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Development of highly reinforced acrylonitrile butadiene rubber composites via controlled loading of sol-gel titania



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ABSTRACT

Remarkable improvement in mechanical properties of acrylonitrile butadiene rubber (NBR) composites is achieved by incorporating nano-titania that is synthesised in solution of the raw rubber using titanium *n*-butoxide (TNB) as the titania precursor. This is achieved by designed and controlled incorporation of titania that resulted in very good dispersion of titania of nanometric dimension in rubber matrix and enhanced rubber-filler interaction. This sol-gel transformation is carried out under optimised reaction condition. Surface modification of titania by a silane coupling agent (bis-(3-triethoxysilylpropyl)-tetrasulfide, TESPT) causes further improvement in filler dispersion and composite properties when added in the reactive solgel system during *in situ* titania generation rather than it's external addition in the titania filled NBR during mixing and compounding. Thorough characterisation of the composites are done that encompasses a wide range of studies on thermal, morphological, mechanical, dielectric, dynamic mechanical, rheological and antifungal properties. The results are analysed on a comparative basis to investigate the effect of *in situ* incorporation and *in situ* surface modification of titania on the composite properties.

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1. Introduction

Titania (TiO₂) has been widely used as a multifunctional [1-4] non-black filler for many polymers to deliver improved physical, mechanical and dielectric properties of the composites [5-12]. Other applications of titania include it's use as a white pigment in the paint, adhesives and as a coatings and colorant material in certain rubber based product. It also finds important applications as a self-cleaning agent, photocatalyst and semiconductor owing to its ability in scattering visible light and thereby imparting whiteness, brightness and opacity when incorporated into a polymer matrix. A literature survey reveals that titania particles could also be used as a potential filler if it is incorporated in elastomer in a controlled and

designed way so that state of dispersion, morphology of the titania and it's intrinsic dielectric properties become favourable in delivering the desired performance of the composite in various directions. Recently Dan-Yang et al. exploited titanium dioxide in nitrile rubber to develope dielectric actuators [13,14]. They modified titania by the use of polydopamine in order to improve the dispersion of titania in the NBR matrix. This resulted in reduction in dielectric loss and enhancement in electrical break down strength. There has been a report that surface modification of sol-gel derived titania improved the physical and thermal properties of styrene butadine rubber (SBR) nanocomposites in a remarkable extent as compared to unmodified titania [15]. Paderni et al. reported the preparation of ethylene-propylene diene monomer (EPDM) based titania composites via nonhydrolytic sol-gel process where presence of titania as a rigid filler in the EPDM matrix led to a significant improvement in mechanical properties such as stiffness and stress at break [12]. In another work, it is reported that the titania filled natural rubber (NR) composite could offer enhanced mechanical properties, strong antibacterial properties as well as good resistance to UV radiation [16]. Javadi et al. developed titania based



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ethylene-propylene rubber to study the dielectric elastomer actuations [17]. Superior antibacterial activity of Ag-doped titania filled natural rubber latex foam, even under visible light condition, is also reported [18]. Significant improvement in composite properties brought by titania loading in different polymeric materials could also be found elsewhere [19–24].

In most of the cases titania is incorporated in polymer by conventional solid state mixing. However, titania particles can be generated in situ in rubber matrix adopting sol-gel method. Poly (amide-imide) (PAI)/titania composite film was prepared by sol-gel derived in situ titania and it was found that glass transition temperature of the polymer was improved which was explained by hydrogen bonding interaction between the amide group of PAI and the hydroxyl group on the titania surface [25]. Walid et al. reported preparation of polypropylene/titania nanocomposites from the hydrolysis and condensation (sol-gel method) of titanium *n*-butoxide premixed with polypropylene under molten condition [26]. Alxandru et al. used solvent free sol-gel technique of in situ filler loading for the preparation of polydimethylsiloxane/silica/titania composites [27]. There are also few reports where sol-gel titania was synthesised along with silica precursor to prepare new hybrid materials containing mixed fillers (silica and titania) [28,29].

In this context, it appears that *in situ* generation of titania in rubber matrix in a strategically designed and controlled condition could be very promising in enhancing the composite properties. It is needless to mention that organic-inorganic hybrid nanocomposites could offer novel and useful properties due to synergistic effect of two components and therefore find many important applications in different technological fields. In recent past, we reported several results on *in situ* generation of silica in rubber matrix adopting different sol-gel techniques along with in situ surface modification of silica that revealed some interesting and significant research findings [30-33]. In present work, titania is generated in situ in NBR by sol-gel method from titanium (IV) nbutoxide (TNB) at low and high content. To the best of our knowledge, this is the first attempt to incorporate titania in situ in NBR which is the most widely used and fastest growing synthetic rubber and finds both specility and general purpose application. Several reaction parameters have been optimised to get appreciable conversion of TNB to titania in the rubber matrix. Thorough characterisations of the composites are done and the results are compared with that of externally filled composites at same filler content. Furthermore, a silane coupling agent viz. bis-(3triethoxysilylpropyl) tetrasulfide (TESPT) is used (both in in situ modification and external mixing) to investigate any further improvement in filler dispersion and composite properties.

2. Experimental

2.1. Materials

Acrylonitrile butadiene rubber (KNB 35L) (acrylonitrile content is 34%) was obtained from Heritage Rubber (Nagpur, India). Titanium (IV) *n*-butoxide 99% (TNB) and *n*-heptylamine were purchased from Acros Organics (New Jersey, USA). Titania powder (P-25) and Bis-(3-triethoxysilylpropyl) tetrasulfide (TESPT) was purchased from Evonik Degussa (Thailand). Tetrahydrofuran (THF) and toluene were purchased from Fischer Scientific Ltd (India). Sulphur, zinc oxide, stearic acid and mercaptobenzothiazole disulfide (MBTS) were collected from Sara Polymer Pvt. Ltd. (Nagpur, India).

2.2. In situ generation of titania into acrylonitrile butadiene rubber by sol-gel process

Titania is generated in situ into NBR matrix by solution sol-gel

process. Reaction condition was optimised with 10 phr titania generation (Discussed in "Result and Discussion" section). 30 gm of NBR, made in small pieces, was dissolved in 400 ml of tetrahydrofuran (THF) with constant stirring till homogenous mixture is obtained. Then measured amount of titanium (IV) n-butoxide (TNB) was added as titania precursor. For composites 2 and 4, 15 ml of TNB (14.7 g) was added in rubber solution to obtain 10 phr of titania since 92% TNB conversion was found during optimisation of reaction condition. For composites **3**, **5** and **6**, 61 ml TNB (59.8 g) was added that resulted in generation of 35 phr titania with 80% conversion. This was followed by addition of water (TNB: water mole ratio 1:2; 1.6 ml of distilled water for composites 2 and 4 and 6.2 ml for composites **3**, **5** and **6**) and *n*-heptylamine (0.096 mol with respect to 1 mol of TNB; 0.21 ml for composites 2 and 4 and 0.85 ml for composites **3**, **5** and **6**), as catalyst, with continuous stirring. For composites **4** and **5**, 0.27 ml (1phr) of bis-(3-triethoxysilylpropyl) tetrasulfide (TESPT) was added in rubber solution during stirring in addition to other reagents. Then the whole mixture was refluxed for 1 h at 80 °C. The refluxing was stopped and the mixture was kept for gelling at room temperature for 4 days which was followed by vacuum drying at 50 °C till the constant weight of the sheet was obtained.

2.3. Compounding of rubber

For the preparation of composites **2–5**, that are differing by *in* situ titania content, same process of compounding and vulcanisation was followed. First, in situ titania filled rubber mixes, obtained from earlier step, were masticated for 5 min on a two roll mill which was followed by the compounding with crosslinking ingredients (ZnO, stearic acid, MBTS, and sulphur) for further 10 min to obtain homogenous rubber mixture. For composite 6, same procedure of compounding and vulcanisation was followed with 35 phr in situ titania filled NBR sheet where TESPT (0.27 ml, 1 phr) was added externally during two roll mixing. Composite 7 is prepared, for comparative study, by mixing raw NBR with externally added titania followed by the addition of TESPT (0.27 ml, 1 phr) along with other crosslinking ingredient added for vulcanisation. Unfilled sample 1 was prepared by same procedure but without adding any filler and TESPT. The resultant compounds were then vulcanized (including unfilled sample), using compression moulding at 160 °C according to their optimum cure time (t_{90}) .

3. Characterizations

3.1. Thermogravimetric analysis (TGA)

Thermal stability and *in situ* titania content of rubber vulcanizates were determined by thermogravimetric analysis (TGA) and derivative of thermogravimetric (DTG) using a thermal analyzer TG-DTA 7200 (Hitachi, Japan). The sample was heated on a platinum pan in the temperature range 40–700 °C under nitrogen at heating rate of 10 °C/min. The titania content in the rubber composites has been determined by comparing the residual weight percentage (obtained from char yield) of a particular composite, relative to the unfilled sample, as obtained from thermogravimetric results. Difference of the residual weight percentage of a composite from that of the unfilled sample gives titania content of the composite in weight percentage that have been converted into phr scale (Eq. (1)) and used in the manuscript throughout.

Content of titania and the conversion of TNB to titania are derived by the following expression and presented in Table 1.

Titania content(in phr) =
$$\frac{W}{W - 100} \times 100$$
 (1)

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