research group, ALOKA (Artificial intelligence and Light assisted Opto-electrochemical-Kinematic Agents) was formed to expand collaborative research in Analytical Chemistry, Materials Physics, Mechatronics and Data Analytics. Developing cost-effective Raman spectroscopy instrumentation combined with machine learning remains a high priority for the group and anticipates wider opportunities to integrate with the industry. Developing new materials for surface enhanced Raman spectroscopy to probe diseases, test food quality and detect environmental pollutants is currently undertaken. For more information, please visit the group webpage at https://aloka.cmb.ac.lk/. For establishing research collaborations, please contact the Director, Center for Instrument Development via email at aloka@sci.cmb.ac.lk.

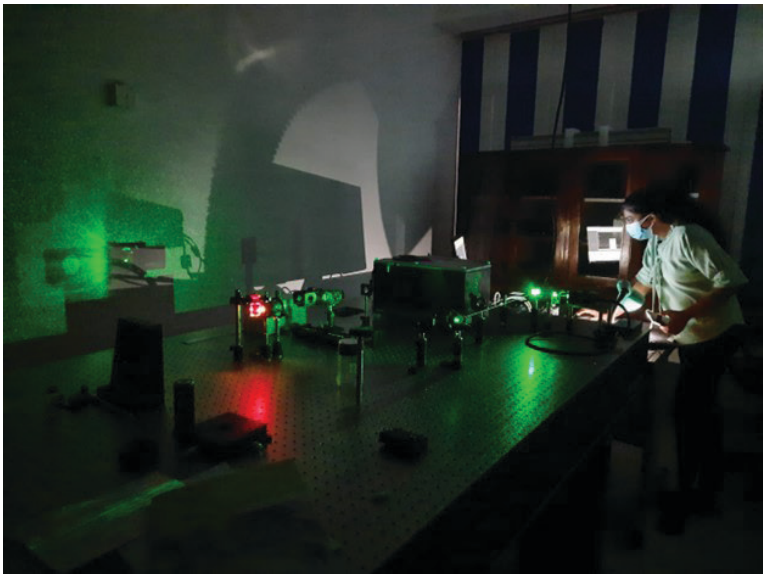

Figure: The Center for Instrument Development Laboratory at the Department of Physics in the Faculty of Science of the University of Colombo now houses a Research grade Raman Spectroscopy setup. The image shows a graduate student initializing Raman spectroscopy. The facility is now open for research collaborators and industrial partners to build partnerships with affiliated researchers at the ALOKA group, Center for Instrument Development. For more information, please visit the group webpage at https://aloka.cmb.ac.lk/

Themed Collection

Nanomatrix Structures Prepared on Natural Rubber Particles in Latex Stage

Asangi Gannoruwa

Department of Materials and Mechanical Technology, Faculty of Technology, University of Sri Jayewardenepura, Pitipana, Homagama, Sri Lanka

Nanomatrix structures are prominent filler network structure which usually improves the mechanical properties of natural rubber or sometimes used to introduce novel properties. The nanomatrix structures have been prepared using both inorganic and organic nanoparticles, such as silica, nanodiamond, and polystyrene, methyl methacrylate, Polyaniline respectively. The nanomatrix structure is a phase separated structure, where, natural rubber particles are dispersed as a major component into matrix of nano-composite with inorganic or organic nanoparticles as a minor component. Mechanical properties of the polymers, which are related to the nanomatrix structure, may be tunable with size, surface area, interaction and dispersion of the inorganic nanoparticles in the matrix.

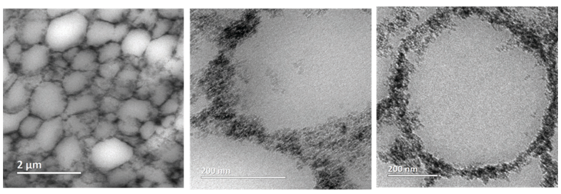

Figure 1. TEM images of Nanodiamond Nanomatrix Structure Prepared onto natural rubber Particles at

different magnifications. The bright domains represent natural rubber particles and the dark domains represents the nanodiamond particles.

The nanomatrix structure consists of rubber particles with a diameter of several micrometers dispersed in filled rubber with a thickness of several tens nanometer as shown by the TEM image of natural rubber with nanodiamond nanomatrix in Figure 1. These filler structures are formed by linking the rubber particles to filler nanoparticles in latex stage, followed by coagulation or solvent casting. Since the chemical structure of natural rubber is cis-1,4-polyisoprene the chemical linkages may generated through radical reactions. For instance natural rubber with polystyrene nanomatrix structure was prepared by graft co-polymerization of styrene onto natural rubber particles in latex stage in the presence of an organic redox initiator, followed by casting and drying. A similar method was used to prepare nanomatrix structures with nanodiamond and graphene. Silica nanomatrix was prepared by graft-co-polymerization of vinyltriethoxysilane in the presence of organic peroxide initiators. Styrene/silica hybrid nanomatrix was prepared with p-styryltrimethoxysilane monomer.

Mechanical properties of natural rubber with nanomatrix structures are high even without conventional sulfur vulcanization. Stress at break for neat deproteinized natural rubber (DPNR) is around 3-4 MPa. The silica nanomatrix structure prepared by grafting vinyltriethoxysilane monomer on to natural rubber at 4.4 phr (parts per hundred dry rubber) silica concentration, the stress at break was reported as 10 MPa. The value for styrene at 14.7 phr concentration was 20 MPa. Formation of a polystyrene/silica hybrid nanostructure at 4.4 phr silica and 6.3 phr styrene concentrations has reported a stress at break of a 23MPa, which is comparable to sulfur vulcanized natural rubber. Thus, the increased tensile strength could be attributed to the nanomatrix structures. A study using nanodiamond nanomatrix structure, mechanical properties were compared with the morphology. When the nanodiamond concentration was 15 phr, where an incomplete nanomatrix was present, the stress at break was 6.5 MPa which was rapidly increased to 15.5 MPa at 25 phr where a complete nanomatrix was observed in TEM images. At 40 phr concentrations the stress at break was around 22 MPa (Figure 2). Interestingly, without the peroxide initiators, even at 40 phr nanodiamond concentration the tensile strength was around 10 MPa and the unique phase separated structure of the nanomatrix was absent in the TEM images. This result proved that not only the morphology the interaction between natural rubber and the fillers also contributes to the mechanical properties of these structures. Storage and loss moduli of the samples reported a similar pattern to the tensile strengths. Further studies based on the 3D-TEM and the AFM analysis (Figure 3 and 4) of the nanodiamond nanomatrix, presence of a glassy rubber region was observed within the nanomatrix. The nanoparticles are heavily dispersed in this glassy rubber region. The Young's modulus of this grassy region was 10- 40 times higher than natural rubber. The enhancement of the tensile strength of the material was found to be due to this layer according to the Takayanagi Principal.

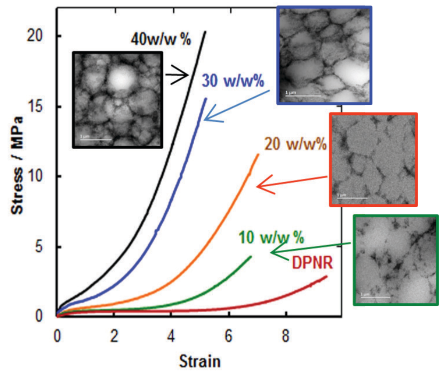

Figure 2. Stress-strain curves of natural rubber with nanomatrix structures with respect to their morphologies.

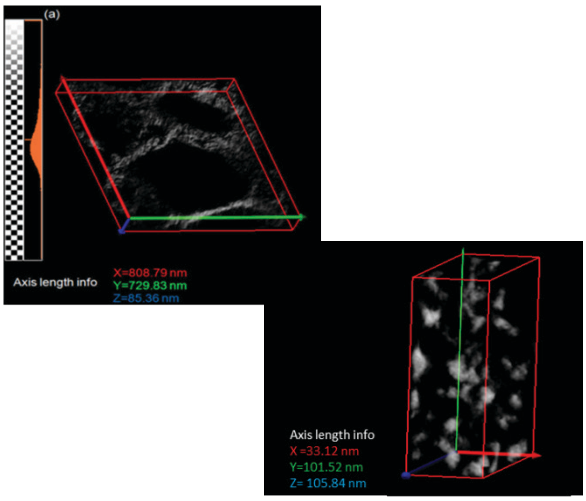

Figure 3. 3D -TEM images of natural rubber with

nanodiamond nanomatrix

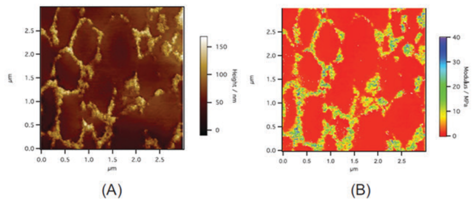

Figure 4. AFM images of nanodiamond–natural rubber film: A) height map and B) Young's modulus map. (Kawahara, S. Et al. Adv. Funct. Mater. 2020, 30, 1909791)

Nanomatrix structures have possibilities to introduce novel properties the natural rubber based materials, which lengthens the industrial applications of them. Natural rubber is an electrical insulating material. However, a nanomatrix structure prepared with anilene grafted epoxidized natural rubber in latex stage showed 6.86 ×10-4 S/cm electrical conductivity. Natural rubber with graphene nanomatrix structure has remarkably improved electromagnetic shielding and mechanical properties which are important for many applications including military applications. It has been reported that sulfonation of polystyrene nanomatrix structure with chlorosulfonic acid, give rise to high proton conductivity and hence could be used as a polymer electrolyte.

Novel nanomatrix structures prepared on to natural rubber particles in latex stage open up for novel applications to natural rubber based industries. The fillers are completely dispersed in natural rubber matrix without forming aggregates; this in turn would prevent unnecessary crack generations in rubber compounds. Hence it is advantageous to use in current natural rubber based products. It was also found by dynamic mechanical analysis, the natural rubbers with nanomatrix structures shows frequency independent viscoelastic behavior, and could be used as materials requiring good damping properties. Thus, natural rubber with nanomatrix structures would play vital role in future natural rubber based materials, expanding its frontiers.

References

- Gannoruwa, A., Sumita, M. and Kawahara, S. (2017) 'Highly enhanced mechanical properties in natural rubber prepared with a nanodiamond nanomatrix structure', Polymer, 126, pp. 40–47. doi:10.1016/j.polymer.2017.08.025.
- Gannoruwa, A., Kawahara, S. (2018) 'Distribution of Nanodiamond Inside the Nanomatrix in Natural Rubber', Langmuir, 34(23), pp. 6861–6868. https://doi.org/10.1021/acs.langmuir.8b00761
- Ha, N. T.et al (2020) 'Preparation of Electromagnetic Shielding Coating Based on Natural Rubber', MaterialsTransactions, 61(8), pp.1544-1549. doi:10.2320/matertrans.MT-MN2019010
- Kawahara, S. et al. (2003) 'Preparation and characterization of natural rubber dispersed in nano-matrix', Polymer, 44(16), pp. 4527–4531. doi:10.1016/s0032-3861(03)00415-4.
- Kawahara, S. et al. (2020) 'Nanodiamond glass with rubber bond in natural rubber', Advanced Functional Materials, 30(15). doi:10.1002/adfm.201909791.
- Nghiem, T. T., Yusof, N.H. and Kawahara, S. (2023) 'A polystyrene/silica hybrid nanomatrix formed in natural rubber', 55, pp. 631–637 (2023). https://doi.org/10.1038/s41428-022-00753-6
- Pham, M.D. et al. (2022) 'Graphene matrix formation in a natural rubber dispersoid', polymer journal, 54, pp. 727–733. https://doi.org/10.1038/s41428-022-00620-4