Bulgarian Chemical Communications, Volume 57, Special Issue E (pp. 83-86) 2025 DOI: 10.34049/bcc.57.E.SIMNS12

Preparation and analysis of epoxy/organoclay composites – structural characterization and mechanical properties

V. A. Angelov[1,2]*, R. K. Krastev[1], T. T. Batakliev[1,2]

[1]*Institute of Mechanics, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl. 4, 1113 Sofia, Bulgaria*

[2]*Center of Competence for Mechatronics and Clean Technologies "Mechatronics, Innovation, Robotics, Automation and Clean Technologies" MIRACle, Bulgaria*

Received: April 02, 2025; Revised: July 09, 2025

The present research aims to obtain epoxy composites with organoclay filler and to investigate some of their mechanical properties. Epoxy composites were obtained at the Laboratory "OLEM" of the Institute of Mechanics-BAS and the mechanical characteristics (Young's modulus and strength in compression) were tested on a TIRAtest 2300 machine. Epoxy composites with fillers - C20A, C30B, 1.44 P, 1.28 E, 1.31 PS showed worse mechanical properties than neat epoxy resin. Composites with organoclay 1.34 TCN showed slightly better mechanical properties, compared to pure epoxy resin. X-ray diffraction (XRD) measurements were performed on the organoclay epoxy composites. Using the peak position (2θ) in the XRD patterns, the inter-layer spacing was calculated through Bragg's law.

Keywords: Preparation, organoclay, epoxy resin, XRD

INTRODUCTION

Polymer-clay nanocomposites (PCNs) are a new class of materials consisting of a polymer matrix and nanoclay as a reinforcing filler [1, 2]. Depending on the application, the polymer matrix can be thermoset, thermoplastic, rubber, or co-polymers. The first PCN, synthesized by the Toyota R & D group in Japan in 1992, used nylon-6 as the matrix and nanoclay as the filler, marking an important milestone in the development of high-performance composite materials.

One of the main reasons for the growing interest in PCNs is the unique reinforcement potential of layered silicate clays, which offer a high aspect ratio, large surface area, and low cost. However, untreated clay is naturally hydrophilic and therefore not easily dispersed in most polymers, which are typically hydrophobic [3]. This incompatibility often results in poor dispersion and limited improvements in the final material properties.

To overcome this challenge, various surface modification techniques have been developed to enhance clay compatibility with organic polymers. Among these, organo-treated montmorillonite clay has emerged as one of the most widely used nanofillers due to its superior compatibility with polymer matrices, high specific surface area, aspect ratio, and improved dispersibility at the nanoscale [4].

Montmorillonite, a nanoclay mineral belonging to the smectite group, has a layered structure and high cation exchange capacity, which enables ion exchange with its environment [5]. This versatile mineral is commonly found in bentonite deposits formed from volcanic ash weathering, with significant sources in the United States, China, and Greece, among other regions [6]. Such properties make it suitable for surface modification to enhance compatibility with epoxy resins.

Despite the advantages of organoclays, challenges remain in maintaining their structure during composite preparation. For example, when used as a nanofiller, Cloisite® 30B (C30B) often undergoes d-spacing collapse, as demonstrated by the shift to wider angles in the XRD basal reflection. This collapse has been attributed to contamination or, more often, to thermal degradation of the organic modifier during processing [7]. Recent work has shown that factors such as filler content, particle size, and environmental exposure can significantly affect the structural stability and performance of these composites [9–11].

In this study, epoxy/organoclay composites were prepared and systematically analyzed to address these challenges. In particular, the work focuses on a comparative investigation of different organoclay fillers in epoxy resin systems — an area that is not widely studied. By comparing the structural

* To whom all correspondence should be sent:
E-mail: *v.angelov@imbm.bas.bg*

characteristics and mechanical properties of composites prepared with various organoclay modifications, this research aims to clarify how different treatments affect clay dispersion, interlayer spacing, and the overall performance of the final material. The goal of this work is to achieve improved compressive strength through the preparation of composites with intercalated structures. This study aims to provide new insights that will support the development and optimization of high-performance epoxy/organoclay nanocomposites.

EXPERIMENTAL

Materials

In the present study, several organoclays were used as fillers in the epoxy resin (matrix) to produce organoclay-epoxy composites. Clay Cloisite® 30B (Southern Clay Products, Inc.), organically modified with methyl tallow bis-2-hydroxyethyl quaternary ammonium chloride (MT2EtOH); Clay Cloisite 20A (Southern Clay Products, Inc.), containing organic modifiers - dimethyl, dihydrogenated tallow, quaternary ammonium; Nanoclay I.44P containing an organic modifier - 35-45 wt. % of dimethyl dialkyl (C14-C18) amine; Nanoclay I.31PS containing 15-35 wt. % of octadecyl-amine, 0.5-5 wt. % of aminopropyltriethoxysilane; Nanoclay I.34TCN containing 25-30 wt. % of methyl dihydroxy-ethyl hydrogenated tallow ammonium; and Nanoclay I.28E containing 25-30 wt. % of trimethyl stearyl ammonium. All nanoclays are produced by Sigma-Aldrich.

Epoxy resin prepolymer Epilox T 19-38/500 (liquid oligomer, η = 450−550 mPa.s at 25 °C) and amine hardener Epilox H 10–30 (η = 200−300 mPa.s at 25 °C) were purchased from Leuna-Harze GmbH (Germany) and were used as received.

Preparation method

All organoclays were dried at 80 ºC for 8 h at the start of the preparation protocol. For the preparation of binary nanodispersions, the appropriate amount of organoclay was added to the liquid epoxy resin oligomer and the mixture was homogenized for 30 min by mechanical mixing at 10 000 rpm, followed by 30 min ultrasonication treatment at 250 W. The obtained clay/epoxy nanodispersions were then degassed in a vacuum set. The solid binary clay/epoxy nanocomposites were prepared from the nanodispersions using an *in-situ* polymerization method. The appropriate amount of the amine hardener was added to the respective dispersions at a molar ratio of *epoxy resin:hardener = 100:49*. The mixture was poured into a cylindrical mold and cured for 24 h at room temperature followed by post-curing at 100 °C for 4 h.

Characterization methods

The moisture content in the organoclays before and after the drying procedure was measured using the moisture analyzer MX-50 from A&D Company Ltd. The moisture content is determined on a wet basis, meaning it is calculated as the difference between the wet sample mass and the dried sample mass, divided by the wet sample mass, and expressed in percentage. The X-ray diffractograms were obtained by using Bruker D8 Advance diffractometer with Cu Kα radiation (λ = 0,15418 nm) and LynxEye detector.

The mechanical properties (Young's modulus and compressive strength) were tested on a TIRAtest 2300 machine at the Institute of Mechanics - BAS. The specimens with 15 mm initial diameter and 29 mm height were compressed at a velocity of 2 mm/min.

RESULTS AND DISCUSSION

Powder XRD analysis

The prepared composites were analyzed using XRD to determine the distance between the organoclay layers in the prepared epoxy-organoclay composites. The inter-layer spacing increases in the intercalated composites shown in Fig. 1b, which is associated with improved mechanical properties of the produced materials [12, 13].

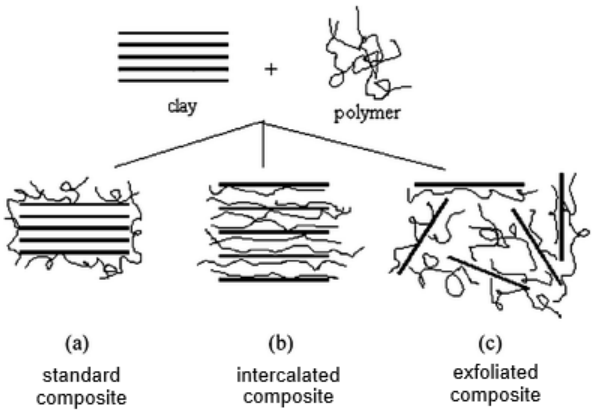

Fig. 1. Types of composites [14]

For all organoclays, the distances between the layers, reported by the producer, are summarized in Table 1. These distances were compared to the measured distances between the layers in the prepared composite. Based on this, the type was inferred, the increase of the inter-layer distance indicating intercalated composite type.

Table 1. Distance between the layers of organoclays

Samples (powder)	Distance (nm)
C30B	1.81
C20A	2.32
1.44 P	2.66
1.34 TCN	1.86
1.31 PS	2.18
1.28 E	2.45

The moisture content in the organoclays was reduced using a drying process to improve the homogenization process. The drying process was controlled by measuring the moisture content before and after the drying.

The results shown in Table 2 indicate that all organoclays were well dried after the drying procedure. The thermal treatment of the organoclays is reported to have an impact on the inter-layer distance [8]. In the current study, the inter-layer distance was not measured after the drying process, but was left as a subject to a future study.

Table 2. Moisture content of organoclays

Samples (powder)	Moisture content (%)	
	Before drying	After drying 80 °C / 8 h
C30B	1.4	0.1
C20A	1.4	0.1
1.44 P	1.0	0.1
1.34 TCN	1.5	0.1
1.31 PS	0.8	0.1
1.28 E	2.5	0.1

The X-ray diffraction patterns of epoxy composites with the six types of organoclays are illustrated in Fig 2.

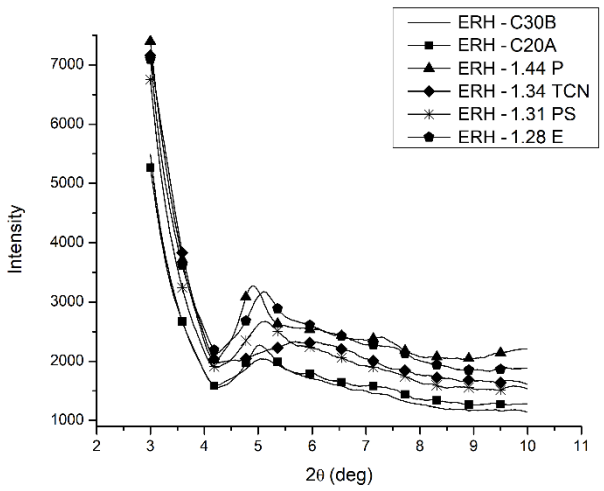

Fig. 2. XRD patterns of the obtained epoxy composites.

Using the peak position (2θ) in the XRD patterns, the inter-layer spacing was calculated through Bragg's law:

$$n\lambda = 2\mathrm{d}\sin\theta$$

where λ is the wavelength of the incident wave (λ = 0.15418 nm), d is the spacing between the layers of organoclay in the composites.

The inter-layer spacing values calculated from the XRD analysis of the six composites are summarized in Table 3. In all six composites, a collapse of silicate layers (decrease in inter-layer distance) was observed. This suggests that the prepared composites are of the standard type indicated in Fig. 1a.

Table 3. Distance between the layers of organoclays in the epoxy composites shown in Fig. 2.

Samples (composites)	2θ (deg)	Distance (nm)
ERH - C30B	5.087	1.74
ERH - C20A	5.028	1.76
ERH - 1.44 P	4.910	1.80
ERH - 1.34 TCN	5.894	1.50
ERH - 1.31 PS	5.126	1.72
ERH - 1.28 E	5.107	1.73

Mechanical properties

The comparison of the Young's modulus of the six composites with that of neat epoxy resin is shown in Fig. 3.

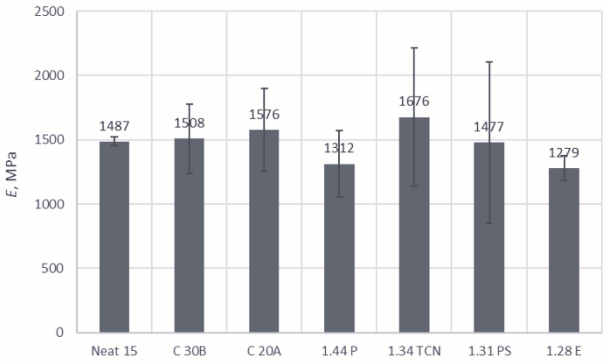

Fig. 3. Young' modulus of neat epoxy resin and organoclay-epoxy composites.

All the composites showed a higher dispersion of results than the neat resin. The 1.34 TCN composite indicated a higher elastic modulus, while 1.44 P and 1.28 E composites had lower moduli.

In Fig. 4 the compressive strength of the prepared composites was compared to that of neat epoxy resin. The results are similar to those for the modulus. There was only a slight improvement in the compressive strength of the composite 1.34 TCN. Composites C30 B and C20 A showed similar strength, and the rest of the composites showed a

decrease in the compressive strength. All tested samples showed elastic behavior up to about 2.6% deformation, with peak compressive strength occurring near 5% strain.

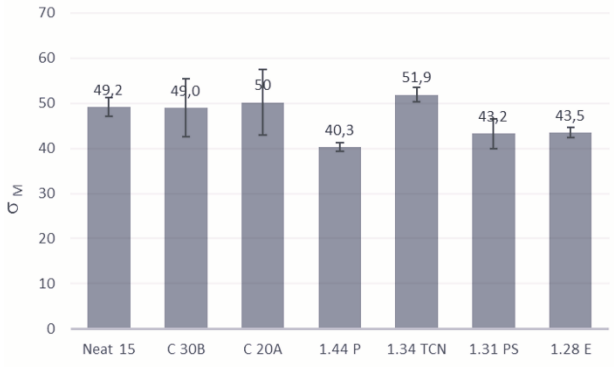

Fig. 4. Compressive strength of neat epoxy resin and organoclay-epoxy composites.

CONCLUSION

In the present study, several different nanofillers (organoclays) were investigated - C30B, C20A, 1.44 P, 1.34 TCN, 1.31 PS and 1.28 E. In all the six synthesized nanocomposites we observed a collapse of silicate layers (inter-layer distance has decreased). Only the epoxy nanocomposite with 1.34 TCN nanofiller showed slightly better mechanical properties than neat epoxy resin. The XRD diagram of the composite with 1.34 TCN organoclay showed the lowest inter-layer spacing compared to the other composites. The measurement of the impact of the drying procedure on the inter-layer spacing in the organoclays and its potential contribution to the collapse of silicate layers, observed in the final composites, is left as a subject for future study.

Acknowledgement: *This work is supported by the Competence Center for Mechatronics and Clean Technologies — MIRACle, developed by the Operational Programme "Science and Education for Smart Growth" (2014–2020) and Program "Research, Innovation and Digitalization for Smart Transformation" 2021-2027 (PRIDST), co-financed by the European Union through the European Structural and Investment Funds. The authors would like to express also their sincere gratitude to the Bulgarian National Science Fund (BNSF) under Grant No. KP-06-H77.*

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