ESSENCE - International Journal for Environmental Rehabilitation and Conservation
Volume VII: No. 1 2016 [36 – 44] [ISSN 0975 - 6272]
[www.essence-journal.com]

Experimental Characterization of Modified Epoxy Resin assorted with Almond shell Particles

Verma, Akarsh and Singh, V. K.

Received: February 28, 2016 | **Accepted**: March 12, 2016 | **Online**: June 30, 2016

Abstract

Experimental investigations have been carried out to study the effect of depolymerised natural rubber at different weight % (0.5, 1, 1.5, 2 and 2.5) to modify the epoxy resin. Mechanical tests are conducted on 100 kN servo-hydraulic universal testing machine under displacement mode of control, digital Rockwell hardness testing machine and impact testing machine. Modifying epoxy resin through blending depolymerised natural rubber and improve mechanical properties is the main focus of this study. Almond shell particles at different wt. % (10, 20, 30 and 40) are filled in modified epoxy resin and the effects of filling almond shell particles on mechanical and thermal properties are reviewed. The modified epoxy resin is analysed on the Scanning Electron Microscopy (S.E.M.) machine for studying the morphology of the composite. The thermal characteristics are investigated by the Thermo Gravimetric analysis as well as the Differential Thermal Analysis.

After carrying out all the above discussed scrutiny, it was observed that on adding 1 wt% of depolymerised natural rubber the impact strength increases by 100% and flexural strength increases by 5%. Filling of almond shell particles by 20 wt% improved thermal stability of material and increased the water absorption and thickness swelling property in comparison of matrix material. The epoxy modified with 1% depolymerized natural rubber and filling of 20 wt% of almond shell particles is found to be better than all other combinations.

Keywords: Biocomposites | Morphology | Scanning electron microscopy (SEM) | Almond Shell Particles | Depolymerised Natural Rubber (DNR)

For correspondence:
College of Technology, G. B. Pant University of Agriculture and Technology, Pantnagar
Email: **akarshverma007@gmail.com**

Introduction

Epoxy resins are very important class of thermosetting polymers that exhibit high tensile strength and modulus, excellent chemical and corrosion resistance, good dimensional stability, low creep and reasonable performance at elevated temperature. Hence, they are widely used as matrix resins for fibre reinforced composite materials and in structural adhesives, surface coatings and electrical laminates. However, such characteristics in an epoxy require moderate to high levels of cross linking which can and usually does result in brittle behaviour. Toughening of epoxy resin has been the subject of intense investigation, because epoxy resins have low fracture energy.

Various rubbers can be used for toughness improvement of epoxy resins, engineering thermoplastics, interpenetrating polymer networks (IPNs) or inorganic particles. Among these, blending epoxy resin with reactive liquid rubber such as carboxyl-terminated butadiene acrylonitrile copolymer, CTBN, amine-terminated butadiene acrylonitrile copolymer, ATBN and hydroxyl-terminated poly butadiene, HTP showed substantial toughness enhancement.

Due to environmental issues, there is growing trend to use bio-fibres and bio-particles as fillers or reinforcement in bio-composites as they are bio-degradable and don't cause negative impact on environment. Also, the bio fibres or bio-particles which are being used in producing composites are generally agricultural waste or by product of some crops and fruits like coir fibre, almond shell particles, walnut shell p almond shell particles, which if nc composites then either they are disposed or burnt as fuel which causes environmental pollution. So, these materials have got significant interest of researchers and scientists to develop new materials which have good mechanical properties as well as less harmful to environment.

Keeping this fact in mind in this work almond shell particles are used as filler and reinforcing material to make the bio-composite which has good mechanical and thermal properties. In this study, the depolymerised natural rubber (DNR) was prepared by a depolymerisation process of natural rubber by adding natural rubber latex to methyl ethyl ketone, and then the resulting mixture was subjected to air oxidation in the presence of potassium per sulphate at 70°C. DNR was blended with epoxy resin in an amount of 0.5, 1, 1.5, 2 and 2.5 wt% of epoxy resin. Blending formulation that showed the highest toughness was applied as matrix for preparation of almond shell particles filled bio composite. The neat epoxy, modified epoxy and almond shell particles filled modified epoxy resin composites were prepared by vertical casting method.

Methods and materials

Matrix material is the material, which holds the relative position of the filler material. The composites shape, surface appearance, environmental tolerance and overall durability are dominated by it. Epoxy resin has wide range of industrial applications because of their high strength and mechanical adhesiveness characteristic. Araldite CY-230 is a liquid solvent free epoxy resin. Curing takes place at atmospheric pressure and room temperature after addition of hardener. Generally, curing shrinkage is very less and may further be reduced by the addition of fillers such as bio-particles, China clay etc. The resin can be easily coloured. Mechanical, electrical properties and higher resistance to chemical and atmospheric attack of fully cured mixture are excellent. Ageing characteristics of the castings are good. Resin can be stored for at least a year if they are stored under cool, dry conditions in the original containers. Hardener HY-951 is a yellowish-green coloured liquid. Hardener (HY-951) was purchased from M/s CIBATUL Limited; India has been used as curing agent. In the present investigation 9 % wt/wt has been used in all material developed. The addition of reinforcing agents to the resin improves the properties of the material. Almond shell particles are used as reinforcing agents to improve the different properties of the composites material.

The almond shell used in the present investigation was arranged from local market. In the present investigation almond shell particles are formed by almond shells that were previously washed and dried in convection oven at 100°C and then by crushing them in Wiley mill and after that almond shell particles were converted into powder form in grinder. After that almond shell particles are mixed in resin and stirred mechanically by means of a high speed mechanical stirrer.

Natural rubber latex was diluted in deionized water to a concentration of 5 wt% based on rubber content in a 1 liter reaction flask. After that $CH_3CH_2COCH_3$ and $K_2S_2O_8$ was added in an amount of 4 v% of total volume and 2 wt% based on the rubber content, respectively. The pH of above solution was adjusted to about 9-10 with 10 wt% aqueous KOH solution. Then, the mixture was mechanically stirred with a spe revolutions per minute (rpm) at 70°C fo under flowing air on the magnetic stirre plate. At the end of reaction, the mixture was coagulated by 1 wt% aqueous $CaCl_2$ solution. The coagulated substance was dissolved in hexane and stirred with magnetic bar for 3 hours. Then, resulting solution was stood overnight and filtered with filter paper and dried at 40°C until weight is constant. The solution obtained by mixing almond shell particles and rubber in resin is kept in the oven at a temperature of 100°C for two hours.

The rubber (DNR) was completely dissolved in epoxy resin at 100°C using magnetic stirrer with hot plate at a speed of 500 rpm for 1 hour. The epoxy resin and rubber mixtures were kept in still air and allowed to reach 40°C. Next, 10 wt% of polyamide (HY 951) was added and stirred at a speed of 200 rpm for 3 min. Thereafter, the blends were poured in different moulds previously coated with releasing agent. Then the mixture was cured at room temperature for 24 hours. After that, each specimen was cut and polished with sandpaper. Finally, the specimen was post-cured at 120°C for 2 h in a mechanical convection oven.

The procedure for casting of almond shell particles filled composites is almost similar to the previous one except mixing of DNR in the epoxy resin first and there after almond shell particles. Almond shell particles were washed with distilled water and dried in oven at 40°C for 24 hours before use. The rubber (1 wt% of DNR) was dissolved completely in epoxy resin at 80°C using mechanical stirrer at a speed of 500 rpm for 1 hour. After that, almond shell particle at different wt% were added and stirred at 200 rpm for 5 min.

Then the mixtures were allowed to reach 100°C in oven and rest of the procedure is same as previous one.

Designation	Epoxy resin (grams)	Hardener (grams)	DNR (grams)	Almond shell particle (grams)
CA1	100	10	1.0	10
CA2	100	10	1.0	20
CA3	100	10	1.0	30
CA4	100	10	1.0	40

Table 1. Design of experiment for almond shell particles filled composites

Results

I. Scanning Electron Microscopy (SEM) :

In the present investigation SEM was carried out for composite containing different weight percentage of depolymerised natural rubber (DNR) to study the dispersion of the depolymerised natural rubber (DNR) in the epoxy resin matrix.

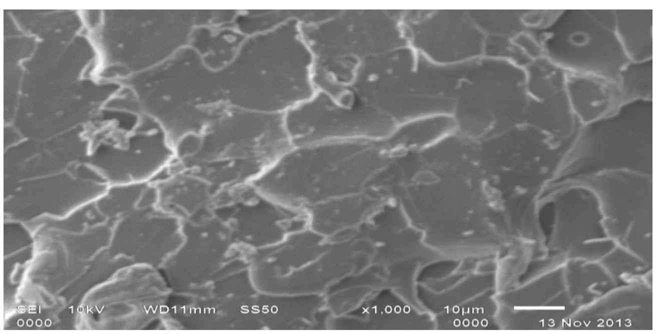

Figure 1: Scanning electron micrograph for 1 wt% depolymerised natural rubber (DNR) composite material at magnification 1000x.

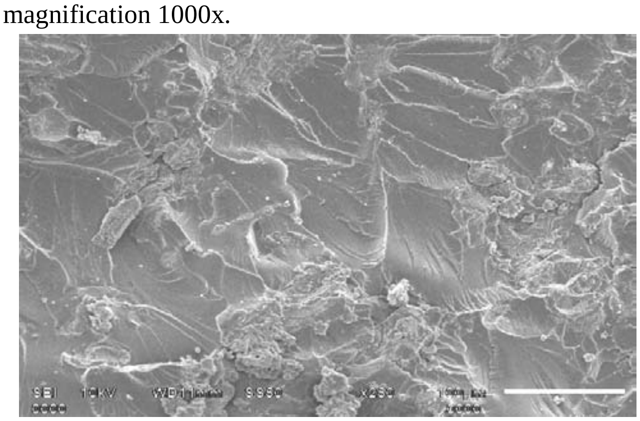

Figure 2: Scanning electron micrograph of 1 wt% DNR & 10 wt% almond shell particles composite material at magnification 250x.

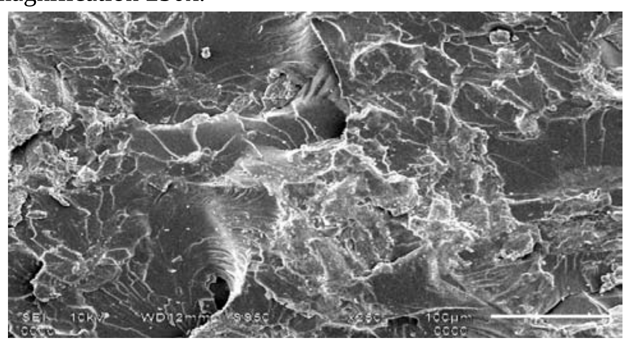

Figure 3: Scanning electron micrograph of 1 wt% DNR & 20 wt% almond shell particles composite material at magnification 250x.

Figure 1 shows the micrograph of 1 wt% of DNR blended in epoxy resin. In this more shearing zone can be seen and the rubber is well dispersed in epoxy resin. Good cross linking of DNR with epoxy resin can be seen here leads to enhanced mechanical properties as this cross linking overcome the brittle behaviour of epoxy resin. Figure 2 shows the micrograph of 10 wt% almond shell particles filled in epoxy resin blended with 1 wt% DNR. In this figure shear bands can be seen which leads to shear yielding of the material. And the dispersion of almond shell particles is good and no cavity can be seen. But at some places matrix cracking has taken place. Figure 3 shows the micrograph of 20 wt% almond shell particles filled in epoxy resin blended with 1 wt% DNR. In is micrograph the cavity which has occurred due to increase in wt% of almond shell particles.

II. Impact test

Depolymerised Natural Rubber (wt%)	Almond shell particles (wt%)	Impact strength (kJ/m^2)
1.0	10	2.288
1.0	20	1.800
1.0	30	1.684
1.0	40	1.451

Table 2. Impact properties of almond shell particles filled composite

The results show that by adding DNR in epoxy resin the impact strength of epoxy resin is increased by 80% on 1 wt% of DNR which is a very remarkable improvement. This might be because DNR which is presented in matrix acted as stress concentrator creating shear yielding and/or crazing in the matrix. In addition, some of rubber molecules might dissolve in epoxy matrix leading to flexibility of epoxy resin. This might be because both toughening and flexibility effects could be operative, resulting in maximum improvement in impact strength. This can also be seen that at higher wt% of DNR the impact strength has been lowered it may be due to the rubber aggregation or accumulation because of which there are internal cavities and internal voids in the material. Similarly, in the case of almond shell particles impact resistance is decreasing with the increase in wt% of almond shell particles. This decrease in the impact properties might be due to the decrease in the bond strength in almond shell particles and matrix material at higher wt% and from SEM micrographs cavities and brittle cracking can also be seen which also decreasing the impact strength.

I. Flexural test

The effect of wt% of DNR and almond shell particles on flexural strength are shown in figures 6 & 7. It is observed that flexural strength increase with an increase in DNR wt% in epoxy.

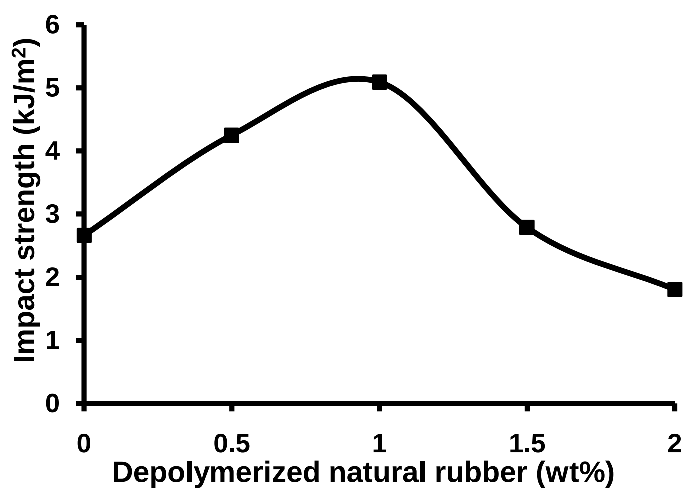

Figure 4: Effect of wt% of DNR on impact strength

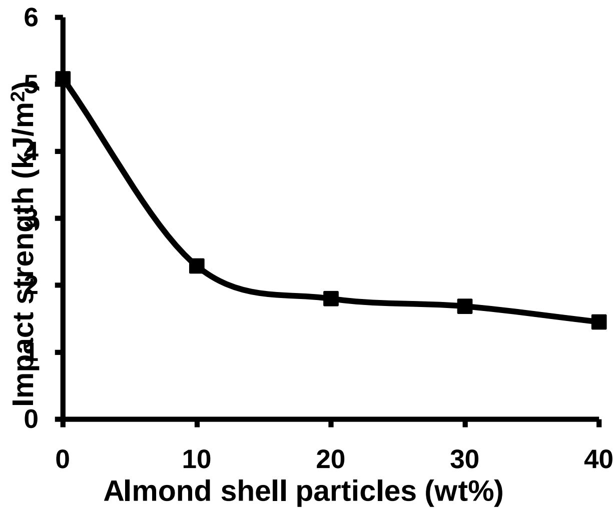

Figure 5: Effect of wt% of almond shell particles with 1 wt% of DNR on impact strength.

II. Flexural test

The effect of wt% of DNR and almond shell particles on flexural strength are shown in figures 6 & 7. It is observed that flexural strength increase with an increase in DNR wt% in epoxy resin and then decreases with an increase in wt%. But in the case of almond shell particles flexural strength keeps on decreasing with the increase in wt% of almond shell particles.

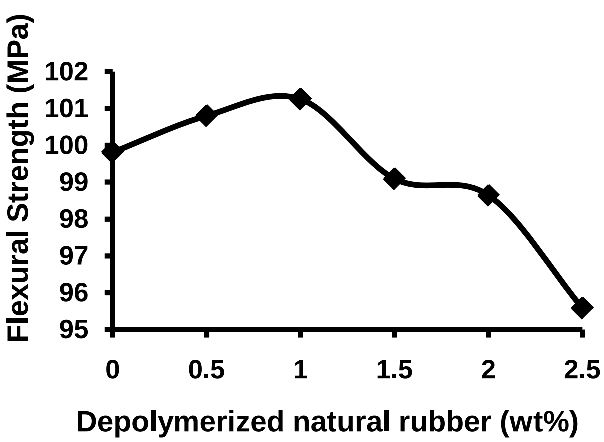

Figure 6: Effect of DNR (wt%) on flexural strength

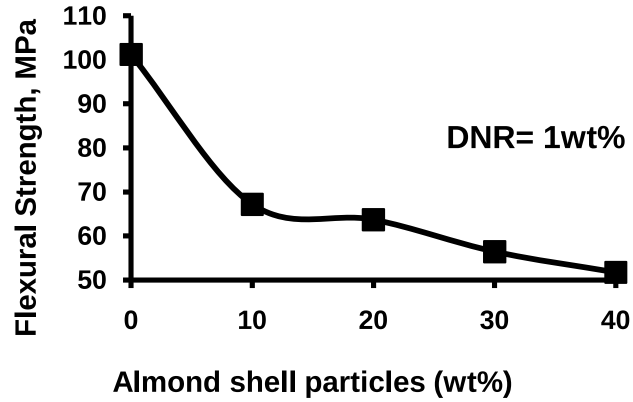

Figure 7: Effect of almond shell particles (wt%) on flexural strength

III. Thermal Analysis

Thermal analysis of the specimen was conducted at Institute Instrumentation Centre, Indian Institute of Technology, Roorkee. For thermal analysis the samples were prepared in powder form by crushing them and the weight of samples were near 10.5 mg and the base material was alumina powder, which was mixed with composite samples in equal amount and medium in which the tests were conducted was air flowing at 20 ml/min. The rate of change of temperature was 10°C/min and range of temperature was room temperature to 1000°C.

Figure 8 shows thermogram of neat epoxy with 10 wt% of hardener. Decomposition of this material has been accomplished under two stages ranging from 356°C to 510°C with corresponding rate of decomposition ranging 1.27 mg/min to 0.72 mg/min. Prior to 200°C, the weight loss of 7.63% may be attributed to the expulsion of the moisture, low molecular mass molecules and volatile matter associated with the material. The maximum rate of decomposition of 1.27 mg/min was observed at 356°C. Such decomposition has been supported with the heat of fusion of -2.487

J/mg centred in the temperature range of 279°C to 511°C with DTA signal of 28.4 µV to 109.2 µV. The decomposition of the material had been concluded at 536°C leaving char residue 3% of initial weight.

Figure 9 shows thermogram of neat epoxy with 1.0 wt% DNR and 10 wt% of hardener. Decomposition of this material has been accomplished under two stages ranging from 354°C to 511°C with corresponding rate of decomposition ranging 1.25 mg/min to 0.74 mg/min. Prior to 200°C, the weight loss of 7.79% may be attributed to the expulsion of the moisture, low molecular mass molecules and volatile matter associated with the material. The maximum rate of decomposition of 1.25 mg/min was observed at 354°C. Such decomposition has been supported with the heat of fusion of -1.88 J/mg centred in the temperature range of 278°C to 511°C with DTA signal of 27.6 µV to 113.3 µV. The decomposition of the material had been concluded at about 530°C leaving char residue 2.2% of initial weight.

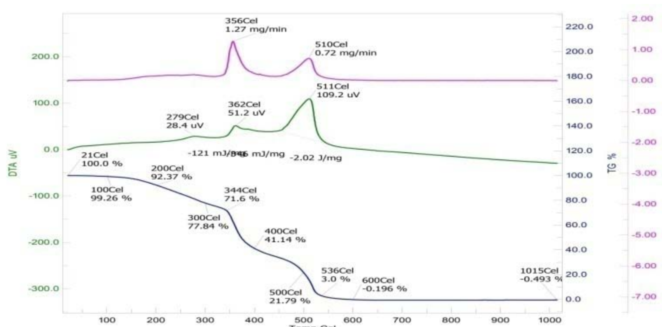

Figure 8: Thermal analysis of epoxy with 0 wt% of DNR

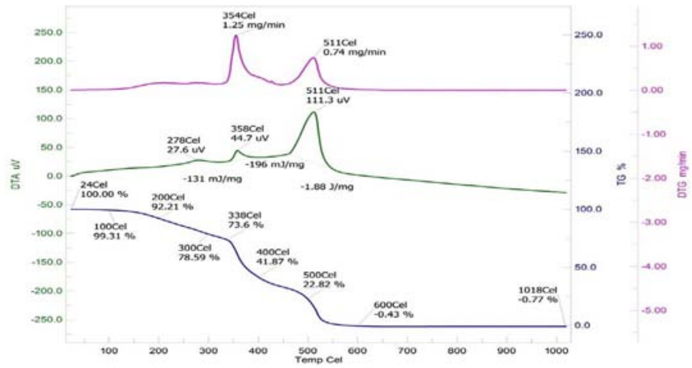

Figure 9: Thermal analysis of epoxy with 1.0 wt% of DNR

Figure 10 shows thermogram of neat epoxy with 1.0 wt% DNR and 10 wt% of almond shell particles and 10 wt% of hardener. Decomposition of this material has been accomplished under two stages ranging from 356°C to 526°C with corresponding rate of decomposition ranging 1.15 mg/min to 0.59 mg/min. Prior to 200°C, the weight loss of 6.81% may be attributed to the expulsion of the moisture, low molecular mass molecules and volatile matter associated with the material. The maximum rate of decomposition of 1.15 mg/min was observed at 356°C. Such decomposition has been supported with the heat of fusion of -1.81 J/mg centred at the temperature 527°C with DTA signal of 92.5 µV. The decomposition of the material had been concluded at about 570°C leaving char residue 2.0% of initial weight.

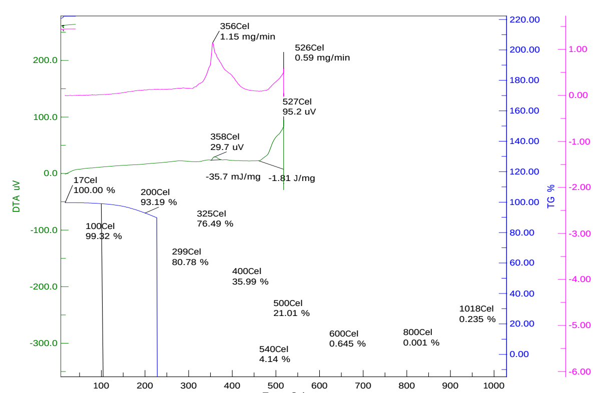

Figure 10: Thermal analysis of epoxy with 1wt% of DNR and 10wt% of almond shell particles

IV. Water Absorption and Thickness Swelling

Water absorption and thickness swell is a very important test for natural particles and fibres reinforced composites to define their potential for outdoor working. The performance of these composites may suffer while they are exposed to environmental conditions for long time. In present work, the specimen filled with DNR and Almond shell particles were tested by dipping them under water for 48 hours to study the effect of water absorption on dimensional stability.

Figure 11 shows that the water absorption increases at constant rate for first 30 hours and the rate of water absorption decreases after 30 hours. This can also be seen that with increasing wt% of almond shell particles the water absorption has also increased, this may be because the addition of almond shell particles wt% the voids and cavities in the materials are more.

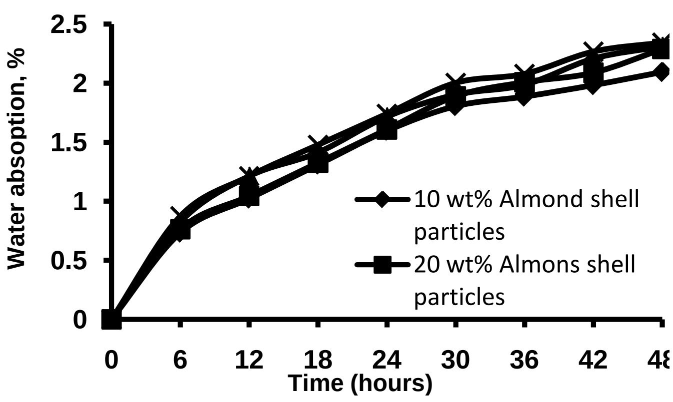

Figure 11: Effect of wt% of almond shell particles on water absorption

Swelling behaviour of almond shell particles and DNR reinforced composite material was studied by dipping the composite material specimen in water, which is a natural for a material if it is being used in open area. The studies were carried out to observe the effect of water on the thickness of the material. Generally, natural particle reinforced composite material swells if they are exposed to aqueous environment. For swelling test the composites were first dried in the oven and then dipped in water at room temperature and the thickness was measured after every 6 hours.

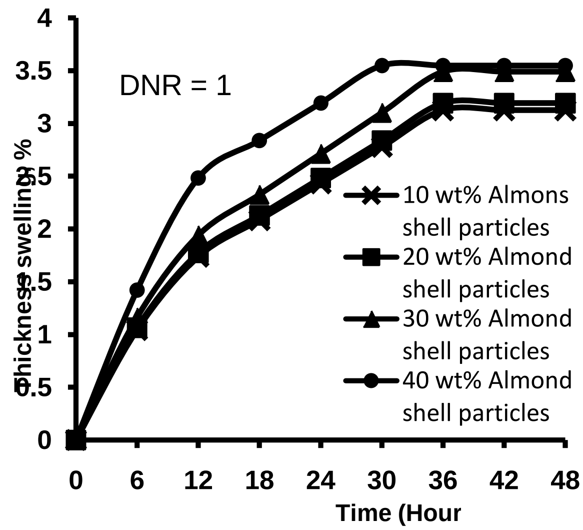

Figure 12: Effect of wt% of Almond she thickness swelling

Conclusions

Effect of blending depolymerised natural rubber

I. The rate of water absorption and thickness swelling increases with the increase in weight percentage of DNR.

II. SEM showed that DNR was uniformly dispersed in the epoxy resin till 1 wt% after that DNR started accumulating at some places and that lead to decreasing mechanical properties.

III. It is also seen that flexural strength increases with increasing wt% of DNR till 1% and after that decreases.

From above this can be observed that 1 wt% of DNR is an optimum concentration for further mixing of reinforcing particles and fibres. Keeping this in mind neat epoxy blended with 1wt% of DNR was taken as a base matrix material and almond shell particles at different concentration were mixed and properties were examined.

Effect of reinforcing almond shell particles

I. The rate of water absorption increases with the increase in weight percentage of almond shell particles. Thickness swelling is approximately same for all type of bio-composites.

II. Increase in the concentration of almond shell particles in epoxy resin enhanced the thermal stability of the material.

From the various mechanical tests it is seen that 20 wt% of almond shell particles is the optimum concentration, at this concentration the material showed optimum mechanical properties. SEM showed the uniform dispersion of almond shell particles in the composite material. And this was also seen that failure of the material is due to matrix cracking or pooling out of almond shell particles.

References

Huang, Y. and Kinloch, A.J. (1992)*(a):* the toughness of epoxy polymer containing micro voids. *Polymer,* 33: 1330-1332.

Huang, Y. and Kinloch, A.J. (1992)*(b):* the sequence of initiation of the toughening micro mechanisms in rubber-modified epoxy polymers. *Polymer,* 33: 5338-5340.

Ramos, V.D. Costa, H.M.D. Soares, V.L.P. and Nascimento, R.S.V. (2005): Modification of epoxy resin: a comparison of different types of elastomer. *Polym. Test.,* 24: 387-394.

Jin, F.L. and Park, S.J. (2007): Improvement in fracture behaviors of epoxy resins toughened with sulfonated poly (ether sulfone). *Polym. Degrad Stab.,* 92: 509-514.

Zhi-hua, L. Yao-peng, H. Dong-yan, R. and Zi-qiao, Z. (2008): Structural characteristics and properties of polyurethane modified TDE-85/MeTHPA epoxy resin with interpenetrating polymer networks. *J. Cent. South University Technology*, 15: 305-308.

Zhou, Y.X. Wu, P.X. Cheng, Z.Y. Ingram, J. and Jeelani, S. (2008): Improvement in electrical, thermal and mechanical properties of epoxy by filling carbon nanotube. *Polym. Lett.,* 2: 40-48.

Bucknall, C.B. and Gilbert, A.H. (1989): Toughening tetrafunctional epoxy resins using polyetherimide. *Polymer,* 30: 213-217.

Chikhi, N. Fellahi, S. and Bakar, M. (2002): Modification of epoxy resin using reactive liquid (ATBN) rubber. *Eur. Polym. J.,* 38: 251-264.

Saadati, P. Baharvand, H. Rahimi, A. and Morshedian, J. (2005): Effect of modified liquid rubber on increasing toughness of epoxy resins. *Iranian Polym. J.,* 14: 637-646.