

**Saeed ISMAELIMOGHADAM, Masih MASOUDIFAR, Babak NOSRATI,
Mohammad SHAMSIAN**

EFFECTS OF INORGANIC NANOPARTICLES ON MECHANICAL AND MORPHOLOGICAL PROPERTIES OF WOOD FLOUR-POLYPROPYLENE NANO COMPOSITES

This research was conducted to examine the effect of SiO₂ and TiO₂ nanoparticles on the mechanical and morphological properties of wood flour-polypropylene nanocomposites. For this purpose, 60 (wt.%) wood flour was mixed with polypropylene. 4% maleic anhydride polypropylene was also used in all the compounds as a coupling agent. In addition, SiO₂ and TiO₂ nanoparticles were used as mineral fillers at 0, 1, 3 and 5%. The mixing process was performed inside an extruder and the test specimens were prepared by injection molding method. Bending and tensile tests were then performed on the specimens according to the ASTM standard. Scanning electron microscopy (SEM) was also used to show the distribution of nanoparticles over the composite substrate. The results showed that the composites containing nano-SiO₂ had more favorable mechanical properties compared to those containing nano-TiO₂. On the other hand, increasing the nanoparticles from 0 to 3% led to an increase in mechanical strength, however, the addition of more nano-fillers resulted in a significant decrease in mechanical strength. The results of SEM also showed a proper dispersion of nanoparticles at 1 and 3% levels, but using 5% nanoparticles caused the particles to aggregate on the composite substrate.

Keywords: wood plastic composite, inorganic nanoparticles, reinforcing additives, particle dispersion

Introduction

Wood plastic composites, a new class of composites classified as green composites, have been drawing the attention of researchers and industries in

Saeed ISMAELIMOGHADAM (saeed.am17358@gmail.com), Islamic Azad University, Chalous, Iran; Masih MASOUDIFAR (masih_masoudifar@yahoo.com), Wood Composite Products, University of Zabol, Zabol, Iran; Babak NOSRATI ✉ (nosrati.babak@uoz.ac.ir), Mohammad SHAMSIAN (mohammadshamsian@uoz.ac.ir), Wood & Paper Science and Industry, University of Zabol, Zabol, Iran

recent years. In the technology by which this class of composites is prepared, there is no material that can improve all properties of the composites. For this reason, nano-scale particles (1-50 nm) are commonly used. Polymer nanocomposites are a class of materials in which inorganic nanoparticles with planar or spherical structures are dispersed in the polymer matrix. This class of composites (nanocomposites) has more acceptable properties compared to pure composites and polymers. Although small amounts of nanoparticles are used to produce polymer nanocomposites, this small amount significantly increases their thermal and mechanical properties [Soon et al. 2012; Njuguna et al. 2008].

Nowadays, polymers reinforced with inorganic nanoparticles are very important: adding these inorganic nanoparticles to the compounds of composites brings many advantages, such as a light weight, enhanced mechanical properties, improved physical properties and easy formability. However, disadvantages include the aggregation of particles in the polymer matrix and a decrease in the impact strength of the composites [Yang et al. 2006; Krueger et al. 2004].

In recent years, some research has been carried out on the effect of mineral nanoparticles on polymer composites. Deka and Maji [2012] studied the effect of silica and clay nanoparticles on the properties of wood-plastic composites. Their results showed that an increase in nanoparticles of 3% resulted in an increase in flexural and tensile strength, as well as flexural and tensile moduli. However, an increase of the nanoparticles to 5% led to a decrease in all the above-mentioned properties. SEM results also showed that adding a large quantity of nanoparticles causes them to accumulate in the polymer matrix and the mechanical strength decreases. Kord and Taghizadeh Haratbar [2014] studied the effect of nanoparticles on wood-plastic composites. Their results showed that by increasing nanoclay to 3%, flexural strength and modulus increased, but with an addition of 6% nanoclay, the mechanical properties decreased. Ismaeilimoghadam et al. [2015] studied the effect of silica nanoparticles on wood-plastic composites. Their results showed that by increasing nanosilica to 3%, the mechanical properties increased, including the flexural and tensile strength and moduli. However, with the addition of 5% nanoclay, the mechanical strength decreased. SEM results also showed that an increase in silica SiO_2 nanoparticles to 5% resulted in aggregation in the polymer matrix. Altan and Yildirim [2010] examined the mechanical and morphological properties of the composite of high density polypropylene and polyethylene strengthened by titanium nanoparticles. Their results showed that increasing the nanoparticles to 5% caused an increase in the flexural strength and modulus of elasticity. The morphological results showed that adding large amounts of nanotitanium causes them to accumulate in the polymer matrix.

Many studies have been conducted concerning the use of SiO_2 , ZnO and CaCO_3 inorganic nanoparticles. Among them, SiO_2 nanoparticles are widely used in polymer industries due to their very small size and large surface area. Researchers believe that SiO_2 particles can improve the strength, hardness,

modulus, crystallinity, viscosity, creep resistance and inter- structural adhesion of polyethylene, polypropylene and thermoplastic elastomers [Zhang et al. 2003a, b; Rong et al. 2004; Guyard et al. 2006; Khatibzadeh et al. 2010; Parvinezadeh et al. 2010]. In some studies, researchers concluded that SiO₂ nanoparticles do not act as the transition core material and barely affect the crystallinity [Bikiaris et al. 2006; Tian et al. 2006; Chae and Kim 2007; Zhang et al. 2008]. But in some other research, a significant improvement of mechanical properties of SiO₂ nanoparticles were noted, in addition to their transition core functionality [Liu et al. 2012]. On the other hand, TiO₂ nanoparticles, used as polymer reinforcers, are inorganic materials with high mechanical strength [Garakani et al. 2007; Ishak Mohd et al. 2008]. In this study, inorganic transition core nanoparticles were compared, and the independent and interaction effects of the factors on the mechanical properties of the composites were studied. Since no research has as yet been devoted to a comparison of the mechanisms of transition core nanomaterials and their effects on nanocomposite properties, it is necessary to study the subject matter in question.

Materials and methods

In this study, grade Pi 800 polypropylene with a melt flow index (MFI) of 8 g/10 min, produced by Arak Petrochemical Company, was used as a polymer matrix, and a 60-mesh wood flour mixed with hardwoods from the northern Iran was used as the reinforcer. Polypropylene grafted maleic anhydride (PP-g-MA) with a melt flow index of 10g/10 min, produced by Krangin Co., was also used, as well as 0.2% maleic anhydride, which was used as a coupling agent. SiO₂ and TiO₂ nanoparticles, produced by US Research Nanomaterials Inc, were used as fillers and their characteristics are presented in table 1 below.

Table 1. Characteristics of SiO₂ and TiO₂ nanoparticles

Type of nanoparticle	Purity (%)	Density (g/cm ³)	Density (g/cm ³)	Specific surface (m ² /g)	Particle size (nm)	Colour
TiO ₂	99	3.9	0.24	200-240	10-25	White
SiO ₂	99	2.4	0.1	180-600	11-14	White

The mixing process was performed using an extruder with two counter current screws at Iran Polymer and Petrochemical Institute according to table 2. The hot formable material obtained from the mixing process was collected after leaving the extruder, and a Wieser WG-LS 200/200 semi-industrial crushing machine(Wieser, Germany) was used on the cooled material to prepare granules. In order to remove the moisture, the granules were transferred to a dryer at 85°C

for 24 hours, and the specimens for the mechanical tests were prepared by injection molding. For this purpose, a semi-industrial injection machine produced by Tehran Imen Machine Company and available at Iran Polymer and Petrochemical Institute was used. 7 treatments were selected, 5 replications of each treatment were considered and, overall, 35 samples were made ($7 \times 5 = 35$). Finally, before performing any test, the specimens were left at room temperature (23°C) with a relative humidity of 50% for 40 hours according to the ASTM standard and D618-99 code.

Table 2. Scheme of the studied mixing treatments

Treatment codes	Wood flour (%)	Polypropylene (%)	Coupling agent (PhC)*	Nano-TiO ₂ (PhC)	Nano-SiO ₂ (PhC)
CS	60	40	4	–	–
S-1	60	40	4	–	1
S-3	60	40	4	–	3
S-5	60	40	4	–	5
T-1	60	40	4	1	–
T-3	60	40	4	3	–
T-5	60	40	4	5	–

*Per hundred compounds

A bending test was performed on the specimens with a 2 mm/min loading speed, according to the ASTM standard and D790 code, while a tensile test was performed on the specimens with a 5 mm/min loading speed, according to the ASTM standard and D 638 code. For this purpose, a HOUNS H 25 KS machine with N 25000 cell capacity was used in the Wood Mechanics Laboratory of the Department of Natural Resources, Zabol University (Iran). After testing each treatment, the computer connected to the machine provided information including the maximum resistance, changes in the specimen's length, proportional limit strength and modulus of elasticity.

Microscopic images were provided to examine the distribution and transmittance of SiO₂ and TiO₂ nanoparticles in the polymer matrix by scanning electron microscopy (SEM, device EM 3200). In this way, cross sections of the fracture point of the bending test specimens were provided. The samples were covered by a thin layer of gold to prevent static charges.

The results were analyzed using SPSS Software and ANOVA. In the case of a significant difference between the levels, Duncan's multiple range test was used at a 95% confidence level to compare the means. Excel software was also used to draw the diagrams.

Results and discussion

The results of the variance analysis showed that there were significant differences between the treatments in terms of bending and tensile strengths at

a 95% confidence level. Figure 1 shows the mutual effect of SiO₂ and TiO₂ nanoparticles on the bending strength of the prepared nanocomposites. As seen in this figure, the highest bending strength was 63.55 MPa for 3 PhC nano-SiO₂, while the lowest was 49.62 MPa for 5 PhC nano-TiO₂. It is worth noting that the composites containing SiO₂ nanoparticles had a higher bending strength than those containing TiO₂ nanoparticles, and increasing these nanoparticles up to 3 PhC resulted in an increase in the bending strength, but beyond this level, it decreased significantly. Figure 2 shows the mutual effect of SiO₂ and TiO₂ nanoparticles on the tensile strength of the prepared composites. According to the figure, the highest tensile strength of the prepared nanocomposites was for 3 PhC SiO₂ and TiO₂ nanoparticles and the lowest tensile strength was for those without nanoparticles (the control).

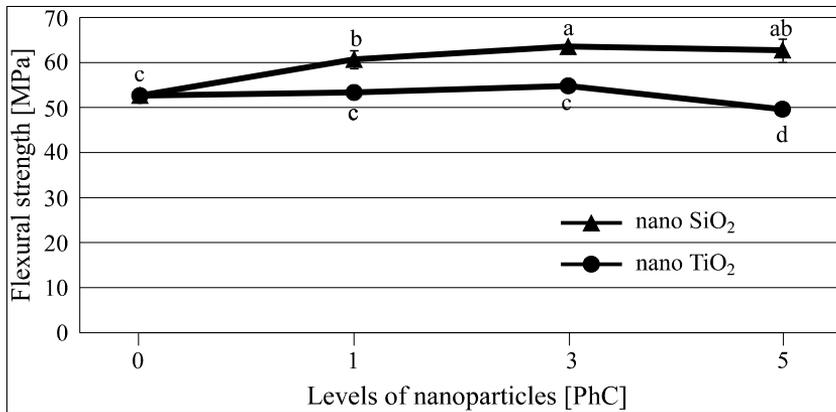


Fig. 1. Mutual effect of SiO₂ and TiO₂ nanoparticles on bending strength

There are, therefore, two mechanisms to increase the bending and tensile strength of nanoparticles up to 3 PhC: the first mechanism is related to the fact that SiO₂ and TiO₂ nanoparticles increase the tension between the fibres and matrix by tolerating stress [Deka and Maji 2012; Ramos et al. 2005] and the second mechanism also suggests that SiO₂ and TiO₂ nanoparticles act as a transition core in crystal growth; hence, the introduction of these nanoparticles increases the number of crystals [Tian et al. 2006; Chae and Kim 2007]. On the other hand, these nanoparticles tend to accumulate and absorb each other due to their high surface energy. Through their chemical groups, these nanoparticles can accumulate on the surface of a polymer by creating hydrogen bonds [Albala et al. 2004; Oburoğlu et al. 2012]. Therefore, the decrease in bending strength by using 5 PhC nanoparticles is due to the accumulation of nanoparticles and their non-uniform distribution, as well as the resulting agglomeration of particles in the composite substrate [Yang and Gu 2007]. Another issue concerns the decrease in polymer moisturizing ability due to the use of a large quantity of

nanoparticles leading to the improper bonding between the lignocellulosic fibres and the matrix. These factors reduce the bending and tensile strength of the nanocomposites made using high doses of SiO_2 and TiO_2 nanoparticles [Deka and Maji 2012]. When the composite materials are finer and their specific surface increases, their static resistance increases significantly. Thus, it seems that the higher bending strength of SiO_2 nanocomposites compared to that of TiO_2 nanocomposites is due to the smaller size of the SiO_2 nanoparticles and their higher specific surface.

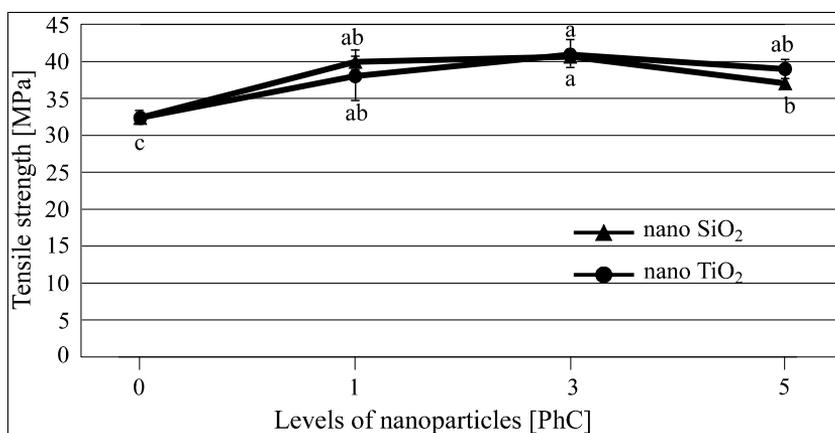


Fig. 2. Mutual effect of SiO_2 and TiO_2 nanoparticles on tensile strength

The results of the variance analysis show that, at a 95% confidence level of there were significant differences between the treatments in terms of bending and tensile moduli. Figure 3 shows the mutual effect of SiO_2 and TiO_2 nanoparticles on the flexural modulus. According to the figure, the highest flexural modulus (6980.7 MPa) was with the use of 3 PhC Nano- SiO_2 , and the lowest (3855.9 MPa) was for the control specimens. Figure 4 shows the mutual effect of SiO_2 and TiO_2 nanoparticles on the tensile modulus. It can be seen that the highest tensile modulus (5787.7 MPa) was with the use of 3 PhC nano- SiO_2 and the lowest (3116.6 MPa) was for the control specimens. Note that the nano- SiO_2 composites had higher flexural and tensile moduli compared to the nano- TiO_2 composites. On the other hand, an increase in the nanoparticles from 0 to 3 PhC resulted in an increase in the moduli, while an increase to 5 PhC led to a decrease in the moduli.

The increase in moduli in polymer nanocomposites largely depends on the dispersion of nanoparticles in the matrix substrate. Hence, the increase in the flexural and tensile moduli when using 3 PhC SiO_2 and TiO_2 nanoparticles may be related to the proper distribution of the particles in the polymer substrate, the decreased mobility of the polymer chains and the subsequent decrease in the

relative elongation of the specimens through loading. On the other hand, the decreased flexural modulus due to the use of larger quantities of these nanoparticles is related to their agglomeration and aggregation in the composite substrate [Chen et al. 2003; Deka and Maji 2012].

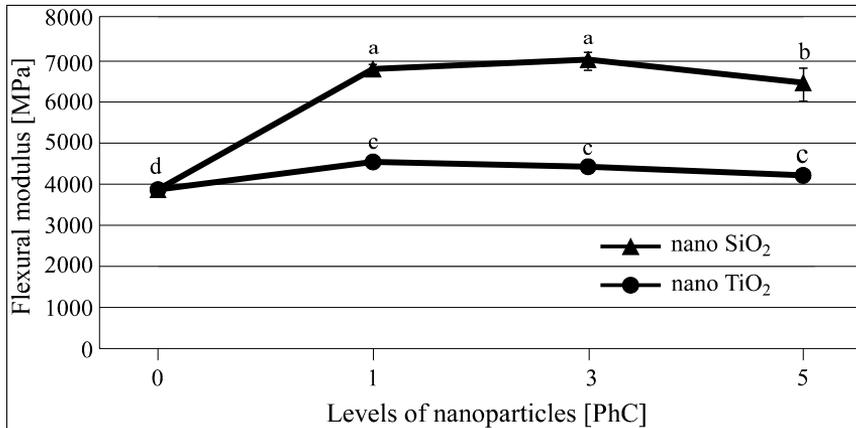


Fig. 3. Mutual effect of SiO₂ and TiO₂ nanoparticles on flexural modulus

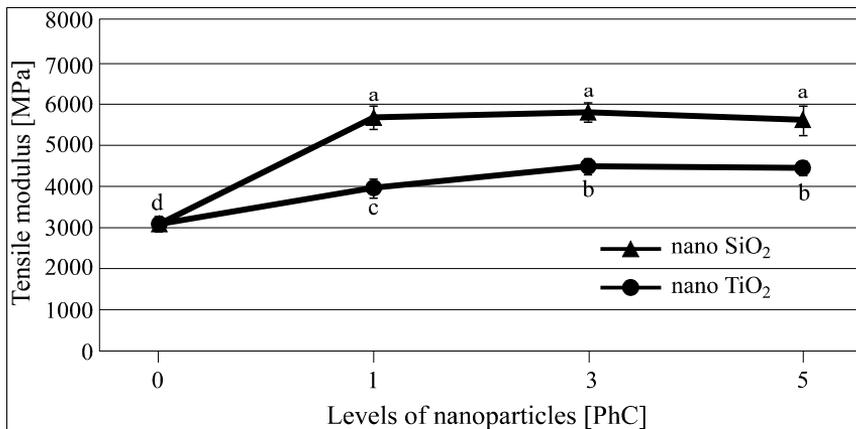


Fig. 4. Mutual effect of SiO₂ and TiO₂ nanoparticles on tensile modulus

Figure 5 shows the distribution of SiO₂ and TiO₂ nanoparticles in a polymer matrix. It can be seen that when using 1 PhC nanoparticles, their distribution was formed well in the polymer matrix. The particle sizes measured in the images related to 1 PhC are less than 20 nm, which is fairly consistent with the manufacturer's claim concerning particle diameter (11-14 and 10-25 nm). This means that the 1 PhC nanoparticles were separately distributed in the polymer matrix without interacting with each other. When using 3 PhC nanoparticles, the distance between the particles decreased compared to the 1 PhC nanoparticles,

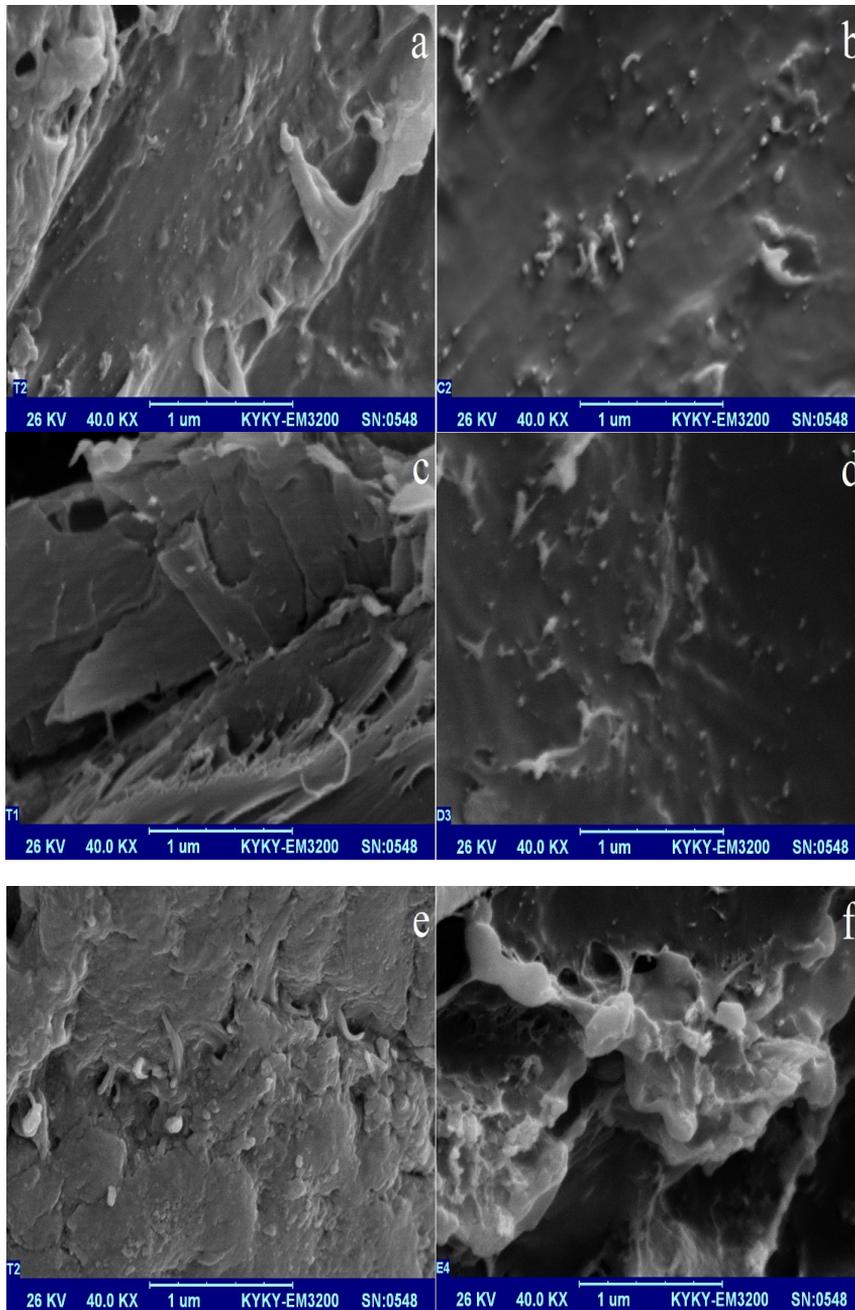


Fig. 5. Distribution of SiO_2 and TiO_2 nanoparticles in a polymer matrix: a – 1 PhC Nano TiO_2 , b – 1 PhC Nano SiO_2 , c – 3 PhC Nano TiO_2 , d – 3 PhC Nano SiO_2 , e – 5 PhC Nano TiO_2 , f – 5 PhC Nano SiO_2

but their distribution improved in the matrix. However, when using 5 PhC nanoparticles, the particles aggregated (agglomeration). The particle size measured in these images is much higher than the manufacturer's claim. This means that SiO₂ and TiO₂ nanoparticles tend to attract each other through hydrogen bonds due to their high surface energy and attracting forces. Thus, with large quantities of these nanoparticles, agglomeration occurs and the crystal size increases, which reduces the mechanical strength of the nanocomposites [Deka and Maji 2012].

Conclusions

In this research, the effects of inorganic nanoparticles on the properties of wood flour–polypropylene nanocomposites were examined. The results showed that:

- By increasing the nanoparticles from 0 to 3 PhC, the mechanical strength increased, including the flexural and tensile strength and moduli. However, an increase in nanoparticles to 5 PhC caused a decrease in mechanical strength.
- The effect of the SiO₂ nanoparticles on the improvement in the mechanical properties was more marked than that of the TiO₂ nanoparticles.
- By increasing the nanoparticles to 3 PhC, their dispersion and distribution improved in the polymer matrix, but the use of 5 PhC nanoparticles resulted in an increase in crystal size and this caused difficulties in their distribution.

References

- Altan M., Yildirim H.** [2010]: Mechanical and morphological properties of polypropylene and high density polyethylene matrix composites reinforced with surface modified Nano sized TiO₂ particles. *World Academy of Science, Engineering and Technology*, 4: 246-251
- Albala R., Olmos D., Aznar A.J., Baselga J., González-Benito J.** [2004]: Fluorescent labels to study thermal transition in epoxy/silica composites. *Journal of Colloid Interface Science* 277: 71-78
- Bikiaris D., Karavelidis V., Karayannidis G.** [2006]: A new approach to prepare poly (ethylene terephthalate)/silica nanocomposites with increased molecular weight and fully adjustable branching or crosslinking by SSP. *Macromolecular Rapid Communications* 27: 1199-1205
- Chae D.W., Kim B.C.** [2007]: Effects of introducing silica particles on the rheological properties and crystallization behaviour of poly (ethylene terephthalate). *Journal of Materials Science* 42: 1238-1244
- Chen X., You B., Zhou S., Wu L.** [2003]: Surface and interface characterization of polyester-based polyurethane/nano-silica composites. *Surface and Interface Analysis* 35: 369-374

- Deka B.K., Maji T.K.** [2012]: Effect of SiO₂ and nanoclay on the properties of wood polymer nanocomposite. *Polymer Bulletin* 10: 60-75
- Garakani M.M., Arefazar A., Nazockdast H.** [2007]: Study on morphological, rheological and mechanical properties of PP/SEBSMA/SGF hybrid composites. *Journal of Applied Polymer Science* 104: 2704-2710
- Guyard A., Persello J., Boisvert J.P., Cabane B.** [2006]: Relationship between the polymer/silica interaction and properties of silica composite materials. *Journal of Polymer Science Part B Polymer Physics* 44: 1134-1146
- Ishak Mohd Z.A., Chow W.S., Rochmadi T.T.** [2008]: Compatibilizing effect of SEBS-g-MA on the mechanical properties of different types of OMMT filled polyamide 6/polypropylene composites. *Composites, Part A*, 39: 1802-1814
- Ismaeilmoghadam S., Shamsian M., Bayat Kashkoli A., Kord B.** [2015]: Evaluation of effect of Nano SiO₂ on the physical, mechanical and morphological properties of hybrid Nano composite from polypropylene-wood flour. *Iranian Journal of Wood and Paper Science Research (Persian)* 30: 266-277
- Khatibzadeh M., Mohseni M., Moradian S.** [2010]: Studying the dyeing of fiber grade PET using a hyper branched polymeric additive. *Journal of Color Science and Technology (Persian)*, 4: 25-32
- Kord B., Taghizadeh Haratbar D.** [2014]: Influence of fiber surface treatment on the physical and mechanical properties of wood flour-reinforced polypropylene bionanocomposites. *Journal of Thermoplastic Composite Materials*, DOI: 10.1177/0892705714551592
- Kruenate J., Tongpool R., Panyathanmaporn T.** [2004]: Optical and mechanical properties of polypropylene modified by metal oxides. *Surface and Interface Analysis* 36: 1044-1047
- Liu X.Q., Wang Y., Yang W., Liu Z.Y., Luo Y., Xie B.H., Yang M.B.** [2012]: Control of morphology and properties by the selective distribution of nano-silica particles with different surface characteristics in PA6/ABS blends. *Journal of Materials Science* 47: 4620-4631
- Njuguna J., Pieliowski K., Desai S.** [2008]: Nanofiller-reinforced polymer nanocomposites. *Polymers for Advanced Technologies* 19: 947-959
- Oburođlu N., Ercan N., Durmus A., Kaşğöz A.** [2012]: Effects of halloysite nanotube on the mechanical properties and nonisothermal crystallization kinetics of poly(butylene terephthalate) (PBT). *Journal of Macromolecular Science Part B Physics* 51: 860-879
- Parvinezadeh M., Moradian S., Rashidi A., Yazdanshenas M.E.** [2010]: Surface characterization of polyethylene terephthalate/silica nanocomposites. *Applied Surface Science* 256: 2792-2802
- Ramos V.D., Helson da costa M., Vera Soares L.P., Regina Nascimento S.V.** [2005]: Modification of epoxy resin: a comparison of different types of elastomer. *Polymer Testing* 24: 387-394
- Rong M.Z., Zhang M.Q., Pan S.L., Lehmann B., Friedrich K.** [2004]: Analysis of the interfacial interactions in polypropylene/silica nanocomposites. *Polymer International* 53: 176-183
- Soon K., Jones E.H., Rajeev R.S., Menary G., Martin P.J., Armstrong C.G.** [2012]: Morphology, barrier, and mechanical properties of biaxially deformed poly(ethylene terephthalate)-mica nanocomposites. *Polymer Engineering and Science* 52: 532-548
- Tian X., Zhang X., Liu W., Zheng J., Ruan C., Cui P.** [2006]: Preparation and properties of poly(ethylene terephthalate)-silica nanocomposites. *Journal of Macromolecular Science Part B Physics* 45: 507-513

- Yang H., Zhang Q., Guo M., Wang C., Du N.R., Fu Q.** [2006]: Study on the phase structures and toughening mechanism in PP/EPDM/SiO₂ ternary composites. *Polymer* 47 [6]: 2106-2115
- Yang Y., Gu H.** [2007]: Preparation and properties of deep dye fibers from poly (ethylene terephthalate)/SiO₂ nanocomposites by in situ polymerization. *Journal of Applied Polymer Science* 105: 2363-2369
- Zhang L., Tam K.C., Gan L.H., Yue C.Y., Lam Y.C., Hu X.** [2003a]: Effect of nano-silica filler on the rheological and morphological properties of polypropylene/liquid-crystalline polymer blends. *Journal of Applied Polymer Science* 87: 1484-1492
- Zhang M.Q., Rong M.Z., Zhang H.B., Rich K.F.** [2003b]: Mechanical properties of low nano-silica filled high density polyethylene composites. *Polymer Engineering and Science* 43: 490-500
- Zhang X., Tian X., Zheng J., Yao X., Liu W., Cui P., Li Y.** [2008]: Relationship between microstructure and tensile properties of PET/silica nanocomposite fibers. *Journal of Macromolecular Science Part B Physics* 47: 368-377

List of standards

- American Society for Testing and Materials. ASTM. [2013]:** Standard practice for conditioning plastics for testing. ASTM D618-99, for testing, Annual book of ASTM standards, Philadelphia, ASTM D618-99
- American Society for Testing and Materials. ASTM. [2010]:** Standard test method for flexural properties of unreinforced and reinforced plastics and electrical insulating materials. Annual book of ASTM standards, Philadelphia, ASTM D790
- American Society for Testing and Materials. ASTM. [2010]:** Standard test method for tensile properties of plastics. Annual book of ASTM standards, Philadelphia, ASTM D638