

RESEARCH ARTICLE | APRIL 19 2018

PVA/NaCl/MgO nanocomposites-microstructural analysis by whole pattern fitting method **FREE**

K. S. Prashanth; S. S. Mahesh ✉; M. B. Nanda Prakash; R. Somashekar; B. M. Nagabhushana



AIP Conf. Proc. 1957, 030002 (2018)

<https://doi.org/10.1063/1.5034326>



APL Energy

Latest Articles Online!

Read Now



PVA/NaCl/MgO Nanocomposites-Microstructural Analysis by Whole Pattern Fitting Method

K.S Prashanth¹, S.S Mahesh^{2*}, M.B Nanda Prakash³, R. Somashekar⁴ and B.M Nagabhushana⁵

¹*Department of Physics, New Horizon College of Engineering, Bangalore, Karnataka, India 560103*

²*Department of Physics, Acharya Institute of Technology, Bangalore, Karnataka, India, 560 107*

³*Department of Studies in Physics, University of Mysore, Manasagangotri, Mysore, Karnataka, India, 570006,*

⁴*RIE, Manasagangotri, Mysore, Karnataka, India 570006*

⁵*Department of Chemistry, M S Ramiah Institute of Technology, Bangalore, Karnataka, India, 560064*

**Corresponding Author: email:maheshphysics1976@gmail.com*

Abstract. The nanofillers in the macromolecular matrix have displayed noteworthy changes in the structure and reactivity of the polymer nanocomposites. Novel functional materials usually consist of defects and are largely disordered. The intriguing properties of these materials are often attributed to defects. X-ray line profiles from powder diffraction reveal the quantitative information about size distribution and shape of diffracting domains which governs the contribution from small conventional X-ray diffraction (XRD) techniques to enumerate the microstructural information. In this study the MgO nanoparticles were prepared by solution combustion method and PVA/NaCl/MgO nanocomposite films were synthesized by the solvent cast method. Microstructural parameters viz crystal defects like stacking faults and twin faults, compositional inhomogeneity, crystallite size $\langle N \rangle$ and lattice strain (g in %), were extracted using whole pattern fitting method.

INTRODUCTION

Polymer nanocomposites have emerged as advanced functional materials particularly in biomedical applications, drug delivery, sensors, food packaging and bone tissue substitutes [1-4]. The prudent properties of polymer nanocomposites can be customized by blending metal or metal oxide nanoparticles with the pristine polymer. MgO nanoparticles are of specific interest as they exhibit excellent biocompatibility. MgO nanoparticles are used in various applications like photo catalysis, as bactericidal, for waste remediation and drug delivery [5-7]. In materials science and technology, the structure - property relationship dictates the functional attributes of the materials which also depend upon the synthesis routes for these materials. Exploration of the microstructure is the key aspect of material technology, any change in the internal structure due to synthesis methods, precursors or due to the chemical environment has the discerning consequences on the different properties of the materials. If we can understand these microstructural changes we can tailor the materials properties.

Novel functional materials usually consist of defects and are largely disordered. The intriguing properties of these materials are often attributed to defects [8]. Naturally the characterization of the materials which are considerably

disordered at the atomic levels assumes greater importance. Essentially, X-ray diffraction data of these materials consists abundant information of defects and disorder enclosed in diffuse scattering.

Nonetheless, there are constrained reports on magnesium oxide nanoparticles as fillers in the PVA matrix and their microstructural characterization in the literature. Henceforth the microstructural characterization of the prepared PVA/NaCl/MgO nanocomposites using whole pattern fitting method is vital for understanding the emerging structure and properties of nanocomposites.

In this study the microstructural parameters of PVA/NaCl/MgO nanocomposites viz crystal defects like stacking faults and twin faults, compositional inhomogeneity, crystallite size $\langle N \rangle$, lattice strain (g in %), are extracted from diffraction lines of polymer nanocomposites.

EXPERIMENTAL

Solution combustion method [9] which is a breakthrough method emerged as a competent, economical and swift technique for the synthesis of high purity, homogeneous and crystalline metal oxide nanoparticles was employed for the synthesis of magnesium oxide nanoparticles. The polymer nanocomposites of different weight percentages were prepared by solvent cast method as reported earlier [9]. Bragg reflection profile with the distribution of crystallite size, lattice strain and stacking faults can be expressed as [9],

$$I_{hkl}(s_{hkl}) = \int_{-\infty}^{\infty} T^{IP}(nd) e^{\left[2\pi i \xi(nd)\right]_g} e^{\left[2\pi i \varphi(nd)\right]_g} e^{\left[2\pi i nd S_{hkl}\right]_g} d(nd) \quad (1)$$

where $I_{hkl}(S_{hkl})$ is the intensity of a profile in the direction joining the origin to the center of the reflection, T^{IP} is the Fourier transform of instrument profile, $e^{\left[2\pi i \xi(nd)\right]_g}$ is the average phase factor due to lattice distortion (ξ) and $e^{\left[2\pi i \varphi(nd)\right]_g}$ is due to crystallite size / stacking faults.

The whole powder pattern of samples were simulated using individual Bragg reflections represented by the above equation using

$$I(s) = \sum_{hkl} (\omega_{hkl} I_{hkl} - BG) \quad (2)$$

wherein ω_{hkl} are the relevant weight functions for the (hkl) Bragg reflection and (s) accounts for the whole range ($2\theta \approx 8^\circ$ to 80°) of XRD. BG represents the limiting factor brought in to contrive the background evaluations. The microstructural parameters were computed using PEAKFIT [10] and SIMPLEX [11] multidimensional minimization program until one obtains a meaningful convergence.

RESULTS AND DISCUSSION

Line profile analysis is one of the potent methods for defect characterization in materials. Presently, various software packages and methods are available to acquire stacking faults, twin faults etc., which make use of whole powder pattern modelling [12].

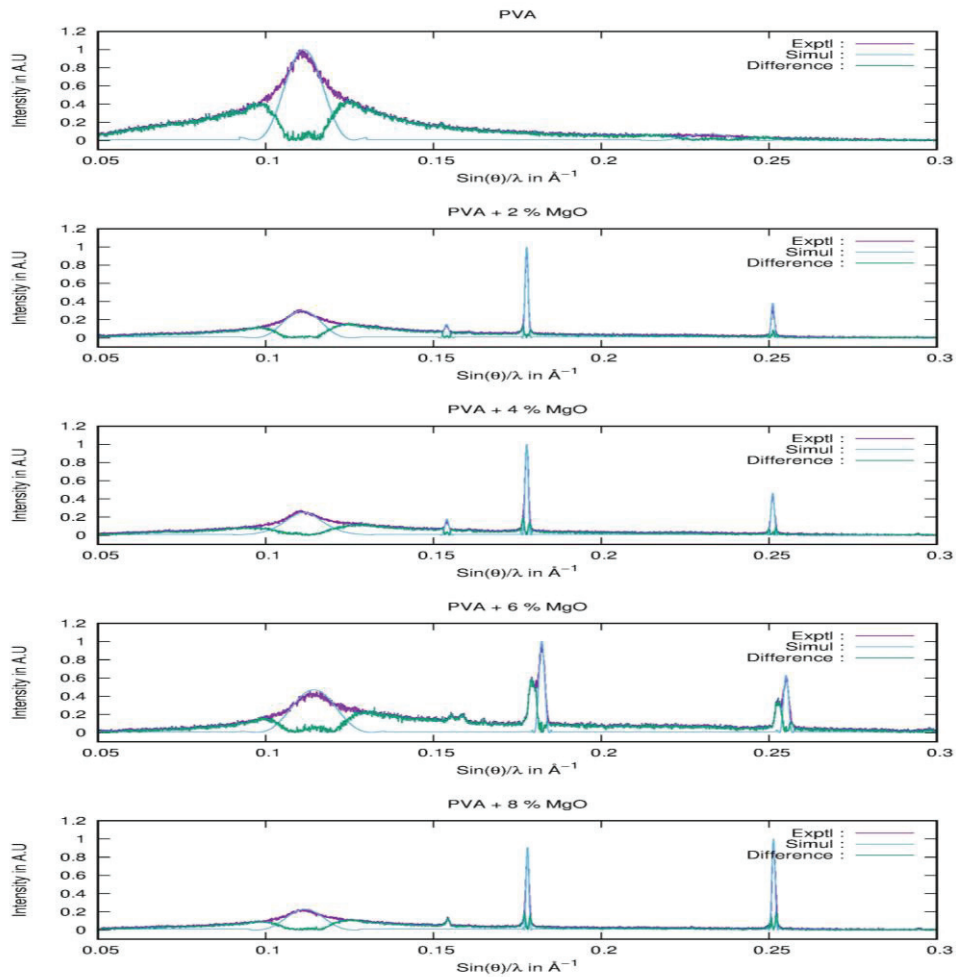


FIGURE1. Experimental and simulated X-ray diffraction pattern of PVA/NaCl/MgO by whole powder pattern fitting technique

Incidentally, most of the methods depend upon multiple-order approach [13]. A multitude of these modelling designs enunciate the significance of line profile analysis [14]. These studies embark on use of single-order method for analysis of microstructure [15]. The whole pattern fitting gives us more reliable microstructural parameters compared to other methods [16]. The experimental and simulated x-ray profiles with different weight percentage composition of PVA/NaCl/MgO nanocomposites using whole powder pattern technique is shown in figure 1. The microstructural parameters evaluated are shown in Table 1 for pristine PVA and PVA/NaCl/MgO nanocomposites using exponential column length distribution. From Table 1 we observe that the average crystallite area increases for 2wt% and decreases upto 6 wt%, but increases for 8 wt% and there is conformity between experimental and simulated X-ray intensity profiles as the standard deviation is about 10% in the current study. From PEAK – FIT program, using Gaussian deconvolution procedure the XRD profiles from samples were extracted. Line profile analysis was carried out for 4 to 6 reflection profiles incorporating instrumental broadening correction. Making use of multidimensional minimization program SIMPLEX intensity of the XRD profiles have been simulated by repetition of the process using above mentioned equations, for significant reflection profiles, until a meaningful convergence is achieved. Apparently it is noticeable from the Table 1 that the innate lattice strain present in the polymer nanocomposites is 0.5%. Owing to the fact that there are an excessive number of layers between two ensuing deformation fault layers, the evaluated microstructural parameters like twin faults, stacking faults and default probabilities didn't change considerably, which

could be attributed to the presence of crystalline domains in the amorphous region of the macromolecular matrix. The noticed disparity in the micro structural parameters as noticed in Table 1 is a result of two-fold refinement [9]. The line profile analysis of the reflection profiles were performed from overlapping domains, on account of being the gold standard to evaluate the micro structural parameters. The extent of overlapping domains dictates the range of broadening of the reflections. The observed trend in the crystallite size values could be attributed to these broadening which in turn depends upon the adjoining reflections.

TABLE 1. Microstructural parameters and stacking faults for pure PVA and PVA/NaCl/MgO nanocomposites using exponential distribution function

Samples	Peaks	2θ (deg)	Crystallite size D_s (Å)	Stacking fault (α^d)	Twin fault (β)	delta (E-03)	Crystallite area (Å ²)
PVA	1	19.7	33.7	3.38E-7	7.21E-5	3.04	1000
	2	41.91	29.7	3.10E-5	8.54E-5		
PVA/MgO 2 wt%	1	19.69	34.6	3.06E-5	6.64E-5	2.44	14144
	2	27.42	260.0	8.27E-6	2.08E-6		
	3	31.78	408.8	2.28E-6	1.67E-6		
	4	45.51	387.8	6.67E-6	7.42E-7		
PVA/MgO 4 wt%	1	19.77	27.7	1.70E-6	2.70E-4	2.45	11323
	2	27.44	313.9	4.83E-6	5.00E-6		
	3	31.78	408.8	3.75E-6	7.47E-6		
	4	45.50	379.0	4.78E-6	6.37E-6		
PVA/MgO 6 wt%	1	20.31	28.7	3.53E-5	1.25E-5	1.86	11020
	2	32.60	219.2	7.00E-6	3.32E-5		
	3	46.27	254.8	8.66E-6	1.73E-5		
	4	57.26	384.0	5.60E-9	4.05E-8		
PVA/MgO 8 wt%	1	19.83	33.9	3.69E-5	4.97E-5	0.77	15661
	2	31.83	462.0	2.97E-8	6.51E-8		
	3	45.55	389.0	9.16E-7	3.88E-6		

CONCLUSIONS

- The MgO nano-particles of average size 12-14 nm was synthesized by solution combustion method.
- The PVA/NaCl/MgO nanocomposites of 2 wt%, 4 wt%, 6 wt% and 8 wt% were prepared by solvent cast method
- The estimated values of microstructural parameters for pristine PVA and PVA/NaCl/MgO nanocomposites using equations mentioned above indicated decreased values relative to neat PVA.
- The noticed disparity in the micro structural parameters is due to a two-fold refinement.
- We observed that average crystallite area varies with the nanoparticle concentration in polymer nanocomposites.

ACKNOWLEDGMENTS

The authors thank department of Chemistry, MSRIT, Bangalore and Department of Physics, University of Mysore, for providing the laboratory facilities

REFERENCES

1. S.A.Mirsalehi,A. Khavandi, S. Mirdamadi, M.R. Naimi-Jamal and S.M. Kalantari, *J. Appl. Polym. Sci* **132**, 42052 (2015).
2. H.D.Vallerie,D.N. Thanh,N. Mangesh,A.D. Nandika and D.G.Teresa, *Mat. Chem. and Phy* **132**,409–415 (2012).
3. A.Alfadhel, B. Li and J.Kosel, *SENSORS*, **2014 IEEE** , 2066-2069 (2014).
4. M.Y.Ahmed, *Poly.Plast. Tech. and Eng* **52**, 635-660 (2013).
5. K.Mageshwari and R.Sathyamoorthy, *Trans. Indian. Inst. Met* **65**, 49–55 (2012).
6. A.H.Faten, A. Fowzia,A.A. Al-Ghamdi, A.Al-Ghamidi. Attieh, M.M. Aly, M.A.T. Reem and E.T. Farid, *Superlattices. Microstruct* **52**, 200-209 (2012).
7. T.Somanathan,V.M Krishna,V.Saravanan, Rajukumar ,Ranadhir kumar, *J.Nanosci. Nanotech* **16**, 9421-943(2016)
8. S. J. L. Billinge, *Curr. Opinion. Solid. State. Mater. Sci* **1**, 477 -484 (1996)
9. K.S.Prashanth,S.S.Mahesh,S.S,M.B.Prakash,N.S.Ningaraju,H.B.Ravikumar,R.Somashekar and B.M. Nagabhushana, *Braz. J. Phys*, **46**, 262-272 (2016).
10. R. Chen, K. A. Jakes and D. W. Foreman, *J Appl. Polym. Sci*, **93**, 2019-2024 (2004)
11. A. R. Stokes, *Proc. Phys. Soc* **61**, 382 (1948)
12. D. Balzar, N. Audebrand, M. R. Daymond, A. Fitch, A. Hewat, J. I. Langford, A. Le Bail, D. Louër, O. Masson, C. N. McCowan, N. C. Popa, P. W. Stephens and B. H. Toby, *J. Appl Crystallogr*, **37**, 911-924 (2004).
13. B. E. Warren and B. L. Averbach, *J. Appl. Phys*, **21**, 595 (1950).
14. I. H. Hall and R. Somashekar, *J. Appl. Crystallogr*, **24**,1051-1059 (1991).
15. R. Somashekar, I. H. Hall and P. D. Carr, *J. Appl. Crystallogr*, **22**,363-371 (1989).
16. A. Leonardi and P. Scardi, *Met. Mater. Trans. A*, **47**,5722–5732 (2016).