroprene rubber (CR), as seen in Table 1. This kind nanocomposites exhibit abrupt stress - strain

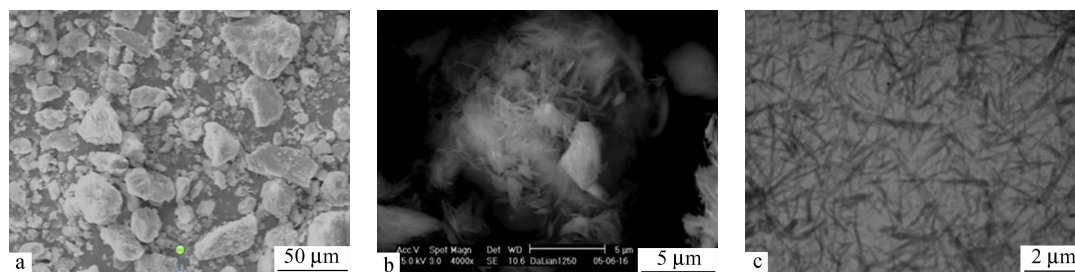


Fig. 1 Representative structure of FS: (a,b) FS micron particles and (c) the exfoliated FS nanofibers in water<sup>[3]</sup> (Copyright © 2006, Rights Managed by Nature Publishing Group)

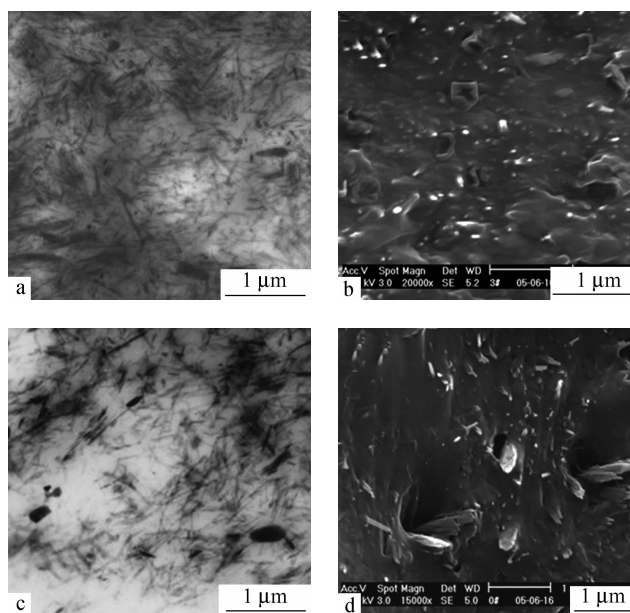


Fig. 2 Representative TEM (a,c) and SEM (b,d) micrographs of SBR/FS nanocomposites (a,b modified; c,d unmodified)<sup>[3]</sup> (Copyright © 2006, Rights Managed by Nature Publishing Group)

**Table 1** The mechanical properties of FS/rubber nanocomposites<sup>a</sup> [3] Copyright © 2006, Rights Managed by Nature Publishing Group

| Properties                  | SBR  | FS/<br>SBR | NR   | FS/<br>NR | NBR  | FS/<br>NBR | CNBR | FS/<br>CNBR | EPDM | FS/<br>EPDM | HNBR | FS/<br>HNBR | CR      | FS/<br>CR |
|-----------------------------|------|------------|------|-----------|------|------------|------|-------------|------|-------------|------|-------------|---------|-----------|
| Shore A hardness            | 45   | 73         | 41   | 74        | 54   | 83         | 61   | 72          | 70   | 78          | 57   | 80          | 51      | 83        |
| Stress at 100% strain (MPa) | 0.8  | 7.6        | 1.0  | 9.1       | 1.2  | 12.1       | 2.3  | 8.3         | 1.4  | 7.0         | 1.3  | 28.6        | 1.1     | 13.8      |
| Tensile strength (MPa)      | 2.3  | 14.7       | 29.3 | 24.5      | 3.2  | 22.7       | 9.7  | 22.7        | 4.7  | 10.7        | 6.1  | 30.4        | 6.6     | 14.6      |
| Elongation at break (%)     | 556  | 344        | 660  | 390       | 308  | 290        | 412  | 237         | 356  | 177         | 270  | 109         | 509     | 113       |
| Tear strength (kN/m)        | 11.6 | 60.8       | 30.3 | 65.4      | 14.3 | 58.8       | 22.9 | 48.5        | 18.1 | 36.1        | 13.9 | 26.4        | no data | no data   |

<sup>a</sup>The FS loading level is 40 g/100g rubber.

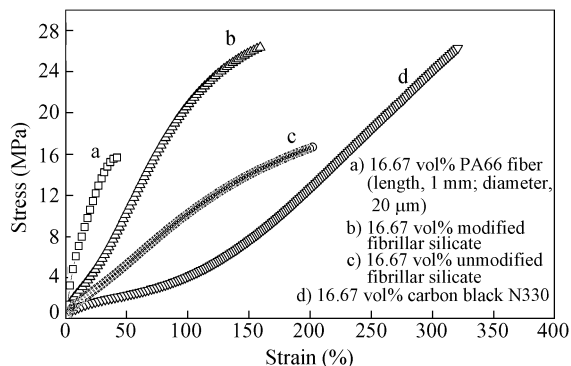


Fig. 3 Stress-strain characteristics of various filler reinforced NBR composites<sup>[3]</sup> (Copyright © 2006, Rights Managed by Nature Publishing Group)

curves that are similar to that of micro-short fiber reinforced rubber, as displayed in Fig. 3. Meanwhile, these nanofibers were orientated along

the shear direction, leading to mechanical anisotropy, as shown in Fig. 4.

## 2.2 Rubber/Graphite Nanocomposites

Rubber/graphite nanocomposites were prepared through blending a comparatively stable aqueous suspension of expanded graphitic (EG) nanosheets with rubber emulsion and then co-coagulating the above mixture (also called latex compounding method, LCM)<sup>[10-12]</sup>. Compared with traditional mechanical blending, LCM resulted in a higher exfoliation of graphite and better dispersion, as implied in Fig. 5. The resultant nanocomposites possess greatly increased modulus and strength, improved wear resistance, better gas barrier property and good electrical/thermal conductivity, as shown in Fig. 6 and Table 2.

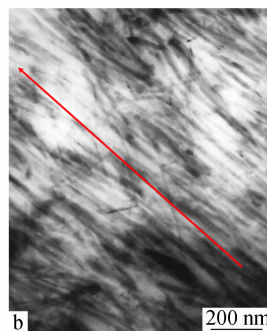
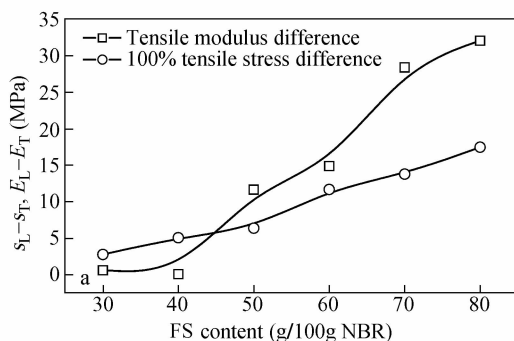


Fig. 4 Mechanical anisotropy of rubber/FS (a) and TEM micrographs of fiber orientation of (b)<sup>[3]</sup> (Copyright © 2006, Rights Managed by Nature Publishing Group)

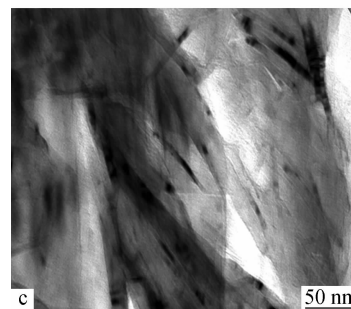
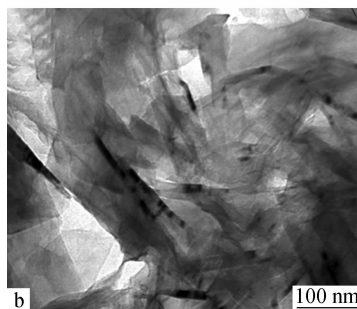
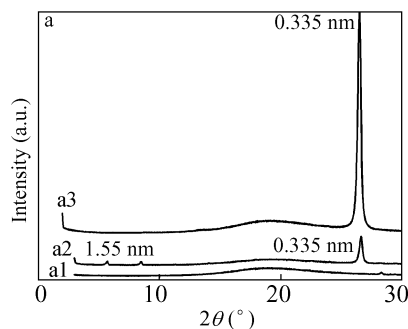


Fig. 5 Structure of NBR/graphite nanocomposites (a) WXR D patterns: (a1) unfilled NBR vulcanizate; (a2) NBR/EG (5 phr) nanocomposite prepared by LCM; (a3) NBR/EG (5 phr) microcomposite prepared by direct blending; (b) and (c) TEM images of the nanocomposite prepared by LCM<sup>[10]</sup> (Copyright © 2007 Acta Materialia Inc)

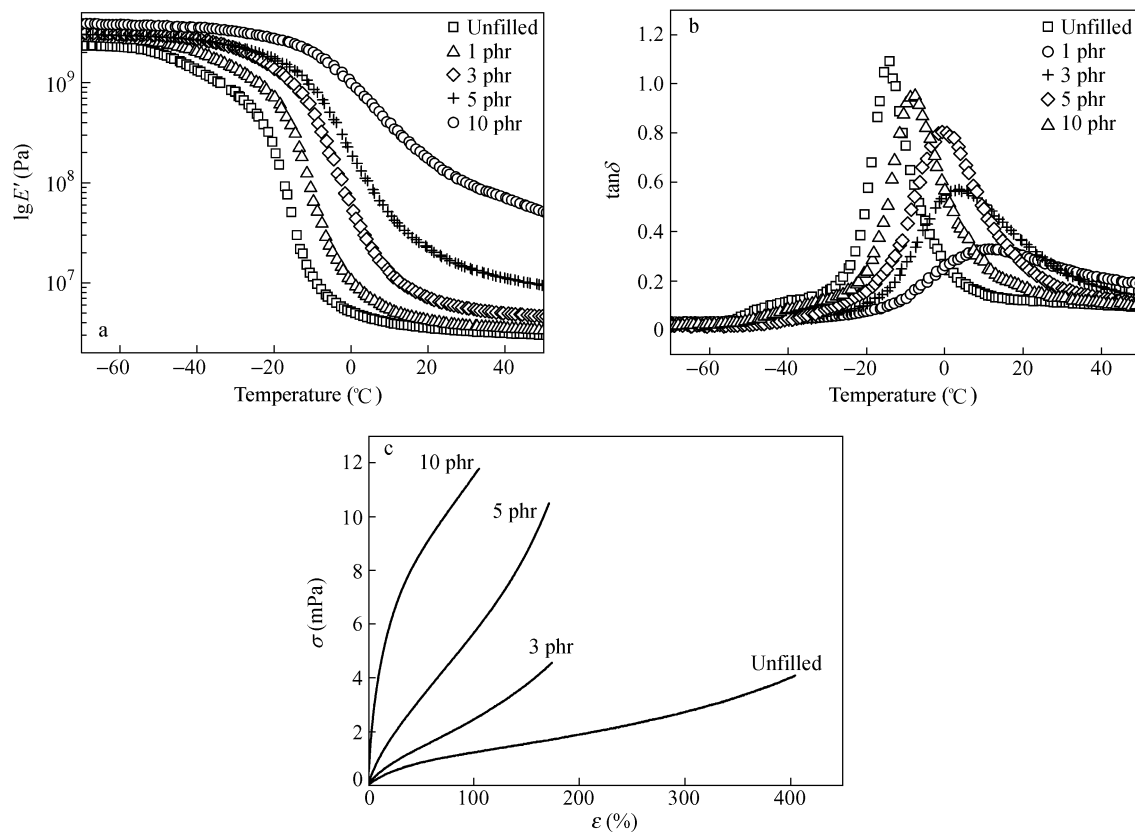


Fig. 6 Mechanical properties of NBR/graphite nanocomposites of different graphite contents prepared by LCM: (a) dynamic storage modulus, (b) loss factor and (c) stress-strain curves<sup>[10]</sup> (Copyright © 2007 Acta Materialia Inc)

**Table 2** Functional properties of NBR/EG nanocomposites prepared by LCM<sup>[10]</sup> (Copyright © 2007 Acta Materialia Inc)

| EG content<br>(phr) | N <sub>2</sub> Permeability<br>$\times 10^{17} (\text{m}^2 \cdot \text{Pa}^{-1} \cdot \text{s}^{-1})$ | Friction<br>coefficient <sup>a</sup> | Wear rate<br>( $\text{mm}^3 / (\text{N} \cdot \text{m})$ ) | Electrical<br>conductivity <sup>b</sup><br>(S/cm) | Thermal<br>conductivity<br>( $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ ) |
|---------------------|-------------------------------------------------------------------------------------------------------|--------------------------------------|------------------------------------------------------------|---------------------------------------------------|-----------------------------------------------------------------------------------|
| 0                   | 3.19                                                                                                  | 1.72                                 | $5 \times 10^{-2}$                                         | × <sup>c</sup>                                    | 0.19                                                                              |
| 5                   | 1.98                                                                                                  | — <sup>d</sup>                       | — <sup>d</sup>                                             | $2 \times 10^{-3}$                                | —                                                                                 |
| 10                  | 1.21                                                                                                  | 1.36                                 | $8 \times 10^{-4}$                                         | $3 \times 10^{-1}$                                | 0.30                                                                              |
| 10 <sup>e</sup>     | 1.83                                                                                                  | 1.38                                 | $3.5 \times 10^{-2}$                                       | ×                                                 | 0.23                                                                              |

<sup>a</sup> Measured under a normal pressure of 0.1 MPa and sliding speed of 0.1 m/s; <sup>b</sup> Flocculated compounds; <sup>c</sup> By direct blending; <sup>d</sup> No test; <sup>e</sup> Out of the range

### 2.3 Rubber/Mg(OH)<sub>2</sub> Nanocomposites

As discussed above, rubber/Mg(OH)<sub>2</sub> nanocomposites were prepared by traditional mechanical blending method, which blended directly nano-Mg(OH)<sub>2</sub> *in situ* modified by silane coupling agent in rubber matrix<sup>[13,14]</sup>. Compared with unmodified ones, modified nano-Mg(OH)<sub>2</sub> presented a better dispersion and more remarkable reinforcement as well as higher limited oxygen index (LOI), as indicated in Fig. 7 and Table 3. As seen in Fig. 8, nano-Mg(OH)<sub>2</sub> showed different improvement effects for different rubber matrices, such as NBR,

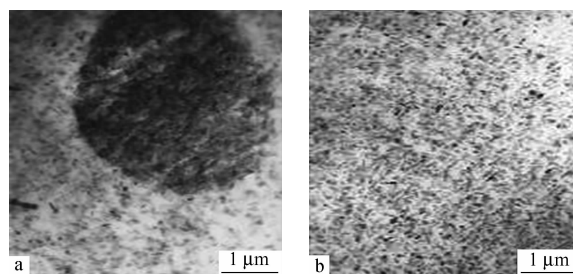


Fig. 7 TEM micrographs of nano-Mg(OH)<sub>2</sub> filled EPDM composites with: (a) unmodified and (b) modified nano-Mg(OH)<sub>2</sub>

ethylene-propylene terpolymer rubber (EPDM), styrene butadiene rubber (SBR) and silicon rubber (SiR), which were caused by the different dispersion levels of the filler. It was also found that

Mg(OH)<sub>2</sub> with smaller particle sizes showed better reinforcement, as illustrated in Fig. 9.

**Table 3** Properties of Nano-Mg(OH)<sub>2</sub> filled EPDM composites<sup>[13]</sup>  
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| Mg(OH) <sub>2</sub><br>loading amount<br>(phr) | Tensile<br>strength<br>(MPa) | Elongation<br>at break<br>(%) | LOI (%) |
|------------------------------------------------|------------------------------|-------------------------------|---------|
| 40 <sup>a</sup>                                | 9.6                          | 432                           | 20.5    |
| 40 <sup>b</sup>                                | 14.1                         | 404                           | 22      |
| 100 <sup>a</sup>                               | 13.8                         | 576                           | 27      |
| 100 <sup>b</sup>                               | 17.7                         | 296                           | 28.2    |

<sup>a</sup> Unmodified; <sup>b</sup> Modified

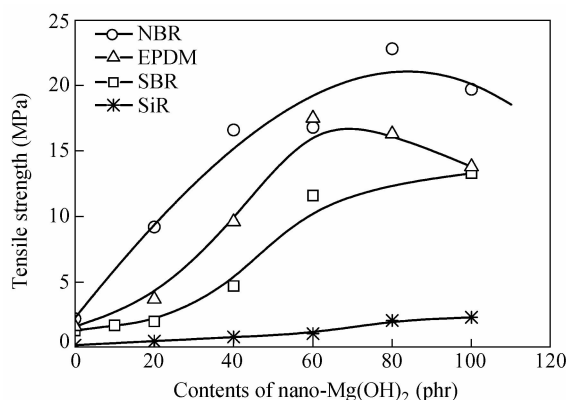


Fig. 8 Tensile strength of rubber/nano-Mg(OH)<sub>2</sub> composites with different loading amounts

## 2.4 Rubber Reinforcement Understanding

A percolation phenomenon is believed to occur in the relationship between mechanical strength and filler volume fractions of composites<sup>[15]</sup>. The percolation phenomenon is inferred to correlate with the elastomer strengthening mechanism. Particle size

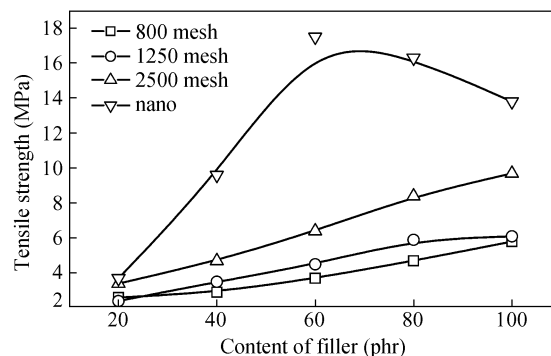
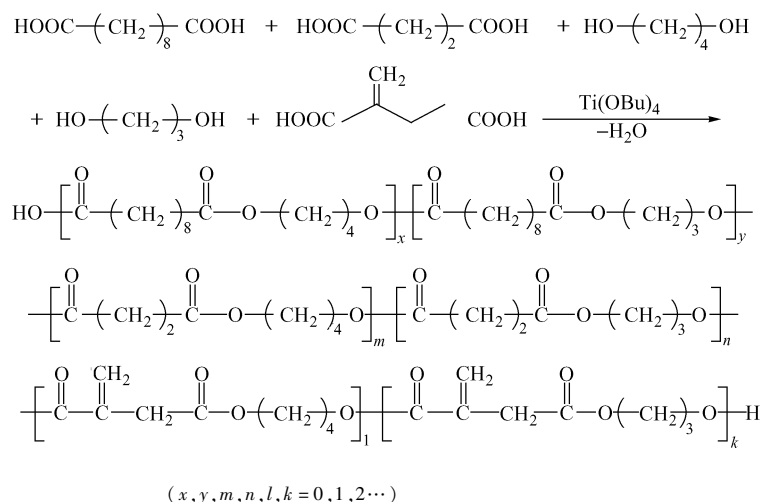


Fig. 9 Tensile strength of EPDM/Mg(OH)<sub>2</sub> with different particle sizes<sup>[13]</sup> (Copyright © 1999 ~ 2012 John Wiley & Sons, Inc)

is an important factor in mechanical performance of strengthening elastomers. The bigger the particle size, the higher the filler content at the percolation point, and the lower the corresponding tensile strength of elastomer nanocomposites. Meanwhile, the occurrence of percolation phenomenon directly depends on the critical particle-particle distance and the critical minimum particle size<sup>[15]</sup>. This is to say, for rubber reinforcement, the particle size is of first importance. The dispersion of filler and the filler-polymer interface should be considered as usual<sup>[16~18]</sup>.

## 2.5 Dielectric Elastomers

A new polyester dielectric elastomer aiming at getting large actuated strains at low electric fields was synthesized through melting polycondensation, as illustrated in Fig. 10. From Fig. 11(a), it is found that the polyester elastomer not only has high dielectric



( $x, y, m, n, l, k = 0, 1, 2, \dots$ )

Fig. 10 The reaction sketch of polyester elastomer

constant, but also shows low glass transition temperature (no figure here). The effect of elastic modulus, which is a key issue for determining actuated strain, was adjusted by tuning crosslink density, as shown in Fig. 11 (b). Although dielectric constant and electrical breakdown strength increase as crosslink density increases, it is surprisingly found from Fig. 12 that, the polyester dielectric elastomer with the lowest crosslink density

shows the maximum actuated strain (11.9%) at a very low electric breakdown field (just 15.6 kV/mm) without any prestrain, even higher than the referred acrylic elastomer VHB4910 and silicon elastomer DC 3481 (as seen in Table 4). It is believed that this elastomer has the lowest elastic modulus, leading to the largest ratio of dielectric constant to elastic modulus.

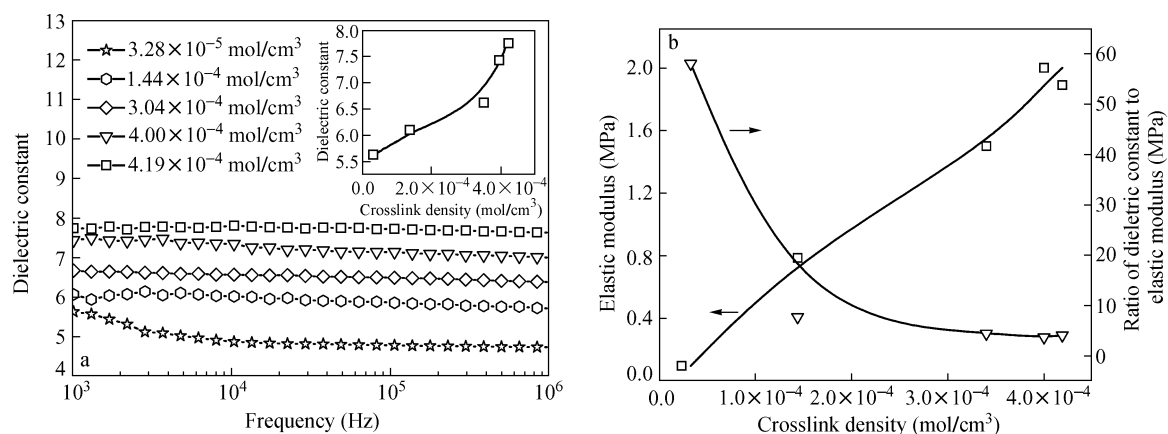


Fig. 11 (a) Dielectric constant and (b) elastic modulus of the polyesters elastomers at different crosslink densities

**Table 4** Actuation behavior of polyester elastomer and other electroactive polymers referred

|                                             | Lateral<br>prestrain at<br>$x$ and $y$ axes<br>(%) | Elastic<br>modulus<br>(MPa) | Maximum<br>area<br>strain<br>(%) | Maximum<br>thickness<br>strain <sup>a</sup><br>(%) | Breakdown<br>electric field<br>(kV/mm) | Energy<br>density <sup>b</sup><br>(MJ/m <sup>3</sup> ) |
|---------------------------------------------|----------------------------------------------------|-----------------------------|----------------------------------|----------------------------------------------------|----------------------------------------|--------------------------------------------------------|
| VHB4910 <sup>[19]</sup>                     | 15, 15                                             | 0.1                         | 40                               | 29                                                 | 55                                     | 0.022                                                  |
| VHB4910 <sup>c</sup>                        | 0, 0                                               | 0.2                         | 7.5                              | 7                                                  | — <sup>d</sup>                         | — <sup>d</sup>                                         |
| DC 3481 <sup>[20]</sup>                     | 40, 40                                             | 0.35                        | 10                               | 9.1                                                | 32                                     | — <sup>d</sup>                                         |
| Polyester with the lowest crosslink density | 0, 0                                               | 0.097                       | 11.94                            | 10.67                                              | 15.6                                   | 0.68                                                   |

<sup>a</sup> The theoretical actuated area strain is calculate by  $S_z = (1 + S_{xy})^{-2} - 1$ ; <sup>b</sup> The elastic energy was obtained as  $e = -P \ln(1 + S_z)$ ; <sup>c</sup> The actuated strain of VHB4910 according to our testing measurement on 15.6 kV/mm without any prestrain; <sup>d</sup> No test

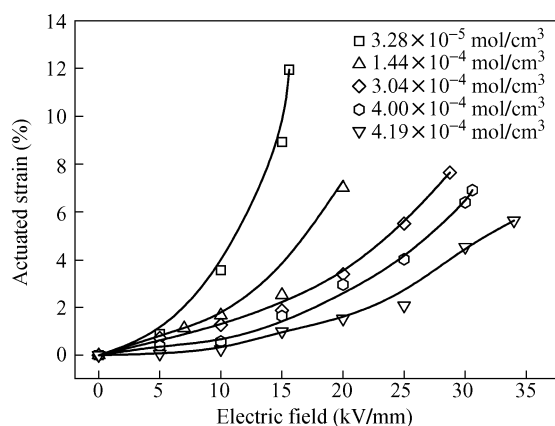


Fig. 12 Electric field dependence of the actuated area strain of polyester elastomers

## 2.6 Functionalized Elastomer Fibers

Silver nanoparticles/elastomer composite fibers with morphological stability were prepared through combination of electrospinning and *in situ* chemical crosslinking method, here including Ag/butadiene rubber (BR), Ag/isobutylene-isoprene rubber (IIR) and Ag/silicon rubber (SiR) composite fibers from hundreds of nanometers to several microns. In this study, Ag nanoparticles were first *in situ* formed by reducing the Ag<sup>+</sup> ions in rubber/DMF/THF solutions under UV-irradiation, then elastomer composite fibers were made by electrospinning the above solution and *in situ* shortly

crosslinking the spun fibers at one time<sup>[21]</sup>. It was found that in-situ chemical crosslinking just after electrospinning was an effective method to

substantially improve the sustainability of fiber morphology<sup>[22]</sup>.

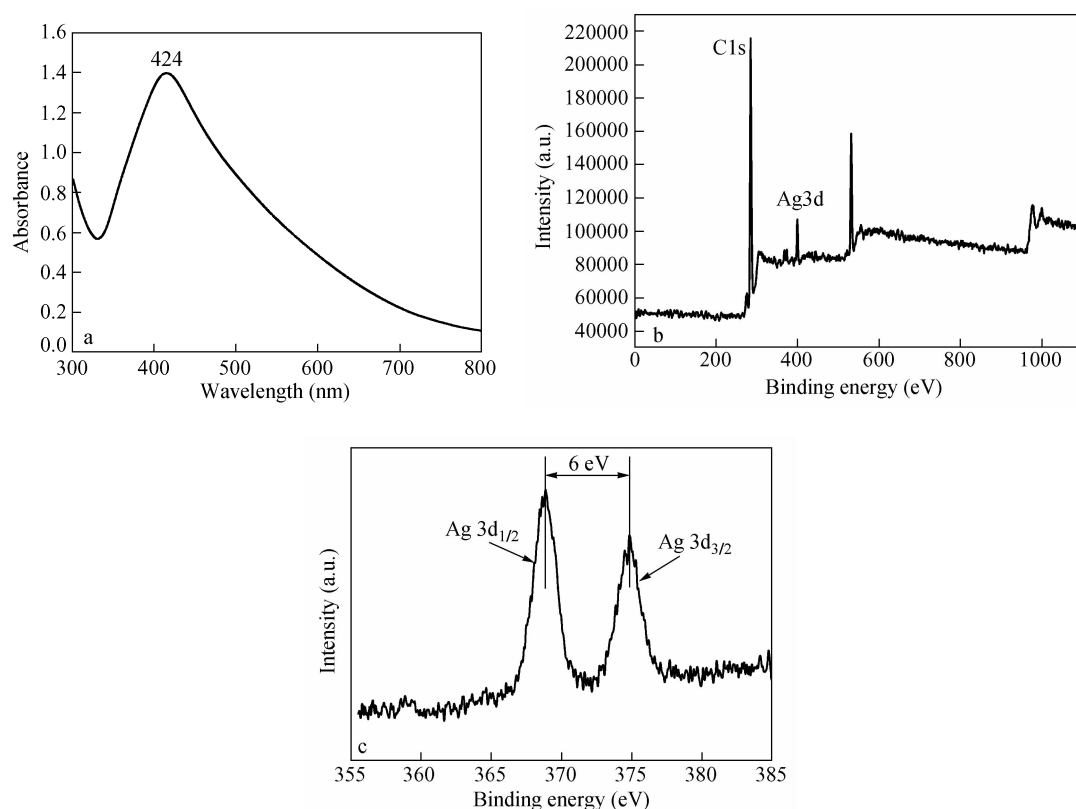


Fig. 13 Characterization of Ag particles in electrospun Ag/BR composite (a) UV spectrum, (b) wide-scan XPS and (c) Ag 3d XPS spectra<sup>[21]</sup>  
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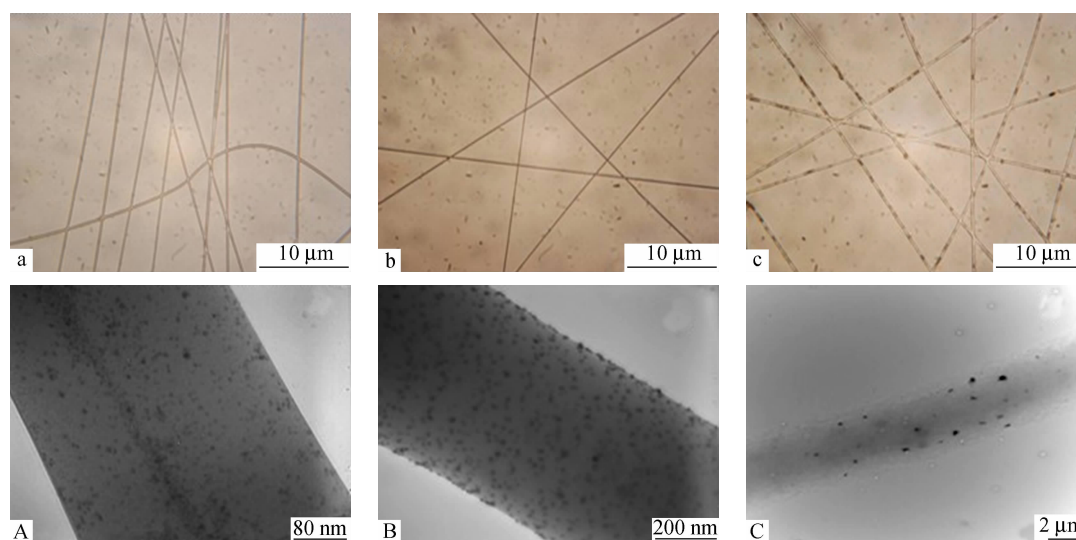


Fig. 14 Optical microscope images (a ~ c) and TEM images (A ~ C) of electrospun

Ag/elastomers, including Ag/BR (a, A), Ag/IIR (b, B) and Ag/SiR (c, C)<sup>[21]</sup> (Copyright © BME-PT)

As indicated from UV absorption spectroscopy, XPS and TEM results in Figs. 13 and 14, Ag NPs with sizes of 10 ~ 20 nm were uniformly dispersed in the elastomer fibers. It was believed that besides the

protection of polyvinylpyrrolidone (PVP), a rapid solvent evaporation and limited motion space for a very fine fiber during electrospinning could obstruct the aggregation of the Ag NPs, resulting in a very

homogenous dispersion. As expected, electrospun BR microfibers with Ag NPs showed very strong antimicrobial activity (99.9%) with very low loading amount of 3 wt% AgNO<sub>3</sub>. This kind of elastomer composite fibers with functionalities would be promising.

### 3 CONCLUSIONS

Rubbers can be reinforced by adding new nano-

particles, such as silicates short nanofibers, graphite nanosheets and Mg(OH)<sub>2</sub> nano-particles rather than traditional nanosized carbon black and silica, resulting in the great improvement in mechanical properties. It is again proved that the particle size of fillers is of first importance for rubber reinforcement. Functional elastomers can be achieved by introducing nanoparticles with functionalities into matrices as well as chemical modification.

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