Characterization and the Pattern of Surfaces of Sealant with nano size Composite Materials

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Abstract
Nano composite sealant is low viscosity, room temperature cured, opaque and flowable nature. They have variety of uses such as potting, pressure sealant and shock resistant. Most important factor influencing use of fillers in polymer composites is their ability to effectively transfer the applied load in the matrix. The effective utilization of fillers in composites for structural applications depends strongly on the ability to disperse the nano fillers homogeneously in the matrix without damaging them. R-Belite supper epoxy adhesive (RBSEA) were formulated with different nano fillers (KCl, Al_2O_3, ZrO_2, SiO_2, ZrO_2) at room temperature. The composite were prepared with the 0.02 to 0.10 weight ratios to promote the nucleation of the nanoparticles in the applied sealant. Two main problems which arise in improving the properties are poor dispersion of the fillers in the composite and weak bonding between nano fillers and the matrix. These problems are solved by mechanical and chemical means. It was observed that mechanical properties like tensile strength, elongation hardness etc and thermal properties were also improved with incorporation of nanofillers in the working applied polymer matrix. The dispersion of nano fillers in polymer matrix is studied by Scanning electron microscopy (SEM). The results confirm the presence of nanomaterial in RBSEA/fillers nanocomposites. SEM is also used to characterize the pattern of surfaces with nano size composite materials.

1. Introduction

Composite resins, first introduced in the 1970s, were typically quartz-filled and did not meet the compressive and tensile force requirements for composite applications. They had relatively high surface roughness and poor bonding at the interface which, in combination with polymerization shrinkage resulted in margin degradation [1].

Early resin composites were difficult to handle due to their manual mixing of the resin paste (A) and the catalyst (B). They were available only in tubs or syringes of pastes (A and B separately), and were always self-cured with a limited working time. Over the time, the strength characteristics of composite resins were improved and the resins were introduced for use in different applications [2-6].

The focus was still on etching and bonding, and early attempts at strong bonding resulted in weak bonding to the layer and a rapidly inside bonding. It was also recommended that, after curing of the resin, the interface over this surface to seal it and help to seal and wear [7-9]. These enabled a more conservative approach during preparation and they were used with improved bonding systems for improved marginal integrity at the interface.

Current composite materials (and bonding systems) are vastly superior to earlier versions due to several types of fillers, advanced enamel and uniform adhesive systems. They offer strength, lower polymerization shrinkage and stress, wear resistance, and excellent bonding [10-12].

Sealant nano composite (SNC) contain crushed particles ranging in size from 0.04 to 1 micron. Filler load is lower in micro filled composite resins, and the internal bonding between the matrix and the

filler is strong, resulting in high strength. This is an important consideration in stress-bearing areas [13, 14].

Nanofilled composite resins have high filler load in order to obtain strength and wear resistance similar to that of micro hybrid composite resins. Nanofilled composite resins contain smaller particles of filler in the range of 0.02 to 0.1 microns. One nanofilled composite contains nanofiller particles that are approximately 0.02 microns in diameter, sintered into nanoclusters of 0.6 to 1.4 microns that contain zirconium particles, in order to improve physical characteristics.

The recent paper in this research work has included reductions in polymerization shrinkage and in polymerization stress. We also report the effect of nano fillers on different properties of SNC. These have been achieved through increased filler loads and novel chemical technology. Polymerization shrinkage, and therefore stress, has been reduced by increasing conversion rate of the monomer [15]. Direct reduction of polymerization stress has now also been achieved through the use of a polymerization process.

2. Experiment

2.1 Materials
R-Belite super (RBS) 2-part epoxy resins were supplied by USA. The chemicals used in this study were Ethyl alcohol C_2H_5OH 99% Aldrich, Zirconium oxide ZrO_2 99.99 % Merck, Aluminum oxide Al_2O_3 99.99 % Merck, Potassium chloride KCl 99.999% Merck and Silicon dioxide SiO_2 99.99 % Merck added to RBS.

2.2 Preparation of Material
All-solid ingredients were dried in an oven at 100 ± 2 °C for minimum 4 h (moisture content < 0.1% by Karl Fischer). R-Belite super 2-part epoxy resins were added in a vertical mixer   for uniform distribution in 30 min.   Fillers were added in two equal installments and mixed for 10 min. The mixing was continued for 60 min without vacuum and then for 60 min in vacuum. All these operations were carried out under controlled humidity 55 ± 5 per cent.

2.3 Characterization of Material
Mechanical properties of the composite formulations were tested according to ASTM- D-638 using tensile testing machine (Instron 1185). Shore hardness was measured by Shore hardness tester (SHR-4 111). SEM (Jeol-JSM-5910LV) and Thermo gravimetric analyses (TGA) were also used for characterizations.

2.4 Processing of composites
 The first step of processing nanocomposites is to determine the right proportion of resin curing agent and nanoparticles, and weighed them carefully as shown in Table-1. A correct ratio of resin and curing agent, when mixed, will make sure that a complete reaction would occur between them. In most of the cases, it would not be possible for a complete reaction to occur between the resin and curing agent where monomers are not mixed in right proportions. Because of the incomplete reaction any unreacted resin or curing agent will remain in the matrix and this will affect the final properties of the composite sealant.

2.5 Curing of Nanocomposites
The mold is prepared by applying the releasing agent. The dispersed mixture of resin, nanoparticles and curing agent should be kept in vacuum before pouring into the mold to make sure that there are no air bubbles in it. The curing of the composite is carried out in two stages. They are cured at room and high temperature.

It was also observed during many experiments that in spite of pouring the mixture into the mold very slowly there were still some air trapped in it. The mold was again kept in vacuum to remove the few air bubbles which might have trapped during the time of pouring of the mixture into the mold. Curing was carried out at room temperature for 30 minutes. The mold and all the parts were tightly fixed with all the screws in position to avoid leakage of the mixture through any of the loosely connected parts.

The properties of the composite to an extent depend on the curing temperature. In all the experiments curing of the nanocomposite samples was carried out at room temperature for 4 hours.

3. Results and discussion

3.1 Formulation designation

Polymer system suitable for sealing purpose must have a low viscosity, a long pot life time, and a cured polymer resin possessing good mechanical properties [6]. R-Belite super (RBS) 2-part epoxy resins have been widely used in many industrial fields because of its good mechanical and relatively low cost properties. Thus, in this study, we selected the RBS as the matrix for the composite sealant. At room temperature, this polymer system has excellent properties because of their low viscosity. The curing agent in this study had to meet all the following requirements: (1) a liquid state at room temperature and low viscosity, (2) low cost and low toxicity, and (3) a long pot life (at least 1 h under 25 °C). Among the many liquid amine curing agents, it was difficult to select one for the epoxy system suitable for this study because many curing agents meet only some of the requirements mentioned previously [4].

Nano composite sealant formed the inner-lining-layer and the outer-wound-layer in the polymerization process. Sealant composites often must endure various inner pressures ranging from 2.5 to 40 MPa according to the different types encountered during long-term use. Therefore, to improve the strength of the products, a toughened polymer sealant nano matrix was required in this study. The toughening agent nano size materials over comes the brittleness of the RBS as the strength property of the layer would depend on the polymer net work. In this study, we used RBS resin with nano materials as the toughening agent. Nano size particles could react with the polymer matrix and become a part of the network. Thus, the cured nano sealant networks obtained better molecule movement capability than the polymer system without nano particles.

Generally, viscosity diluter is often added to the epoxy system. However, the strength is reduced on the addition of diluter.

The formulations of the polymer system for the sealant nano composite is listed in Table-I.

Table-1. Compositions of The Nanoparticles Based Composite Materials.

Ingredient (%)	sealant nano composite (SNC-1)	sealant nano composite (SNC-1I)	sealant nano composite (SNC-1III)	sealant nano composite (SNC-1V)	sealant nano composite (SNC- V)	sealant nano composite (SNC-VI)	sealant nano composite (SNC-VII)
RBS resin	49	49	49	49	49	47	45
RBS hardener	49	49	49	49	49	47	45
KCl	2	-	-	-	-	-	-
Al$_2$O$_3$	-	2	-	-	-	-	-
ZrO$_2$	-	-	2	-	2	6	10
SiO$_2$	-	-	-	2	-	-	-

Nano particles of ZrO$_2$, Al$_2$O$_3$, KCl and SiO$_2$ were added in the polymer matrix sealant formulations (Table-1). The shear strength (MPa) and nano particles distribution were improved. A possible reason could be attributed to the fact that the incorporation of nano particles into the polymer system

introduced a few flexible chains containing chemical bonds inside the network structure of the sealant. During the formulation of RBS, nano particles reacted with the matrix nearly at the same time. Thus, many flexible chain segments were expected cross linked to the nano composite sealant structure and finally embed into the structure of the polymer system. The improvement in the shear strength could be due to fact that few flexible chains containing chemical bonds were introduced into the nano sealant composite.

3.2 Mechanical properties

The mechanical properties of the sealant nano composites (SNC I-VII) were evaluated through shear strength, hardness, density and thermal properties (Table-2). It has been reported [6] that low-interfacial interaction between the embedding nano particles and the matrix results in good mechanical properties. This observation can be seen in the sample SNC-I to IV in the range of 1.04 to 1.05 MPa. The maximum property of the shear strength was obtained in the sample no SNC-VI.

Table-2.   Mechanical Properties of Nanoparticles base composite materials.

Compositions	Thickness (mm)	Particles size (Micron)	Hardness (Shore A)	Density (gcm^{-3})	Tensile shear strength (MPa)	Thermal Temperature range (°C)
SNC-1	4	500 pass	92	1.04	1.0	280-570
SNC-1I	4	500 pass	90	1.04	1.0	280-570
SNC-1II	4	500 pass	91	1.04	1.2	280-570
SNC-1V	4	500 pass	89	1.05	0.9	280-570
SNC -V	4	500 pass	90	1.06	1.4	280-570
SNC -VI	4	500 pass	90	1.10	1.6	280-570
SNC -VII	4	500 pass	90	1.09	1.4	280-570

This was an indication of bonding with polymeric matrix and the nano materials were improved. On the basis of these results, this   formulation SNC-VI was chosen as the candidate because of its good overall mechanical properties. Viscosity and pot life of this formulation is practically feasible during the application of the sealant. With respect to the sealing of the component in the applied process, the viscosity and pot life of the polymer system are crucial because a low viscosity and a long pot life make the nano sealant process easier.

It is due to the formulation that the viscosity of the polymer system has to be kept as low as possible to seal the assembly completely. If the pot life is too short, it is difficult to finish the sealing operation because the parts cannot be wetted fully by the sealant; the short pot life causes many air bubbles to be trapped inside the sealing during the wet process if the viscosity increases quickly.

3.3 Morphological studies

Figure 1(a, b, c) presents the SEM images of the SNC V to VII system respectively. The images show irregular boundaries in the range of 10 to 100 nm. In the case of the polymer Fig. 1(a) the pattern was found to be non uniform type, whereas in the case of the Fig. 1(b) nano composite sealant, the micrographs show regular patterns. Dispersed particles and some large agglomerates in the matrix were also observed. The spherical particles can clearly be seen in the polymer matrix. From these various observations, it can be deduced that the formation of the regular is probably the result of uniform distribution of the nano particles.
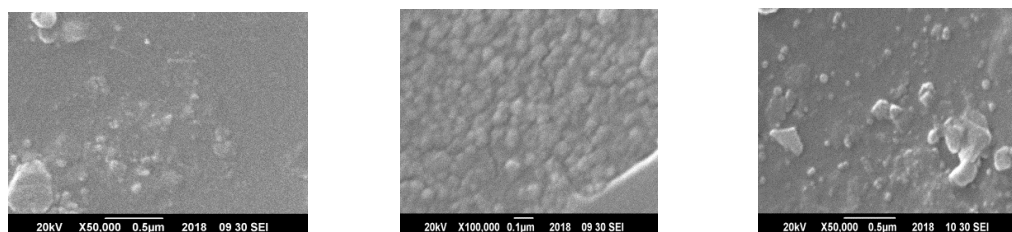
Figure 1. Scanning electron micrographs **(a)** Sealant nano composite (SNC- V)
(b) Sealant nano composite (SNC- VI) and **(c)** Sealant nano composite (SNC- VII).

The interface plays a vital role in stress transfer from nano particles to the polymer nano composite matrix. Optimal interfacial adhesion is required for taking advantage of the excellent mechanical properties of nano composite sealant.

The addition of nano particles to the polymer matrix has an effect on the mechanical properties of nano composites through the interface because the toughness, shear strength, and viscosity of the resin matrix are affected by the bonding strength and interfacial behavior between the matrix and nano particles.

4. Conclusion

Sealant nano composites   were successfully prepared by one-step blending. The results show that polymeric materials effectively improves the compatibility between filler and matrix, forming chemical bonding between the active end of monomer and the surfaces of nano particles, which make them well distributed in matrix. The results of mechanical properties show that nanocomposite improves   shear strength. When the content of nano-ZrO_2 is 2%, the shear strength is the highest, improving 1 to 1.6 MPa, compared with traditional composite systems, nano-composite systems.

Scanning electron micrographs (SEM) have demonstrated the smoother surface resulting in a more uniform pattern, predicting the uniform distribution of nano particles in the host matrix.

5. References

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