Available online at http://www.journalcra.com

International Journal of Current Research
Vol. 9, Issue, 05, pp.49846-49850, May, 2017

INTERNATIONAL JOURNAL OF CURRENT RESEARCH

ISSN: 0975-833X

RESEARCH ARTICLE

CURE CHARACTERISTIC STUDIES OF NR-COMPOUNDS REINFORCED WITH NANO ZINC OXIDE CURE ACTIVATOR- SYNTHESIZED VIA SOL-GEL METHOD

Sambhu, R., Christy Augustine, P. A. and *Prema, K. H.

Department of Chemistry, S.D. College, Alappuzha-688003, Kerala, India

ARTICLE INFO

Article History:
Received 22nd February, 2017
Received in revised form
16th March, 2017
Accepted 04th April, 2017
Published online 19th May, 2017

Key words:

Sol-gel method, Zinc oxide,
Natural rubber, Vulcanization,
Cure rate index.

ABSTRACT

ZnO nano particles are synthesized using sol-gel method. Crystal structure of the samples prepared at different annealing temperature is analysed using XRD. Natural rubber vulcanisates are prepared using different series of nano ZnO (Z0, Z1, Z2, and Z3) as cure activator. A control compound is also prepared with commercial ZnO at high phr loading. Cure characteristics as well as cure rate kinetic values of NR-nano ZnO vulcanisates are compared with that of the commercial sample. Appreciable reduction in phr of ZnO is possible with the usage of nano ZnO.

Citation: Sambhu, R., Christy Augustine, P. A. and Prema, K.H., 2017. "Cure Characteristic Studies of NR-Compounds Reinforced with Nano Zinc Oxide Cure Activator- Synthesized via Sol-Gel Method", *International Journal of Current Research*, 9, (05), 49846-49850.

INTRODUCTION

Zinc oxide nano materials have wide range of application in the field of electronics, optics and photonics. ZnO is a semiconductor material with wide band gap energy (3.37 eV) (Sanjeev Kumar *et al.,* 2014, George Varghese *et al.,* 2014, Sridevi and Rajendran, 2009). Depending on the method of synthesis it has a diverse group of growth morphologies such as nanocombs, nano rings, nano wires and nano cages. ZnO crystals have wurtzite structure with lattice parameters a = 0.3296 and c = 0.52065 (JCPDS 36-1451). It is a transparent electro conductive and piezoelectric material. Its UV absorption capacity makes it an excellent optoelectronic material (Nanda Shati and P.S. Gupta, 2010, T.D Malevu and R.O Ocaya, 2015, Ratheesh R Thankalekshmi *et al.,* 2013, Ruby Chauhan *et al.,* 2010). It has application in photocatalysis, solar cells, chemical sensors, gas sensors and other electroluminescent devices. Another important application of ZnO is in the vulcanization reaction of natural rubber. It is one of the basic materials of the rubber compound formulation. Rubber chains are generally cross-linked by sulphur and sulphur donor compounds. During this process ZnO acts as an activator. Several studies are being carried out to find efficient cross-linking agents, activators and co-activators which can bring about economy in rubber industry by reducing the vulcanization time (cure time) and quantity of vulcanizing ingredients. Sofar the role of ZnO (commercial grade) is intact as an activator along with stearic acid as co-activator in cross linking reaction of natural rubber (NR) with sulphur. In view of reduced environmental polution, it is highly essential to study the possibility of reducing ZnO content in rubber products. Replacement of commercial ZnO with nano ZnO can surve this purpose to a certain extent. Effficiency of ZnO as cure activator can be improved by maximizing contact between ZnO particles and rubber chains. This is highly depend on the size, shape and surface area of the particles which on the other hand influenced by the method of preparation.

As the particle size decreases surface area increases and the crosslinking contact between rubber chain increases. Studies are being carried out in this way to replace commercial ZnO with nano ZnO (Bindhu Panampilly and Sabu Thomas, 2010, Suchismita Sahoo *et al.,* 2007). Several methods are available from the literature for the synthesis of ZnO nano particles (Yendrapati Taraka Prabhu *et al.,* 2013, Virendra Chandore *et al.,* 2013). In this particular study ZnO nanoparticles are synthesized by sol-gel auto combustion method. ZnO nano particles are incorporated in natural rubber and cure characteristics are analysed.

****Corresponding author: Prema, K.H.***
Department of Chemistry, S.D.College, Alappuzha 688003, Kerala, India.

Table 1. Recipe used for the preparation of NR vulcanisates with different loading of Nano ZnO

Ingredients (phr)	Z (Commercial)	Z0 (a,b,c)	Z1 (a,b,c)	Z2 (a,b,c)
NR	100	100	100	100
ZnO	5.0	(1.5,2.0,2.5)	(1.5,2.0,2.5)	(1.5,2.0,2.5)
Stearic acid	3.0	(0.75,1.0,1.25)	(0.75,1.0,1.25)	(0.75,1.0,1.25)
MBTS	0.8	0.8	0.8	0.8
TMTD	0.2	0.2	0.2	0.2
Sulphur	2.5	2.5	2.5	2.5
Aromatic oil	1.0	1.0	1.0	1.0

MATERIALS AND METHODS

A modified sol-gel auto combustion method is adopted for the synthesis of ZnO nano particles using Zinc nitrate as the precursor. As such prepared samples are annealed at 200, 400, and 600 degree celsius and the samples are designated as Z0, Z1 and Z2 respectively. These samples are used in rubber vulcanization at different phr loading. All the chemicals used for the synthesis of ZnO and vulcanization of natural rubber are of analytical grade. Natural rubber used for the preparation of NR vulcanisates is of ISNR-5 grade (mooney viscosity ML (1+4) at 100^{o}C equal to 85 is purchased from Rubber Research Institute, Kottayam, Kerala, India.

Preparation of NR compounds with nano ZnO and commercial ZnO

Incorporation of various ingredients into natural rubber is carried out in a two roll mill according to the recipes given in Table 1. A control compound with commercial ZnO is also prepared with 5phr loading.

Determination of Cure Characteristics

Cure characteristics of the mixed compounds are determined using a rubber process analyser (RPA 2000), Alpha Technologies, USA, as per ASTM D2084-01 at 150^{0}C for time duration of 30 minutes. From the RPA data, parameters like optimum cure time (t_{90}), scorch time (t_{10}), maximum torque (Dmax) and minimum torque (Dmin) are determined.

Characterization Techniques

XRD patterns of the powdered samples annealed at different temperature are recorded using a X-ray diffract meter using Cu Kα radiations. The wavelength of Cu Kα radiation is 1.5405 A^{0} and the scan rate used is 5^{o}/minute. The FTIR spectra is recorded on a Thermo Nicolate Avatar370 (Model) spectrophotometer in KBr medium in the region 4000-400 cm^{-1} having DTGS detector. TGA studies are carried out on a TGA analyzer: model Perkin Elmer STA 6000 at SAIF, CUSAT, COCHIN. Samples are subjected to the TGA analysis from 40^{o}C to 750^{o}C at a heating rate 10^{o}C/min. The chamber is continuously swept with nitrogen at a rate of 200 ml/min.

RESULTS AND DISCUSSION

Figure 1 represents the XRD of the samples prepared at different temperature. All the samples exhibit typical XRD pattern of ZnO and matches well with the JCPDS data file no. 36-1451. Reflecting planes are indexed in the figure, which ensures the formation of crystal planes and the formation of hexagonal wurtzite structure. XRD patterns are considerably broadened which indicates the formation of nano particles. From the peak width average particle size is calculated using Debye-Scherrer equation $t = \dfrac{0.9\lambda}{\beta\cos\theta}$.

Where 't' is the thickness of the crystallite (particle size), λ is the wavelength of the X-radiation, β is the angular width which is equal to the full width at half maximum. Slight reduction in particle size is observed at higher annealing temperature. This may be due to the breakdown of agglomerated particles. Average particle size of the samples is tabulated in Table 2.

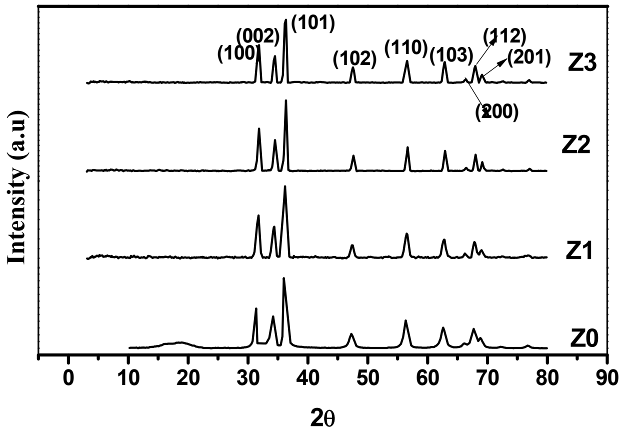

Figure 1. XRD pattern of ZnOnano particles at different temperatures

Table 2. Average particle size of ZnO

Sample	Temperature (^{o}C)	Average particle size (nm)
Z0	200	13.17
Z1	400	15.73
Z2	600	25.64
Z3	800	19.43

IR spectra of samples fired at 200^{o}C and 600^{o}C is represented in figure 2. The broad peak at 3430 cm^{-1} in Z0 sample is the characteristic of O-H stretching vibration of adsorbed water molecules. Peaks observed at 1588 and 1385 cm^{-1} are due to O-H deformations. All these peaks are almost disappeared at higher firing temperature as shown in the IR spectrum for the sample Z2.The broad peak observed below 500 cm^{-1} ensures the formation of ZnO particles. TGA and DTA curves for the ZnO particle prepared at 200^{o}C are given in Figure 3. Two minor decomposition stages are observed in the TGA curves, one is at 104^{o}C and the other one at 361^{o}C. Initial weight loss is due to the loss of adsorbed water molecules and the weight loss at higher temperature may be due to the decomposition of other molecular impurities that may retain with the sample during the synthesis. Overall weight loss is very small which indicates about the purity of the sample prepared at 200^{o}C.

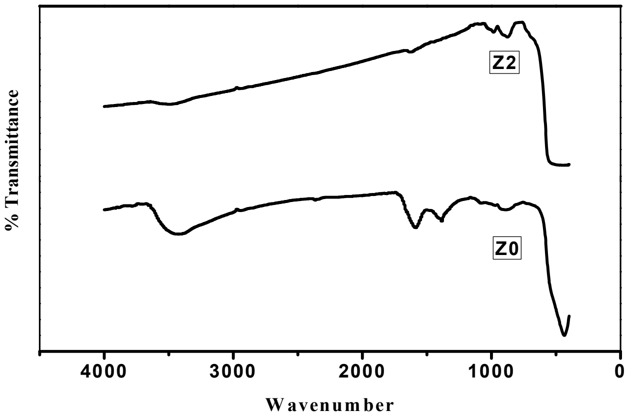

Figure 2. IR spectra of Z0 and Z2 samples

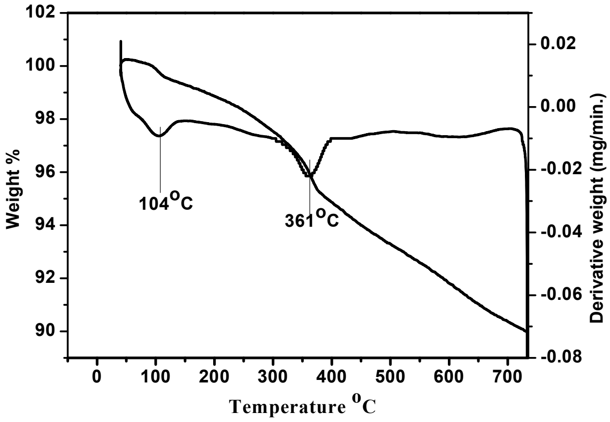

Figure 3. Thermogravimetric and derivative thermogravimetric curves of sample Z0

Table 3. Cure time analysis

Loading (phr)	ZnO (commercial)	Z0	Z1	Z2
1.5		7.20	6.07	5.54
2.0		6.55	6.65	6.33
2.5		7.70	7.10	7.01
5.0	7.39	…..	….	…

Representative cure curve for the NR-vulcanisates with nano ZnO is shown in Figure 4. Initial part of the cure time graph indicates about the induction period during which the change in torque value is small. Sharp increase in torque value during the second stage indicates the cross link formation between the rubber chains. The third plateau like portion in most of the case is due to the maturation of cross linking. Nature of cure curve is identical for both the commercial ZnO and the prepared nano ZnO samples. This indicates that mechanism of cure reaction is not affected by nano zinc oxide. Cure time of the samples prepared with nano ZnO is compared with commercial ZnO as given in table 3. From the analysis results it is clear that cure time increases with increase in phr loading of nano ZnO. But even at 2.5 phr this value is comparable with that of commercial ZnO with a higher loading of 5 phr. Cure time is found to decrease as the particle size increases from sample Z0 to Z2. Reduction in cure time cannot be taken as the only criteria for the selection of the nano ZnO as a curative. Various other parameters are also to be considered. Commercial ZnO sample give maximum torque value of about 2.4. Dmax value is one of the important parameters for the vulcanisates as this determines the mechanical properties of the composites.

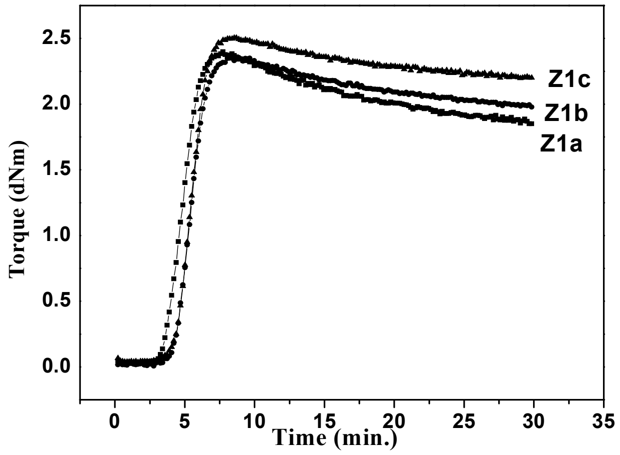

Figure 4. Cure curves for Z1 _NR vulcanisates with different loading

Table 4 represents the scorch time for the NR-ZnO vulcanisates. Variation of scorch time of different samples is identical with that in the case of cure time. Scorch time is found to decrease with the size of the ZnO particle. At higher loading (2.5phr) the scorch time values are comparable with that of commercial ZnO. Nano ZnO-NR compounds provide enough scorch safety in par with that of commercial ZnO sample.

Table 4. Scorch time results

Loading (phr)	ZnO(commercial)	Z0	Z1	Z2
1.5		4.51	3.64	3.34
2.0		4.01	4.35	3.96
2.5		4.49	4.44	4.32
5.0	4.19	….	….	…

Higher the Dmax, better is the stress-strain properties. From the analysis results it is clear that other than the Z0 samples all other samples give higher Dmax values, hence better mechanical properties are expected. Compiling all these results it can be seen that loading of nano ZnO can be optimized to 1.5 phr with Z2 sample. This is supported from cure kinetic studies. Kinetics of cure reaction can be followed from rheometric data using the equation $\ln (M_h-M_t) = -kt + \ln (M_h-M_0)$ where M_h is the maximum torque, M_0 is minimum torque and M_t is the torque at time t. The straight line plot of $\ln (M_h-M_t)$ against time indicates that the cure reaction follows first order kinetics. The cure reaction rate constant (k) is then directly obtained from the slop of the straight line plot. Plot of $\ln(M_h-M_t)$ against time for different phr loading of ZnO is given in figure 5a-5c. The nature of all these curves is similar and the straight line portion of all these curves indicates that cure reaction follows first order kinetics. Initial portion of these curves is slightly bent which corresponds to the scorch period. Slope of the straight line portion of the curves is determined from linear fit method from which the cure rate constant is obtained.

Table 5. Dmax values of NR vulcanisates with commercial and nano ZnO

Loading (phr)	ZnO(commercial)	Z0	Z1	Z2
1.5		2.036	2.399	2.487
2.0		2.298	2.357	2.569
2.5		2.334	2.507	2.523
5.0	2.409	….	…	…

Cure rate index CRI = 100/ (cure time-scorch time). All the NR-nano ZnO vulcanisates have better CRI values than for the commercial ZnO sample. Variation of CRI values with particle size for different loading of ZnO is depicted in figure 5a-5c. Better CRI values are obtained for compounds with 1.5 phr loading of different nano zinc oxide particles.

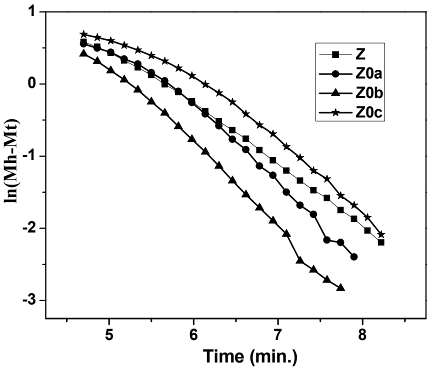

Figure 5. (a) cure kinetic curves for commercial and Z0 series of ZnO

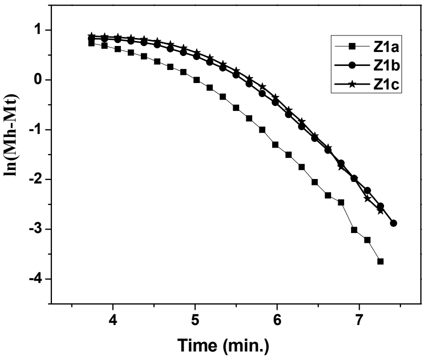

Figure 5. (b) cure kinetic curves for Z1 series of ZnO

Cure rate index and cure reaction constant for various samples with different ZnO nano particles are shown in figure 6a, 6b and 6c. Cure rate index and cure reaction constant found to increase with increase in particle size, attain a maximum value and then decreases. Maximum value is obtained for samples with 1.5 phr loading of Z2 (particle size 25nm). But at 2.0 and 2.5phr loading this maximum is shifted to the samples with lower particle size 15 nm (Z1b & Z1c). Better cure properties of NR compounds vulcanized with nano ZnO can be attributed to the high surface area of thes samples compared with commercial ZnO. As the particle size decreases surface area increase and cure ingredients are better adsorbed on the surface which enhances the cure reaction.

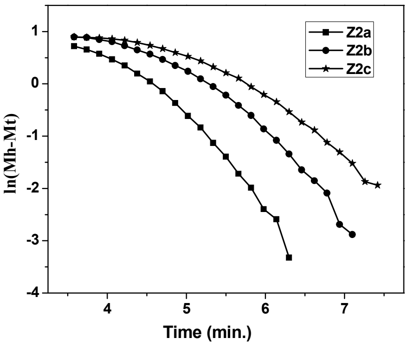

Figure 5. (c) cure kinetic curves for Z2 series of ZnO

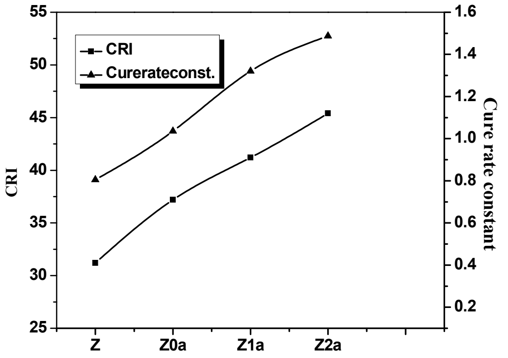

Figure 6. (a) CRI and cure rate constant for different ZnO particles at 1.5 phr loading

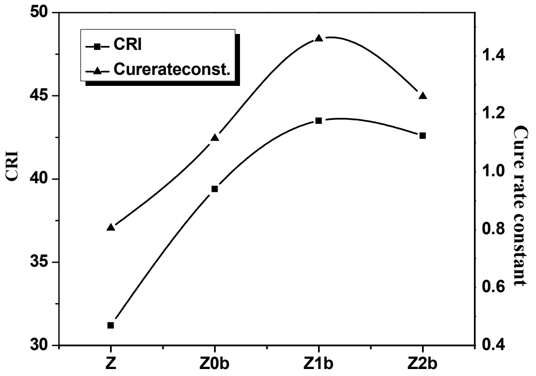

Figure 6. (b) CRI and cure rate constant for different ZnO particles at 2.0 phr loading

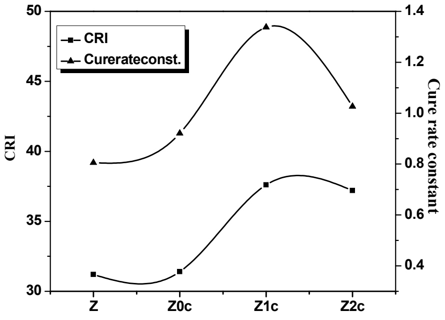

Figure 6. (c) CRI and cure rate constant for different ZnO particles at 2.5 phr loading

Thus better cure characteristics can be obtained by the reduction in particle size of cure activator to nano regime.

Conclusion

Zinc oxide nano particles are synthesized using a modified sol-gel process. Size of the particles is varied by annealing the as such prepared samples. XRD analysis of all the samples reveals the formation of phase pure wurtzite crysatal structure for ZnO. TGA and FTIR studies ensure the absence of impurities in the sample. Cure characteristic studies show that nano ZnO is a better cure activator than the commercial ZnO for the cross linking reaction of natural rubber. Conventional vulcanization of NR uses 5.0 phr of ZnO as a cure activator. Using nano ZnO this can be reduced to about 50 percentage without any compromise in stress-strain properties of NR vulcanisates. One of the other major ingredients, stearic acid can also be reduced to about 50% of conventional recipe. Rate of cure reaction is found to increase with decrease in particle size and maximum value is obtained for 1.5 phr loading of nano ZnO. Use of nano ZnO as a curing agent can bring about revolutionary changes in rubber industry.

Acknowledgment

Authors thank Technicians of SAIF, CUSAT for providing the XRD, TGA and FTIR results. We thank H.O.D, PSRT, CUSAT for providing facility to do the polymer mixing and cure characteristic studies at this centre.

REFERENCES

BindhuPanampilly and Sabu Thomas, 2010. “Nano ZnO as Cure Activator and Reinforcing Filler in Natural rubber”, Polymer Engineering and Science, pp. 1337-1346.

Free Route”, *International Journal of Environmental Science*: Development and Monitoring 4, pp. 45-47.

George Varghese, K.T. Usha and A.S Kumar, 2014. “Characterisation And Band Gap Energy of Wurtzite ZnO:La Nanocrystalites”, *International Journal of Latest Research in Science and technology*, 3, pp. 133-136.

Malevu, T.D and Ocaya, R.O. 2015, “Effect of Annealing Temperature on Structural, morphology and optical PropertiesofZnO-Needles Prepared by Zinc-AirCell System method”, *Int. J. Electrochem. Sci.,* 10, pp.1752-1761.

Nanda Shati and P.S. Gupta, 2010, Applied Physics Research, “Structural and Optical Properties of Sol-Gel ZnO Thin Film”, 2, pp. 19-28.

Ratheesh, R. Thankalekshmi, Samwad Dixit and A.C. Rastogi, 2013, “Doping Sensitive optical Scattering in Zinc oxide nano structured films for Solar Cells”, *Adv. Mat. Lett.,* 4, pp. 9-14 .

Ruby Chauhan, Ashvani Kumar and Ram Pal Chaudhary, 2010 “Synthesis and Characterisation of Silver Doped ZnO nanoparticles”, *Archives of Applied Science Research*, 2, pp. 378-385.

Sanjeev Kumar, Fouran Singh and A Kapoor 2014, “Synthesis and Characterisation of Nano-Crystalline ZnO Quantum Dots via Sol-Gel Route for Dye-Sensitized Solar Cells”, International Journal of Recent trends in Electrical & Electronics Engg., 4, pp. 25-29.

Sridevi, D. and Rajendran, K. V. 2009 “Synthesis and Optical Characteristics of ZnO nanocrystals”, Bull. Mater. Sci., 32, pp.165-168.

Suchismita Sahoo, Madhuchhanda Maiti, Anirban Ganguly, Jinu Jacob and Anil K Bhowmick, 2007, “Effect of Zinc Oxide Nanoparticles as Cure Activator on the Properties of natural Rubber and Nitrile Rubber”, Journal of Applied Polymer Science, 105, pp. 2407-2415.

Virendra Chandore, Gopal Carpenter, Ravindra Sen and Nitish Gupta, 2013, “Synthesis of nano Crystalline ZnO by Microwave Assisted Combustion method:An ecco Friendly and Solvent

Yendrapati Taraka Prabhu, Kalgadda Venkateswara Rao, Vemula Sesha Sai Kumar and BandlaSiaKumari, 2013, “Synthesis of ZnO nanoparticles by a Novel Surfactant Assisted Amine Combustio Method”, Advances in nanoparticles, 2, pp. 45-50.

Zhong Lin Wang, 2004, “Zinc Oxide nanostructures: Growth, properties and Applications*”, J. Phys.:*Condens. Matter 16, pp.829-858.

****