

Characterization of Biocomposites Based on Mussel Shell Wastes

Suheyila Kocaman, Gulnare Ahmetli, Alaaddin Cerit, Alize Yucel, Merve Gozukucuk

Abstract—Shell wastes represent a considerable quantity of byproducts in the shellfish aquaculture. From the viewpoint of ecofriendly and economical disposal, it is highly desirable to convert these residues into high value-added products for industrial applications. So far, the utilization of shell wastes was confined at relatively lower levels, e.g. wastewater decontaminant, soil conditioner, fertilizer constituent, feed additive and liming agent. Shell wastes consist of calcium carbonate and organic matrices, with the former accounting for 95-99% by weight. Being the richest source of biogenic CaCO_3 , shell wastes are suitable to prepare high purity CaCO_3 powders, which have been extensively applied in various industrial products, such as paper, rubber, paints and pharmaceuticals. Furthermore, the shell waste could be further processed to be the filler of polymer composites. This paper presents a study on the potential use of mussel shell waste as biofiller to produce the composite materials with different epoxy matrices, such as bisphenol-A type, CTBN modified and polyurethane modified epoxy resins. Morphology and mechanical properties of shell particles reinforced epoxy composites were evaluated to assess the possibility of using it as a new material. The effects of shell particle content on the mechanical properties of the composites were investigated. It was shown that in all composites, the tensile strength and Young's modulus values increase with the increase of mussel shell particles content from 10 wt% to 50 wt%, while the elongation at break decreased, compared to pure epoxy resin. The highest Young's modulus values were determined for bisphenol-A type epoxy composites.

Keywords—Biocomposite, epoxy resin, mussel shell, mechanical properties.

I. INTRODUCTION

GOOD mechanical strength, electrical and chemical resistance, good thermal insulation and good adhesion to most fibers and fillers have made that epoxy resins are attracting as thermosetting resins. Nowadays, it is possible to find epoxy resins in a wide variety of products; aerospace industry, automotive industry, adhesives, glues, paints, surface coatings, nautical materials, electrical and electronic components [1].

Canning industry generates great amounts of seashell wastes from different mollusks such as barnacles, mussels, clams, scallops and oysters. Calcium carbonate is the primary mineral content in the seashell of mollusks. Also, mussel shell is a hard ceramic material which can be used in the

formulation of medicine, in construction or as filler in polymer materials [2]. World production of mussels in the last twenty years has increased almost two-fold. Mussel shell recycling plants converts it into calcium carbonate of 96% purity, which can then be used in the chemical industry as fertilizer, an animal feed additive or in construction [3]-[5]. But there are limited studies in mussel shell used as filler in epoxy based composites. Hamester et al. [6] used calcium carbonate from mussel and oyster shells as filler in polypropylene. Chong et al. [7] obtained fire-retardant plastic material from oyster-shell powder and recycled polyethylene. The seashell reinforcement in poly(methyl methacrylate) improves compressive strength and wear resistance [8].

The aim of this study was to preparation of biocomposites reinforced with mussel shell using various epoxy resins and to investigate its mechanical properties.

II. EXPERIMENTAL

A. Materials

A commercially available bisphenol A-type diluted epoxy resin NPEK 114, polyurethane modified bisphenol A-type epoxy resin NPER-133L and CTBN rubber modified bisphenol A-type epoxy resin NPER-450 (Konuray Chemical Co.) were used during the experimental studies (Table 1).

TABLE I
TYPICAL PROPERTIES OF USED EPOXY RESINS

	NPEK-114L	NPER-133L	NPER-450
Physical state	Liquid	Liquid	Liquid
Epoxy equivalent weight (g/eq)	190~210	195~240	450~500
Color (Gardner)	1.0 max	1.0 max	12.0 max
Hydrolyzable chlorine content (ppm)	0-400	-	-
Flash point (°C)	>150	-	-
Viscosity (cps at 25 °C)	550~750	10000~16000	250000~400000
Density (g/cm ³ 25°C)	1.16	-	-

MNA (Methyl Nadic Anhydride): A mixture of methyl isomers of methyl-5-norbornene-2,3-dicarboxylic anhydride and 2,4,6-Tris(dimethylaminomethyl)phenol (Sigma-Aldrich) were used as curing agent and epoxy embedding medium accelerator, respectively.

The mussel shell (MSh) used in this experimental research was obtained from Black Sea Region (Fig. 1), washed with hot soapy water, dried and crushed into smaller pieces manually. Thereafter, the shell powder was obtained by grinding in a mill and sieved. Table II presents the chemical composition of MSh.

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Fig. 1 MSh waste

TABLE II
CHEMICAL COMPOSITION OF MSH [3]

Oxides	%
CaO	95.7
K ₂ O	0.5
SiO ₂	0.9
SrO	0.4
Fe ₂ O ₃	0.7
MgO	0.6
Al ₂ O ₃	0.4

B. Composite Preparation

The bio-based MSh filler (particle size < 63 μm) with various wt% (10-50 wt%) and epoxy matrices were mixed with mechanical stirring (stirring rate of 2000 rpm) for 3 h and ultrasounded for 1 h at 60 $^{\circ}\text{C}$ in order to obtain a good dispersion. Afterwards, the curing agent at 40 wt% and epoxy accelerator (1 wt%) were added, and the mixture was degassed

for 60 min at room temperature and then transferred into the mold. Samples were prepared in stainless-steel molds according to ASTM D 638 standard. The curing temperature for MNA is 120 $^{\circ}\text{C}$.

C. Analysis and Testing

The FTIR spectra of the composites were recorded with Bruker-Platinum ATR- vertex 70 between 500 and 4000 cm^{-1} wavenumbers at a resolution of 4 cm^{-1} using an attenuated total reflectance (ATR) accessory.

A Shore Durometer TH 210 tester was used for measuring the hardness of the samples.

The resistances to stretch properties were determined by Stretch and Pressing Equipment TST-Mares/TS-mxe.

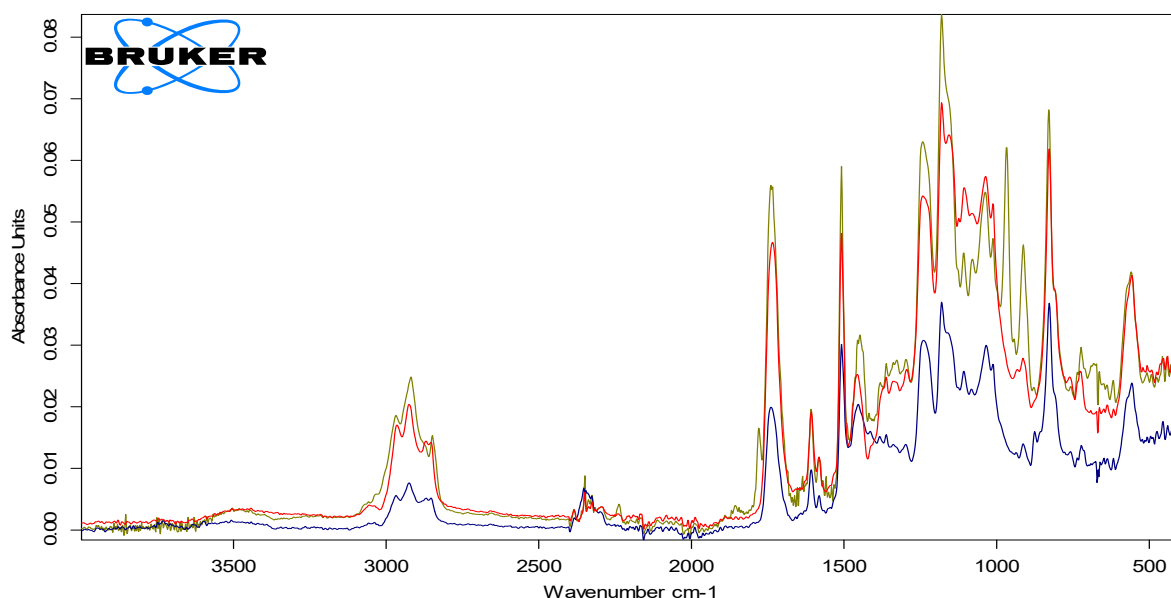
According to the Beer-Lambert law, the absorption peak at 1600-1616 cm^{-1} of a benzene ring can be regarded as an internal standard; thus, the degree of curing can be determined from the FTIR spectra of uncured and cured epoxy [9].

III. RESULTS AND DISCUSSION

A. Curing Degrees

FTIR spectra of cured epoxy resins and composites with 50 wt% MSh were shown in Figs. 2 and 3.

The presence of epoxide groups is characterized by the appearance of typical bands at 1250, 913, and 830 cm^{-1} . The absorption assigned to C–O stretching of the epoxide at 906 cm^{-1} almost disappeared after curing in the neat epoxy resin.



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Fig. 2 FTIR spectra of cured neat epoxy resins

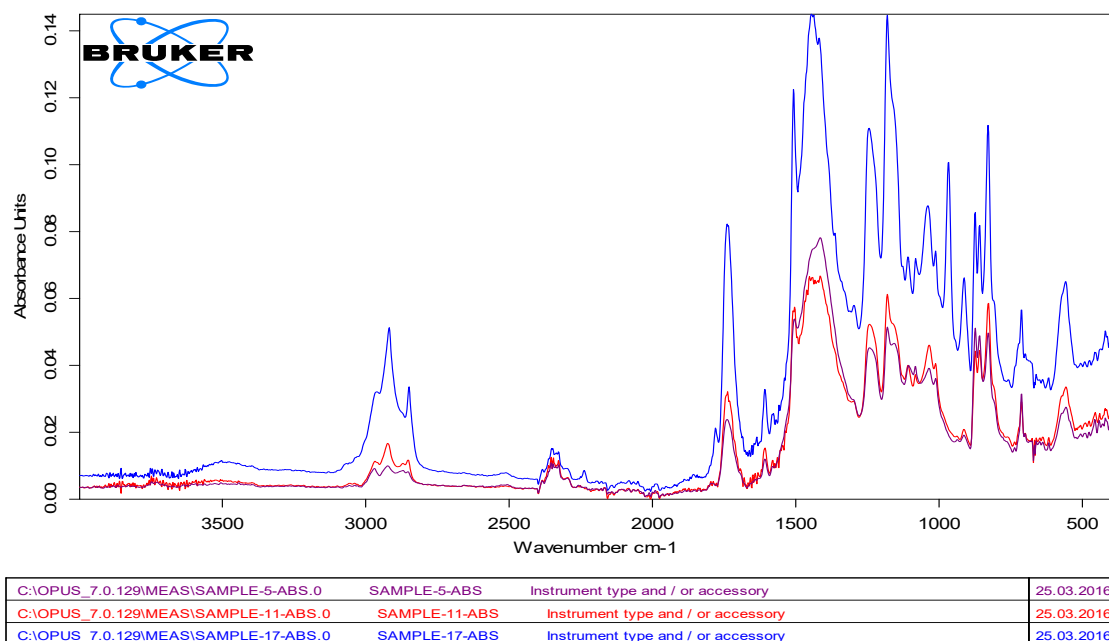


Fig. 3 FTIR spectra of composites with 50 wt% MSh

As can be seen from Figs. 2 and 3, the band at 906 cm^{-1} decreased in neat epoxies and composites in the order of PU modified epoxy > CTBN modified epoxy > Bisphenol-A type epoxy resin.

The calculated curing degrees of bisphenol-A type, CTBN modified and PU modified epoxies were 99%, 97% and 83%, respectively. Curing degrees of composites changed in the range of 98-79%.

B. Mechanical Properties of Composites

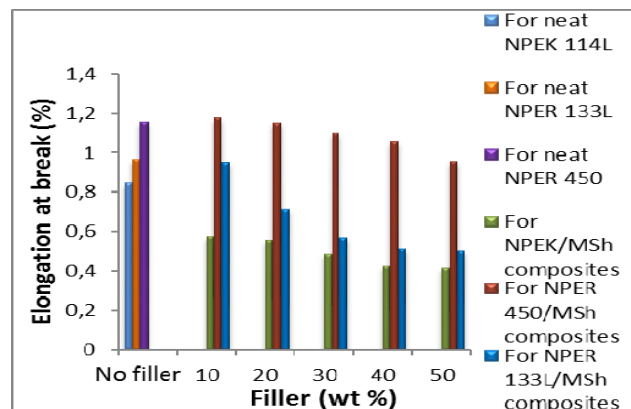


Fig. 4 Elongation % of composites

The mechanical properties of composites are critically based on the microstructure and performance of the interface between the reinforcing filler and matrix. The strength of the bond between the resin and fiber is not solely dependent on the adhesive properties of the resin system, but is also affected by the surface coating on the reinforcement fibers. Among the other resins, such as polyesters or vinyl ester resins, epoxy systems offer the best performance due to their chemical

composition and the presence of polar hydroxyl and ether groups.

To investigate the tensile strength, elongation at break, and hardness of the composites, mechanical testing was performed. The results are summarized in Figs. 4-7. It can be seen from Figs. 4-7, that all composites show higher elastic (Young's) modulus and tensile strength than the neat epoxy matrices. The improvement in strength and modulus can be attributed to the high strength and high aspect ratio of MSh particles as well as to the uniform distribution and good interfacial adhesion between the particles and the epoxy matrices. As the MSh wt% increased, the hardness of the composites increased, too. The hardness measurements showed similar results to the tensile strength, since there is a co-relationship between the hardness and the tensile strength in terms of mechanical property. The rigid filler usually decreases the elongation of the matrix. As seen from Fig. 4, the elongation of neat epoxy resins decreased in all MSh contents. The tensile strength values were determined for bisphenol-A type epoxy (NPEK), PU modified epoxy (NPER 133L) and CTBN modified epoxy (NPER 450) as 62 MPa, 46 MPa and 25 MPa, respectively. Reinforcement of epoxies with bio-based filler increased its tensile strength. The appropriate amount of rigid filler for optimal tensile strength values for composites was determined as 40 wt%. The tensile strength values at this MSh dose were 86 MPa, 56 MPa and 43 MPa (Fig. 5). Also, Young's modulus and hardness of composites were found higher than neat epoxy resins (Figs. 6 and 7)

In many materials, the applied stress is directly proportional to the resulting strain (up to a certain limit), and a graph representing these two quantities is a straight line. Brittle materials, such as ceramics, do not experience any plastic deformation and will fracture under relatively low stress [10].

For practical purposes, it is often useful to divide polymeric materials into five common classes depending on their stress-strain behaviour. As the polymer is hard and brittle, the e-modulus is high and elongation at break is low. For soft and tough polymer, the e-modulus is low and elongation at break is high value [11].

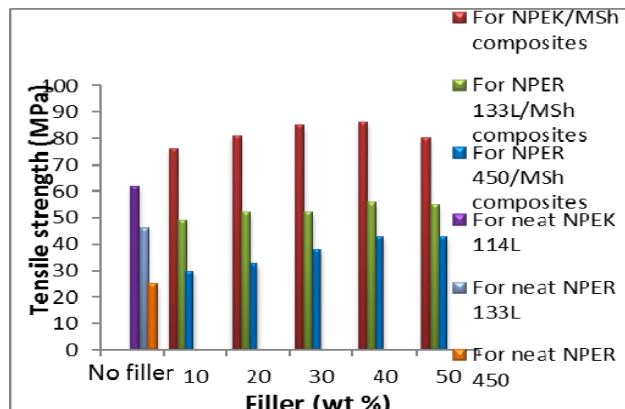


Fig. 5 Tensile strength of composites

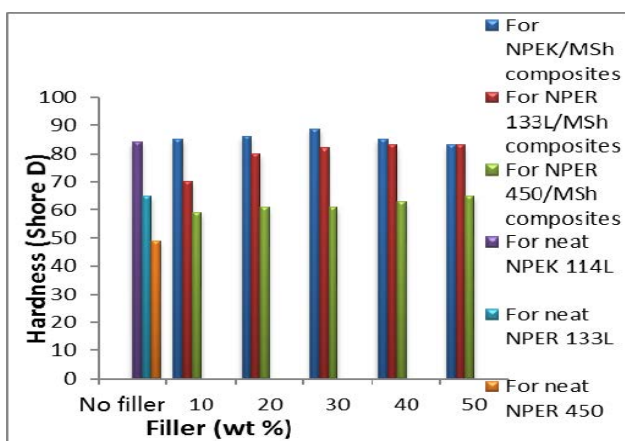


Fig. 6 Hardness of composites

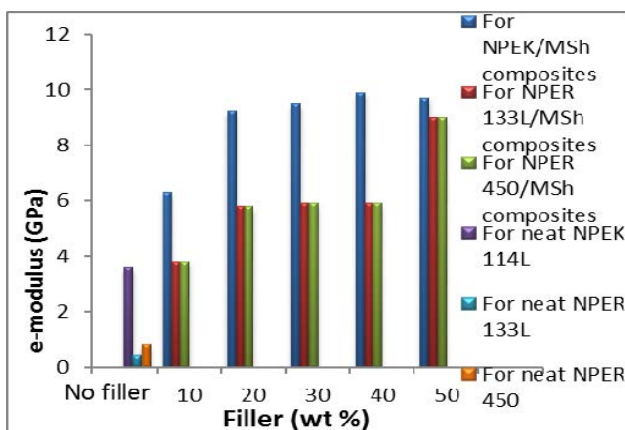


Fig. 7 Young's modulus of composites

The main conditions influencing the ductile/brittle aspect of composites are the temperature, the nature of the polymer matrix and fillers. The nature of the polymer matrix is strongly dependent upon its degree of cross-linking. Therefore, epoxies are generally less ductile than thermoplastic materials. Unlike strictly elastic materials, polymer-based materials can show limited or even no linearity in the stress-strain behavior [12]. The tensile stress-strain curves of MSh composites are shown in Fig. 8.

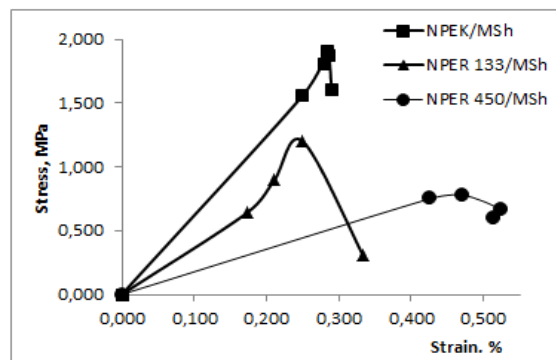


Fig. 8 Stress-strain curves of composites

IV. CONCLUSION

Mussell shell waste was used to prepare 10-50 wt% MSh/epoxy composites. Curing degree and tensile properties of a various epoxy resins reinforced with waste filler were determined experimentally. Mechanical properties were enhanced in all filler amounts.

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