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Analysis of Variance (ANOVA) for Optimizing the Nano-SiO_2 Content of High Performance Epoxy Nanocomposites

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Epoxy based nanocomposite samples containing SiO_2 nanoparticles (0.0–3.0 %w) were prepared for physical and mechanical evaluation. Some thermomechanical and physical properties of samples were investigated using dynamic mechanical analysis (DMA), tensile strength, hardness and abrasion tests. The main aim of experimentation was to realize the optimum amount of nano-SiO_2 which would demonstrate the best improving effect on mechanical and physical properties of nanocomposite samples and finding how significant a factor is for improving in physical and mechanical properties. Analysis of variance (ANOVA) was applied for optimization of SiO_2 content in epoxy based nanocomposites.

Keywords: Nanocomposite, SiO_2, epoxy, mechanical, analysis of variance

1 Introduction

There are several reports indicating the improvement in characteristics of thermosetting resins by inorganic nanoparticles e.g. SiO_2, TiO_2, Al_2O_3 *etc.* (1). High performance polymer composite materials are used increasingly for engineering applications under hard working conditions. The materials must provide unique mechanical and tribological properties combined with a low specific weight and a high resistance to degradation in order to ensure safety and economic efficiency (2). Epoxy based composites are used in a variety of applications since their excellent properties. The molecular architecture, curing conditions and the ratio of the epoxy resin and the curing agent were previously introduced as the main important factors influencing their performance. Nowadays, the use of nanometer inorganic fillers has been shown to strengthen the physical properties of polymer resins (e.g. epoxy) such as thermal stability, wear resistance, mechanical response and electrical resistance (3–9).

Nanoparticles can fill up the weak micro-regions of resins to boost the interaction forces at the polymer–filler interfaces. A dramatic increase in the interfacial area between fillers and polymer can significantly improve the properties of the polymer (10). The reinforcement efficiency is reported to show strong dependence on dispersion of nanoparticles. Well-dispersed nanoparticles can effectively enhance the comprehensive properties of nanocomposites, which are unique and different from any other current composites (11,12). Of course the addition of a nano-sized material would not always play an improving role for characteristics of the nanocomposite. It is required to optimize the amount of doped nanoparticles which would result in the best properties and maximum improvement. In the present work, we discuss how to compare the experiments which allow sufficient improving in epoxy based nanocomposites' mechanical properties, using analysis of variance (ANOVA), in order to determine the significance of a given factor. It has been tried to apply SiO_2 nano particles in epoxy formulation as a reinforcing agent which would result in better performance in the industry. According to high active surface and surface:diameter ratio in nanoparticles, they would act as stress concentrators and a binding bridge at the inter-phase (13). An important route would be introduced providing numerical information about the significance and the nano-SiO2 content of the epoxy based composite would be optimized. As one of the main applications of epoxy based materials is in field of coating, corrosion protection, cothodic protection etc., modifying

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application of nano silica in epoxy based system would be interesting and useful for coating and paint industry.

2 Experimental

2.1 Materials and Characterization Apparatus

The epoxy resin was bisphenol-A (Araldite® GY 6010) from Jana CO., Saudi Arabia (epoxy value: 0.5208–0.5498 eq per 100 g; weight per epoxide: 182–192 g per eq; residual epichlorohydrin: <100 ppm). A cycloaliphatic polyamine hardener (Aradur 43) was from Huntsman Co. (amine value: 260–280 mg KOH per g). Resin/hardener ratio was 100/60 pbw. Nano-SiO_2 was AEROSIL® 200 (specific surface area:200 m^2g^{-1}; average particle size: 12 nm) from Degussa. A coupling agent with γ-aminopropyltriethoxysilane structure (Amino A-100) was supplied from Silquest® Chemicals. It was added 5 pbw to the epoxy resin. Water free acetone was from Merck®.

The tensile strength of cured samples was determined, using an Instron testing machine at a crosshead speed of 5 mm min^{-1} at room temperature, according to ASTM D638. Three specimens of each sample were tested. The thermomechanical properties were investigated by a DuPont Instrument operating in the three-point bending mode (atmosphere: N_2; temperature range: −20 to 200°C; scanning rate: 5°C min^{-1}; frequency: 10 Hz). Abrasion resistance was determined according to DIN 53516 standard method by a Bareiss® instrument and applied weight was 10 N during all tests (path length: 350 mm; rate: 2 mm s^{-1}). The grit abrasive sheet was checked by a comparison standard elastomer. It would abrade approximately 220–240 mg of the comparison sample. The sheet was used as long as the abrasive loss of a comparison elastomer sample was less than 180 mg. It was then replaced by a new one (according to manual operation documents of instrument). Test sample was a 10 mm diameter disk with 10 mm thickness. Hardness of samples was determined in Shore D scale. Thermal gravimetric analysis was performed by a DuPont instrument and heating rate was 5°C min^{-1}.

2.2 Nanocomposite Preparation

One of the main issues in preparation of nanocomposites is to disperse the nanoparticles in resin media which has been reported to increase the resin's viscosity. SiO_2 nanoparticles were pretreated by coupling agent in acetone. In the next step, epoxy resin was added to the mixture. Acetone would decrease the viscosity of the preparing mixture providing well dispersed sample. Using a "high shear" laboratory-mixing device for mechanical mixing (2 h) and an ultrasonic homogenizer (30 min) it was tried to reach as complete as possible dispersion. Acetone content of the sample was removed by vacuum at 40°C (12 h). The mixture was again homogenized by ultrasonic apparatus (30 min). The hardener was added to the formulation, being mixed by mechanical (30 min) and ultrasonic (15 min) equipments. The prepared composite sample was degassed (2 h), being cured in a chamber at room temperature. After 48 h, the mechanical tests were performed in order to investigate the effect of different amount of nano-SiO2 on composites' properties.

2.3 Statistical Approach

Analysis of variance (ANOVA) is a useful technique for comparing more than two methods or treatments. The variation in the sample responses (treatments) is used to decide whether the sample treatment effect is significant (14,15). Analysis of variance ANOVA is similar to regression in that it is used to investigate and model the relationship between a response variable and one or more independent variables. However, analysis of variance differs from regression in two ways: the independent variables are qualitative (categorical), and no assumption is made about the nature of the relationship (that is, the model does not include coefficients for variables) (16,17). In the present work, it was tried to model the variation in several physical-mechanical properties according to the nano-SiO_2 content of the nanocomposite samples. The modeled variations were investigated together. Finally, the optimum nano-SiO_2 content was concluded, which would demonstrate the maximum improving influences on the nanocomposites characteristics.

3 Results and Discussions

3.1 Investigating the Mechanical-Physical Properties by ANOVA

As shown in Table 1, reinforcement of epoxy flooring by SiO_2 nanoparticles would dramatically improve the tensile properties of these coatings. Generally, nanoparticles inherently possess high module and would strengthen the polymeric matrix when dispersed in the nano scale level. However, improvement from 3.22 MPa (unmodified sample) to 12.59 MPa (2.5% nano-SiO_2) is really excellent as much more interfacial surfaces can be generated between polymer and nanoparticles, which assists in absorbing the physical stress. The maximum tensile strength and elongation was in EP-5 which would drop in EP-6 sample with higher amount of SiO_2 nanoparticles. Figures 1 and 2 show the quality of fitting for tensile strength and elongation results after application of several fitting model and selection of best simulated model for these two parameters with minimum norm of residual. In our investigation, a second-order model, which shows reasonable correlation with experimental data, was used to build the relation between mechanical properties (X) and amount of nano-SiO_2 (Y). The model for tensile strength is according to Equation 1:

$$Y = -1.440 + 0.349\ X - 0.007\ X^2 \qquad (1)$$

Table 1. Variations in physical-mechanical properties of epoxy nanocomposites via reinforcement by nano SiO_2

	SiO_2 (%)	*Tensile Strength (MPa)*	*Standard Deviation (%)*	*Elongation (%)*	*Tg (°C)*	*Tan-Delta*	*Abrasion (mm^3)*	*Hardness (Shore D)*
EP-0	0.0	3.22	1.8	5.94	43.2	0.70	490	58
EP-1	0.5	3.36	2.1	7.17	45.8	0.68	426	61
EP-2	1.0	5.08	1.7	6.99	46.0	0.63	416	61
EP-3	1.5	5.14	2.5	8.47	47.7	0.59	397	62
EP-4	2.0	8.72	2.8	14.29	50.3	0.57	368	62
EP-5	2.5	12.59	2.2	31.58	50.8	0.44	318	63
EP-6	3.0	11.19	2.1	33.04	55.2	0.30	256	67

While for elongation, it is as Equation 2:

$$Y = -1.869 + 0.759\ X - 0.033\ X^2 \qquad (2)$$

The standard deviation data for tensile tests has been shown in Table 1. Reliable data of tensile strength indicates that the mixing technique was effective and dispersion was uniform in prepared nanocomposites, since agglomerates of nano silica would act as stress concentrators causing premature failure in tensile tests.

As mentioned previously, the EP-6 sample's tensile strength is in opposition to the improving trend of previous samples. There are several possible reasons for this decrement in tensile strength. One would be the weak boundaries between nanoparticles and probable micronized trapped bubbles. The other dependable reason may be the effect of high amounts of nanoparticles on homogeneity in crosslinking of the epoxy network. As the interfacial area of the particles is high, their interaction with epoxy chain would cause the lower homogeneity in crosslink density. Finally, the heterogeneous dispersion of nanoparticles according to increment of resin's viscosity could also be mentioned as an important factor in mechanical failure.

Achieving the abrasion resistant composite by addition of more SiO_2 nano particles is expected. The composite surface if filled by more amounts of nanoparticles. The inorganic filler is a well known abrasive agent. This would prevent any surface damages during the physical contact.

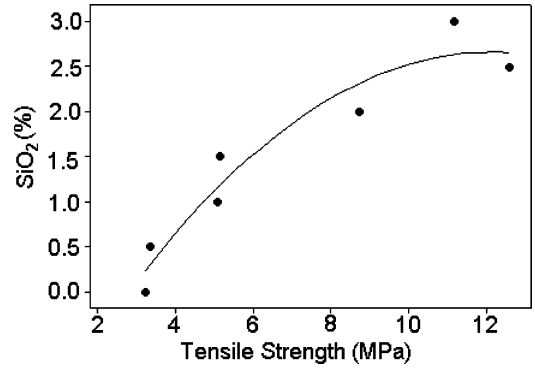

Fig. 2. Best statistical model with a minimum norm of residual for nano-SiO_2 content versus improvement in tensile strength.

It is mentionable that the abrasion tests were performed sequent from EP-0 to EP-6. Also, the hardness of nanocomposite is improved according to the nano-SiO_2 content. The ANOVA model was as Equation 3:

$$Y = -80.24 + 759\,X + -2240\,X^2 + 2120\,X^3 \qquad (3)$$

for abrasion resistance and as Equation 4:

$$Y = 6.257 - 49.764\,X + 131.579\,X^2 - 115.636\,X^3 \qquad (4)$$

For hardness, while X is the mechanical property and Y is nano-SiO_2 content. The models are shown in Figures 3 and 4 for abrasion and hardness, respectively. It is also

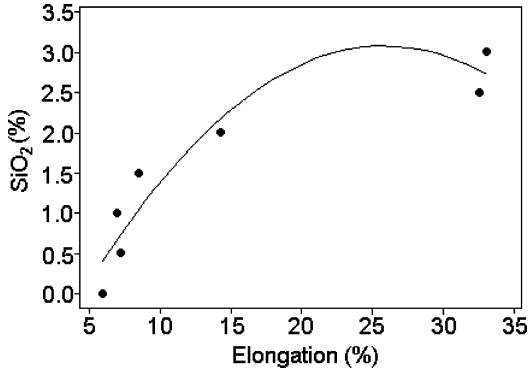

Fig. 1. Best statistical model with a minimum norm of residual for nano-SiO_2 content versus elongation enhancement.

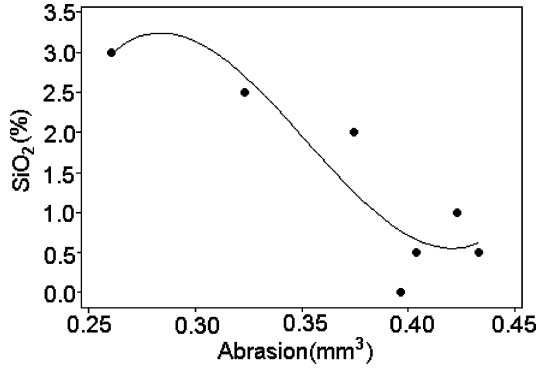

Fig. 3. Best statistical model with a minimum norm of residual for nano-SiO_2 content versus improvement in abrasion resistance.

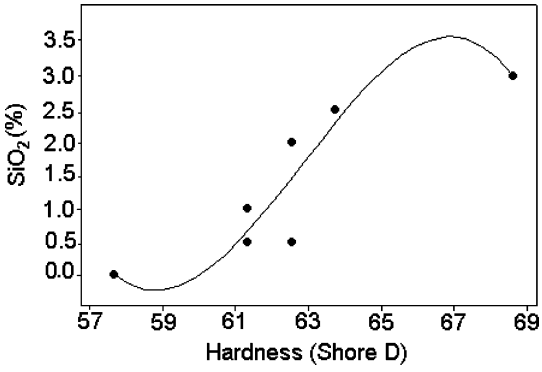

Fig. 4. Best statistical model with a minimum norm of residual for nano-SiO_2 content versus increment in hardness.

observed in Table 1 that Tg would increase in accordance with amount of SiO_2, while variations in δ_{tan} would be vise versa. Chemical bonding at the interface of the nanoparticles and polymer matrix according to the presence of coupling agent could lead to hindered relaxational mobility in the polymer segments near the interface, which leads to an increase of Tg. ANOVA modeling equations are:

$$Y = 134.5 - 9.570\,X + 0.218\,X^2 - 0.002\,X^3 \qquad (5)$$

and

$$Y = 25.31 - 147.9\,X + 315.9\,X^2 - 222.6\,X^3 \qquad (6)$$

for Tg and δ_{tan}, respectively (Figures 5 and 6).

Thermal gravimetric analysis (TGA) was performed on prepared nanocomposites. There was no mass loss in 25–150°C temperature region. Interestingly, the main TGA signal which is due to polymer structure would shift from 480 to 537°C (EP-0 to EP-6) gradually in accordance with nano-SiO_2 content of samples. On the other hand, residual mass of samples after 750°C was the same as filled nano silica. In order to confirm that the final ratio of nano SiO_2 to neat epoxy in each sample is the same as start formulation, samples were tested 3 times by thermogravimetry and furnace, results were reliable.

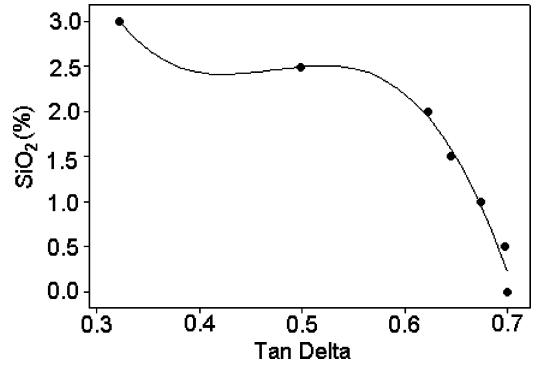

Fig. 5. Best statistical model with a minimum norm of residual for nano-SiO_2 content vs. δ_{tan}.

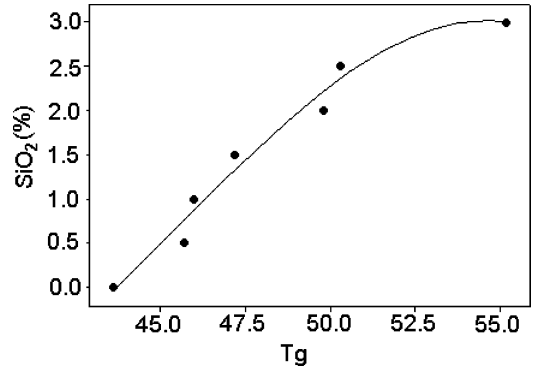

Fig. 6. Best statistical model with a minimum norm of residual for nano-SiO_2 content vs. increment of glass-transition temperature (Tg).

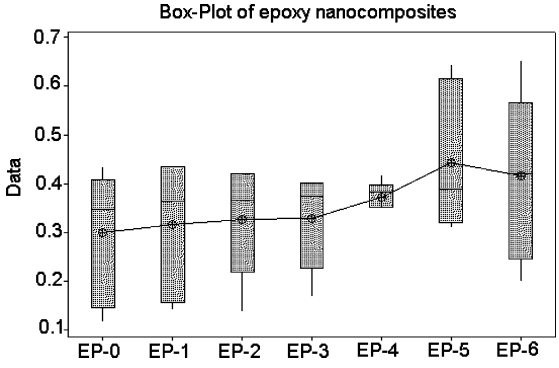

Fig. 7. Application of ANOVA for comparing the result of all experiments together, illustrating the most great improvement in properties for EP-5 samples (2.5%w nano-SiO_2).

3.2 Optimizing the Nano-SiO2 Content According to Cumulative Analysis by ANOVA

The effect of amount of nanoparticles on epoxy composite samples due to evaluating the best stage for best properties of end products was studied by ANOVA. If the p-value is small, this casts doubt on the null hypothesis and suggests that at least one experiment mean is significantly different than the other experiment means. The choice of a critical p-value to determine whether the result is judged "statistically significant" is left to the researcher. In this study the minimum of p-value has been selected than the other values. The results were illustrated that with step by step addition of nano particle to the polymer matrix, best characteristics with minimum amount of p-value would be observed in EP-5 sample which contains 2.5% of SiO_2 nanoparticles. Figure 7 shows the Box-Plot of total investigations.

4 Conclusions

Analysis of variance as a statistical approach assisted the determination of optimum content of nano SiO_2 which yields the best thermophyscial characteristics in epoxy based composites. Improvement in these properties due to

addition of SiO_2 nanoparticles was a principle which is again demonstrated.

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