

Prediction of Resulting Properties from Adding Nanoparticles to Polymers by the Aid of MATLAB Software

Nika Nasiri^{1*}, Amir Mosayebi²

¹Chemistry Engineering Group, Technical and Engineering Faculty, Islamic Azad University, Tehran North Branch, Tehran, Iran, ²Assistant Professor in Chemistry Engineering Group, Tafresh University, Tafresh, Iran.

* Corresponding Author

Abstract: The empirical findings of this study show that glass transition (Tg) temperature is increased by adding $MgO-Al_2O_3$ mesopore particles to polymer's matrix and module of adjusted system is decreased. The impact strength and tensile strength of hybrid materials are increased up to 53.5% and 14% respectively as $MgO-Al_2O_3$ content includes weight percentage. The structural morphology of impact fracture surface and hybrid surface was observed by Scanning Electron Microscopy and Atomic Force Microscopy (AFM) respectively. Similarly, experimental databases were presented for better assessment of the given system. The neural networks were utilized for modeling behavior of conversion system. The results indicated that the model with correlation coefficient (R^2 =0.97) could anticipate thermal efficiency of the conversion system.

Keywords: Propylene Nanoparticles, Nano-Fluid, Morphology, Thermal Properties, SEM Morphology

INTRODUCTION

The sol-gel technique, including hydrolysis reactions and density of alkoxide precursor materials, is a reliable method for synthesis of micro-fine metallic oxides (Li et al., 2004). Several researchers have employed sol-gel technique in various forms. Li et al. (2002) added tetra n-butyl titanate to deionized water and prepared a gel by adding hydrochloric acid or ammonia from which TiO_2 nano powder was extracted after dehydration, grinding and calcination at different temperatures. Zhang et al. (2002) utilized sol-gel micro emulsion method. They synthetized TiO_2 nanoparticles by hydrolysis of tetra titanium isopropyl-oxide in micro emulsion content (80 Tween-Span) and calcinated them under different temperatures. Given these findings, it was observed that the particles were spherical with relatively suitable particle size distribution. In some cases, a surfactant is used in sol-gel process.

By adding Lauryl Amine Hydrochloride (LAHC) as a surfactant to precursor solution and stirring up and drying the given solution, Pavasupree et al. (2005) synthetized TiO_2 mesopore. The resulting powders were calcinated at temperature 400°C for 4h. Using a similar method, Colon et al. (2002) increased specific level of particles from $13m^2/g$ to $110m^2/g$ by addition of activated carbon to the solution. XRD results only showed presence of anatase phase in powders. In 2014, Al2O3 nanoparticles were synthetized using sol-gel technique by Oliveira et al. They employed propylene matrix in their studies. Their findings indicated that producing inorganic nanoparticles did not need to a solvent in a polymeric solution through reaction in molten metal.

Nanocomposite synthesis

The mesopore MgO-Al₂O₃ materials were prepared by a sol-gel process using polyethylene glycol as a pore constituent agent. The mineral sol-gel was prepared by stirring up a mixture including calculated quantity of Al (NO₃)₃, Mg (NO₂), ethanol, water and HCl at room temperature for 3h. In a normal synthesis, 10g of polyethylene glycol and 0.1mol of Mg (NO₂) in ethanol (ethanol's molar ratio: Mg (NO₂) =0.5) were utilized as partial hydrolytic catalyst by a magnetic mixer with the presence of aqueous HCl. We used water content to the extent that the molar ratio of (MAl₂O₃+MMgO): HCl: H₂O to amount to 0.01: 1: 0.5. This solution was stirred up at room temperature for about 20min. As the color of solution became bright, formerly-calculated amount of Al (NO₃)₃ was added in drops and the solution was stirred at room temperature for 2h. The mixture was transferred to a 200cc-beaker and covered by parafilm for a few days to evaporate small molecules. The resulting aerogels were dried under temperature 60°C for 24h. Finally, the organic substance was omitted during calculation process at temperature 600°C for 4h (heating rate: 10degrees/min).

The Al_2O_3+MgO particles were dispersed using ultrasonic cleaner into propylene solution at certain weight percentage. Then, three weight parts of DDS baking agent were slowly mixed with 10 parts of PP into this system. The given mixtures were degasified in vacuum at temperature 130°C for about 20min. Afterwards, the given mixture was transferred into preheat die coated with silicon resin. All specimens were baked at temperature 130°C, 170°C and 190°C for 2h.

Analysis on properties of nanocomposites

Using FTIR spectrometry is the simplest technique for determination of formation of Al-O-Mg bonds. FTIR spectra for pure PP, Al_2O_3+MgO and PP/ Al_2O_3+MgO hybrid materials are shown in Fig 1. Fig 1 (a) shows that the characteristic peak points of symmetric tensile al C-C band of PP appear in 3507cm-l and absorption rate of 915cm-l. IR absorption spectra were utilized at low wavelength for finding characteristics of Al_2O_3+MgO mixed oxides after entering Al_2O_3+MgO non-organic part. With respect to the data (Figure 1 (a) and (b)), vibrational bands are observed as strong and wide absorption bands within range (400-850cm-l) belongs to Al-O-Al and (920-110cm-l) relating to characteristic of Mg-O-Mg and Ti-O-Ti matrices and the band locating in range (952cm-l) was created due to vibrations of magnesium caused by presence of alumina and as a sign of formation of these bands. The characteristic band for Mg-OH and Al-OH is a band close to range (3400cm-l) in hybrid materials.



Figure 1: FTIR results: (a): Pure propylene; (b) Al₂O₃+MgO; and (c) Nanocomposite

XRD patterns are given for Al_2O_3+MgO mesopore and Al_2O_3+MgO/PP hybrid material in Fig 2. XRD analysis was conducted on mixed oxides of Al_2O_3+MgO mesopore at temperature of 600°C and the Al_2O_3+MgO sample (25/75 weight/ weight). XRD pattern indicates a very wide protuberating peak in Fig 2 (a) where contact angle (2 θ) is placed within 15-35 degrees that is due to amorphous phase of Al_2O_3+MgO and it does not appear in crystalline form. This fact may be probably justified according to extensive relationship for Al_2O_3+MgO ; namely, alumina fields are extremely small so they could not be crystallized. The dispersion pattern for Al_2O_3+MgO/PP hybrid material (Fig 2 (b)) only shows a wide amorphous peak (2θ = 10-30 degrees) driven from amorphous homogeneous Al_2O_3+MgO matrix. This finding denotes full and homogeneous Al_2O_3+MgO mixture and matrix and mineral phase cause by interaction of balanced hydrogenous bond in hybrid systems is led to disappearance of crystalline form in Al_2O_3+MgO/PP . This also indicates that Al_2O_3+MgO material does not create adequately great clusters for XRD during PP baking process. Thus, entering Al_2O_3+MgO may disrupt PP molecular order.



Figure 2: XRD results: (a) Pure propylene; (b) Nanocomposite

SEM technique was employed for describing dispersion of particles and fracture in surfaces of pure PP and hybrid materials using various amounts of porous Al₂O₃+MgO. The growing fracture areas are shown in Fig 3. It is visible in image of (Fig 3 (a)) that fracture surface has been completely different for control system from adjusted systems in which this surface is very fine with uniform fracture direction and properties of fragile fracture and this has led to weak impact resistance in this system. The hard fracture has occurred in the adjusted systems in Fig 3-4 (b-d). Likewise, the fracture cross section in all hybrid materials indicates favorable dispersion of Al₂O₃+MgO particles. The facture surface includes some branches in Fig 3 (b) and it seems to be coarser than in pure propylene system. Consequently, the given impact strength is noticeably improved. The fracture surface in Fig 3 (c &d) denotes large and deep pores and this is generally assumed as properties of adjusted rubber PPs. These pores show the initial position of plastic particles that have been extruded and or broken during fracture process. These pores have been stably and tightly connected to PP matrix and this is led to good adhesion and strong connection between Al₂O₃+MgO particles and phase of PP matrix. Resistance is increased to fracture because of great dissipated deformation energy takes place adjacent to tip of fracture. Such findings may justify rising coarseness of polypropylene. The result shows that appearance of branches and cavities on fracture surface has played important role in improving resistance to impact. The coarse fracture surface has been created in hybrid materials due to separation of smaller phase and special interaction between Al₂O₃+MgO particles and polymer that may restrict mobility of polymeric chain and productivity of rearrangement.



Figure 3: SEM results: (a) Pure propylene; (b) Al₂O₃+MgO nanocomposite 1%; (c) Al₂O₃+MgO nanocomposite 3%; and (d) Al₂O₃+MgO nanocomposite 5%

Whereas mechanical properties in composite extremely depend on dispersion level of Al_2O_3+MgO porous powder in polymeric matrix therefore TEM technique was adapted for analysis on dispersion of Al_2O_3+MgO powder in PP matrix. Fig 4·4 displays TEM micro graph of Al_2O_3+MgO porous powder and the given hybrid materials. The micro graph indicates irregular spherical particles for Al_2O_3+MgO powder (Fig 4 (a)) with loose and discrete structure. Distribution of size particles was seen in Al_2O_3+MgO mesopore with average size of 42nm in a wide spectrum. It can be seen similar to hybrid materials (Fig 7 (b)) that Al_2O_3+MgO may keep the main spherical morphology. It was also observed that it had been homogeneously dispersed in PP matrix. The derived results from TEM indicated that the average particle size was approximately 80nm for 1 weight percentage mode in Al_2O_3+MgO particles and it was seen nanoparticles were not agglomerated. Nonetheless, the quantities of Al_2O_3+MgO particles were increased 3% and 5% of weight percentage respectively. Agglomeration has occurred only at small level. The individual great nanoparticles and small agglomeration were seen in polymeric matrix which has been shown in Fig 4 (c & d). The particle size was calculated by TEM images and it was about 100-200nm.



Figure 4: TEM results: (a) Pure propylene; (b) Al₂O₃+MgO nanocomposite 1%; (c) Al₂O₃+MgO nanocomposite 3%; and (d) Al₂O₃+MgO nanocomposite 5%

Discussion and Analysis

In Fig5 indicates DSC diagrams for PP along with various quantities of Al₂O₃+MgO hybrid materials. All three samples include glass transition temperature (Tg) of 156°C for pure polymer. In addition, Tg rate is increased by rise of Al₂O₃+MgO quantities. This is due to this fact that PP matrix may penetrate through Al₂O₃+MgO mesopore particles and is converted into Al₂O₃+MgO lattice. The Al₂O₃+MgO stringer matrix may result with higher amounts of Al₂O₃+MgO in the matrix which is composed of the link between inert PP chains with Sio₂-TiO₂ nanoparticles. Similarly, glass transition behavior was also confirmed by DMA.

Fig 6 shows TGA thermo-grams resulting from thermal synthesis of pure PP and hybrid materials of Al_2O_3+MgO polymer. It is obvious that the initial temperature of thermal analysis is higher in Al_2O_3+MgO polymer than in pure PP i.e. 379°C while it is 394°C in Al_2O_3+MgO/PP . When Al_2O_3+MgO content includes 5% weight percentage these findings may be related to strong interaction between polymeric chains and mineral particles and this is subsequently led to prevention from thermal synthesis of PP. At temperature 700°C, the efficiency rate is 7.81% weight percentage in pure PP char and it is 19.8% weight percentage for Al_2O_3+MgO at 5% level. The empirical residues have greater amounts than theoretical quantities because some of PP chains are entrapped in Al_2O_3+MgO particles and this may confirm the strong mutual effect between two phases.



Figure 5: DSC results: (a) Pure propylene; (b) Al₂O₃+MgO nanocomposite 1%; (c) Al₂O₃+MgO nanocomposite 3%; and (d) Al₂O₃+MgO nanocomposite 5%



Figure 6: TGA results: (a) Pure propylene; (b) Al₂O₃+MgO nanocomposite 1%; (c) Al₂O₃+MgO nanocomposite 3%; and (d) Al₂O₃+MgO nanocomposite 5%

The mechanical properties of hybrid materials are given in Table 1. Compared to pure PP, impact strength and tensile al strength are increased in hybrid materials up to 53.5% and 14% following to rise of loading Al₂O₃+MgO particles up to 3% weight percentage but as loading of Al₂O₃+MgO was further increased, both impact strength and tensile al strength were reduced. Strength and toughness of hybrid materials depend on density of traversal joints within suitable limit of traversal density and cross links may lead to strength and toughness effects. A probable justification for these results may be due to some special reactions among PP and Al₂O₃+MgO particles (it is more unlikely due to interaction between oxidant groups belonging to PP and surficial hydroxyl groups of Al₂O₃+MgO particles). As the material is treated by an impact test, some micro-phase separations have taken place to import Al₂O₃+MgO particles in the Al₂O₃+MgO particles and to be remarkably increased by entering Al₂O₃+MgO particles and to lead to toughness of nanocomposite. Nevertheless, more than 3% of weight of Al₂O₃+MgO content was reduced in impact strength due to agglomeration of Al₂O₃+MgO particles in propylene matrix.

Al ₂ O ₃ +MgO percentage in specimen	Tensile strength	Bending strength	Impact strength
	MPa	MPa	Kj/m ²
0	55.9	35.8	11.6
1	58.1	37.1	14.9
2	61.2	39.2	16.8
3	63.7	41.5	17.8
4	58.2	38.8	16.3
5	56.3	37.6	14.9

 Table 1: Results of mechanical tests

Thermal dependency of dynamic properties for Al_2O_3+MgO/PP hybrid materials including various quantities of alumina and magnesium matrices is shown in Fig 7. Following to addition of Al_2O_3+MgO to PP, in glass area and deformation zone, small increasing rate was shown in module for storage of hybrid materials. This behavior is probably due to this fact that some special interactions (more unlikely because of interaction between factor groups of PP and surficial hydroxyl groups in SiO₂-TiO₂) have been formed among polymer and Al_2O_3+MgO and matrix- building density of composite (compared to pure propylene) has been improved by adding Al_2O_3+MgO particles. The results indicate that the mobility of polymeric chain has been constrained due to interaction between dispersed particles of Al_2O_3+MgO and polymeric matrix and also rate of matrix-building has been increased by rising quantities of Al_2O_3+MgO particles.



Figure 7: DMA results: (a) Pure propylene; (b) Al₂O₃+MgO nanocomposite 1%; (c) Al₂O₃+MgO nanocomposite 3%; and (d) Al₂O₃+MgO nanocomposite 5%

Fig 8 displays dynamic-mechanical spectrum for tan δ in propylene and Al₂O₃+MgO/PP hybrid materials. Compared to pure PP, it seems tan δ peak quantities for the adjusted systems to be reduced slightly by rise of Al₂O₃+MgO amount. The tan δ peak temperature for hybrid materials is noticeably higher than in pure system. Adding Al₂O₃+MgO to matrix made difficult the motion for polymeric chain. Hence, tan δ peak quantities were reduced and glass transition (Tg) temperature was transferred to higher temperature. This operation may be attributed to loss of mobility in polymeric parts of PP which is due to some specific interactions (interaction between Al₂O₃+MgO particles). The surface-to-surface distance should be relatively small between particles and motion may be restricted in chain related parts.



Figure 8: DMA tanδ results: a) Pure propylene; (b) Al₂O₃+MgO nanocomposite 1%; (c) Al₂O₃+MgO nanocomposite 5%

The three-layer feed forward neural network and Levenberg- Marquardt Back Propagation (BP-LM) training algorithm were utilized for modeling of conversion system. Parameters of temperature and concentration of nanoparticles were selected as input data and number of properties as target parameter. The target parameter is one for which we tend to predict it for the system.



Figure 9: Topology of neural network model

Diagram in Fig 10 indicates the predicted quantities for efficiency of conversion system versus the acquired amount from the results *in vitro*. As it characterized, data in diagrams follow Y=X line in which the signal of network could predict absorption efficiency at high precision level. In other words, the gradient of line fine should be at 45 degrees angle when the predicted quantities are the same as correspondent experimental amounts. The lesser dispersion in quantities around Y=X line is led to better performance in the system.



Figure 10: Results of neural network model

Conclusion

The hybrid materials were prepared for MgO/Al₂O₃- propylene in three types by interaction of covalent bonds between polymeric and mineral phases in this study using MgO/Al₂O₃ mesopore particles. These particles were prepared by means of sol-gel process from magnesium nitrate hexahydrate and aluminum nitrate as precursors. The hybrid particles derived from azotic physical absorption, X-Ray Diffraction (XRD) and Fourier Transform Infra-Red (FTIR) spectrometry etc. were characterized. The empirical results indicate that glass transition (Tg) temperature is increased and module of adjusted system is reduced by adding MgO/Al₂O₃ mesopore particles. As MgO/Al₂O₃ content is considered by weight percentage, impact strength and tensile strength are increased in hybrid materials up to 53.5% and 14% respectively. The structural morphology was observed for impact fracture surface and hybrid surface respectively by Scanning Electron Microscopy (SEM). Similarly, we could predict experimental data correlation coefficient (R²=0.995) using neural networks

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