

# Preparation and Characterization of Transparent Advanced Smart Nanocomposites Reinforced by Nanofibrillated Cellulose/Poly(methyl methacrylate)/Methyl methacrylate/Benzoyl Peroxide

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Transparent smart nanocomposites, which are among the advanced materials, were developed with the synergistic effect of nanofibrillated cellulose (NFCs) as a natural bionanomaterial, polymethyl methacrylate (PMMA) as a biocompatible microcapsule, methyl methacrylate (MMA) as a monomer, and benzoyl peroxide (BPO) as an initiator and catalyst. Epoxy resin was reinforced with NFC, PMMA, MMA, and BPO. Casting, which appears to be an industrially promising method that allows for cost-effective and high-quantity production, was used for producing transparent advanced nanocomposites. The properties of the nanocomposites, including yield strength, modulus of elasticity, hardness, impact energy, and self-healing capability, were determined. Increases in the yield strength (136.4%), modulus of elasticity (260%), hardness (28.3%), and impact energy (75%) were observed in the transparent smart nanocomposites reinforced with NFC, PMMA, MMA, and BPO, compared to pure epoxy composites. Furthermore, the transparent advanced smart nanocomposites self-healed by about 7% after the notch/scratch defect. It has the potential to be used in a variety of applications, such as interior and structural components for the aerospace and automotive industries, packaging, flexible screens, and lightweight transparent materials.

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*Keywords:* Epoxy resin; Mechanical properties; Nanofibrillated cellulose; PMMA; Self-healing; Transparent advanced smart nanocomposites

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## INTRODUCTION

The expected properties of materials change along with advancements in technology and production methods. Material science is developing at a much faster rate day by day and aims to produce the most resilient, lightest, and most effective materials with smarter solutions than anticipated.

A composite is a material consisting of two or more different materials that, when combined, have higher performance properties than those individual materials by themselves. A wide variety of industries, including the aerospace, automotive, architectural, marine, and military sectors, use composite materials. However, recovering composite material in the case of damage could not be possible or would be highly expensive. The presence of microcracks in composite materials can result in structural

weakness and vulnerability, as they are difficult to detect and nearly impossible to repair. In addition to external factors, the material can be exposed to mechanical or thermal stresses that result in microcrack formation. The ensuing fracture results in serious damage mechanisms, especially the mechanical deterioration of composites. There are several strategies to eliminate these issues, including distributing the modifier particles throughout the matrix and enhancing the interface properties between the matrix and the reinforcing component (Seyyed Monfared Zanjani *et al.* 2017; Yildirim *et al.* 2021, 2023a, 2024a).

Smart materials, also referred to as intelligent or stimulus-sensitive materials, have emerged as a new class of materials that have a wide range of application areas and solve material problems *in situ* because of their unique properties and responsive nature (Basheer 2020). Advanced materials, known as smart materials, are created to react to external stimuli similarly to biological systems, mimicking their behavior. A new age of materials has begun with recent advances in smart materials, which have the potential to shift several research areas (Yildirim *et al.* 2023b). Smart materials respond to external factors, including pH, pressure, humidity, temperature, and electric and magnetic fields. The advantage of developing these smart materials is that they become stronger, have a longer service life, and/or require reduced repair costs.

Epoxy resin is an important thermosetting polymer. It is commonly utilized as a composite matrix for adhesives and structural materials in the aerospace and electronics industries (Jin *et al.* 2015). The reaction of epichlorohydrin and bisphenol A in the basics produces 95% of epoxy resins. However, epoxy resins are inherently brittle and notch-sensitive due to their highly cross-linked structure (Chi *et al.* 2022). Due to their low impact strength, fracture toughness, and poor resistance to crack propagation, cured epoxy systems are restricted in their use in high-performance applications. As several studies have indicated, adding fiber reinforcements can actually make the material more brittle, which poses a big problem for researchers. Various materials have been utilized to improve the toughness of epoxy resins, including inorganic nanoparticles, carbon-based nanomaterials, block copolymers, and natural macromolecules (Zweifel *et al.* 2023). While there are inherent challenges to dealing with fragile behavior, efforts are being made to develop novel approaches and formulations that can reduce fragility while utilizing the advantages of NFC reinforcement for transparent smart nanocomposites.

The significance of bio-based polymers has increased recently, and research into them has become increasingly important. Sustainable development and environmentally friendly products are gaining popularity on a global scale day by day (Yildirim *et al.* 2024b). Globally, green biomaterials have become a new image for both products and brands. Lignocellulosic materials have been referred to by the international scientific community as “biomaterials.” The three main structural components of lignocellulosic biomaterials are cellulose, lignin, and hemicellulose. A natural and sustainable biopolymer, cellulose is one of the most abundant materials in the world. A linear semi-crystalline homopolymer, it consists of anhydroglucose units linked by  $\beta$ -(1-4)-d-glucosic bonds (Dufresne 2020). Plants are the main source of cellulose, but it can also be produced by algae, tunicates, and some types of bacteria.

The word “nanocellulose” describes cellulose with a nanostructure. Nanocellulose is commonly divided into three main categories based on its shape, size, source, and preparation method (Candan *et al.* 2022). These are nanofibrillated cellulose/cellulose nanofibril (NFC/CNF), nanocrystalline cellulose/cellulose nanocrystal (NCC/CNC), and bacterial nanocellulose (BNC) (Yildirim and Candan 2021a; Yildirim *et al.* 2021b). Nanofibrillated cellulose is an effective filler among many other sustainable lignocellulosic

bionanomaterials for reinforcing transparent plastics without impeding their transparency. NFC has nanometer-scale size, a reflecting index that is similar to that of plastics, cost-effectiveness, a high specific surface area, an excellent aspect ratio, excellent mechanical qualities, and an inherent low density and low thermal expansion coefficient (Yildirim *et al.* 2023b).

Poly(methyl methacrylate) (PMMA), also known as acrylic or plexiglass, is widely utilized in a variety of areas, including automotive, construction, lighting, biomedical, optical, and sensor applications, due to its unique properties such as optical transparency, low density, excellent chemical resistance, low moisture absorption, and good insulation (Ali *et al.* 2015; Erbas Kiziltas *et al.* 2015; Pawar 2016). PMMA transmits 92% of the sunshine and has a refractive index of 1.492. The two main factors that affect light scattering by the composite are the particle size, or aggregation of particles, and the difference in refractive indices between the matrix and the fillers. Various methods have been developed to minimize the amount of light scattered by the particle in order to achieve optimal composite transparency. The strategies most frequently used include particles much smaller than a wavelength of light, greater compatibility at phase boundaries so that no particles are stuck in the composite, an absence of clusters of reinforcing particles, and components with matching refractive indexes (Loste *et al.* 2018). In terms of optical transparency, PMMA is comparable to glass and polycarbonate (PC) (Ibeh 2011). PMMA is lighter than glass and less costly than PC (Ali *et al.* 2015; Pawar 2016). Despite the strong mechanical properties of PC, PMMA is the preferred material for nanocomposite formulation due to its transparency, compatibility with additives, and ease of processing. The global market for PMMA is expected to reach 14 billion USD by 2027, with a compounded annual growth rate of close to 5% and prices starting at 4.5 dollars per kilogram (De Tommaso and Dubois 2021; Chub *et al.* 2022). PMMA, a highly transparent thermoplastic composed of polymerizing methylmethacrylate (MMA) monomer, has a lot of potential, but its mechanical-dynamic properties (low strength, impact resistance, storage modulus, *etc.*) limit its effective use in engineering applications (Liu *et al.* 2010). The mechanical strength of PMMA is still inadequate for many modern applications. These drawbacks can be addressed by reinforcing with nano- and micro-fillers (Nussbaumer *et al.* 2003; Chen *et al.* 2009; Tang *et al.* 2010). Also, it is generally necessary to maintain PMMA composites' optical transparency while increasing their mechanical strength and stiffness (Day *et al.* 1997). Furthermore, peroxides are highly effective initiators of polymerization; for example, benzoyl peroxide is utilized as an initiator when polymerizing MMA to form PMMA.

The presence of hydroxyl functional groups in NFC makes it easier to agglomerate. A homogeneous distribution and dispersion of NFC inside the PMMA matrix are required to maximize its mechanical and thermal properties while minimizing its effect on optical properties. Many strategies are used to get around problems such as fiber aggregation in PMMA-based composites reinforced with NFC. These include surface modification, optimizing processing parameters, using dispersion agents, using controlled solvent casting or mixing methods, and adding compatibilizers.

There are some studies of the effects of nanocellulose and PMMA nanocomposites on the optical, viscoelastic, thermal, and tribological properties. According to Banerjee *et al.* (2013) and Sain *et al.* (2014), the addition of modified NFC improved the thermal stability of PMMA due to enhanced bonding between NFC and PMMA. According to Littunen *et al.* (2013), the higher level of compatibility between modified NFC and PMMA lowered transmittance. Erbas Kiziltas *et al.* (2015) determined the increase in storage

modulus, especially at higher temperatures, to be due to nanocellulose's capacity to inhibit PMMA chain movements. Anju and Narayanankutty (2017) found that adding more than 10% NFC lowered storage modulus and attributed the loss to NFC agglomerations. According to Shi *et al.* (2022), the higher tribological performance of NFC/PMMA composites is principally due to the NFCs' longer length and aspect ratio, which enhances mechanical entanglement with the PMMA matrix and hence improves toughness. The mechanical properties of PMMA- and NFC -reinforced composites are still unclear. Moreover, most of the research on self-healing that has been published has to do with nanocellulose hydrogels (Zhang *et al.* 2022; Berglund *et al.* 2023; Cheng *et al.* 2023; Heidarian and Kouzani 2023).

The scientific novelty of this study is to evaluate the synergistic effects of incorporating NFC/PMMA/MMA/BPO filler into the epoxy at different loadings to enhance the mechanical and self-healing properties, thereby expanding the application areas of the transparent nanocomposites.

## EXPERIMENTAL

### Materials

AC510, a two-component, UV-protected, solvent-free transparent epoxy, was used as the matrix. The resin and hardener were supplied from Armor Chemical (Istanbul, Türkiye). Nanofibrillated cellulose (NFC), polymethyl methacrylate (PMMA), methyl methacrylate (MMA), and benzoyl peroxide (BPO) were used as reinforcing components for the epoxy matrix composition. The NFCs were produced at the University of Maine's Advanced Structures and Composites Center (Orono, ME, USA). NFCs have a diameter of 20 nm and a length of one micron. These values are average and do not convey the fact that the structure of the cellulose fibrillar material produced through mechanical refinement is highly complex, with many branches. PMMA, as a biocompatible microcapsule; MMA, as a monomer; and benzoyl peroxide (BPO), as an initiator and a catalyst, were used as reinforcements for the epoxy matrix composition. PMMA (CAS No. 9011-14-7), MMA (CAS No. 80-62-6), and BPO (CAS No. 94-36-0) were supplied from Sigma-Aldrich (Merck KGaA, Darmstadt, Germany).

### Methods

The NFC loading level was used up to 5% in this study, since several other studies indicate that there is a reduction in agglomeration and strength values when the nanomaterial loading level is over 5% in polymer reinforcements. This also makes sense when considering the cost of the product. The producing design of experiments (DoE) for the transparent advanced smart nanocomposites is shown in Table 1.

**Table 1.** Design of Experiments for Control Group and NFC/PMMA/MMA/BPO-reinforced Transparent Advanced Smart Nanocomposites

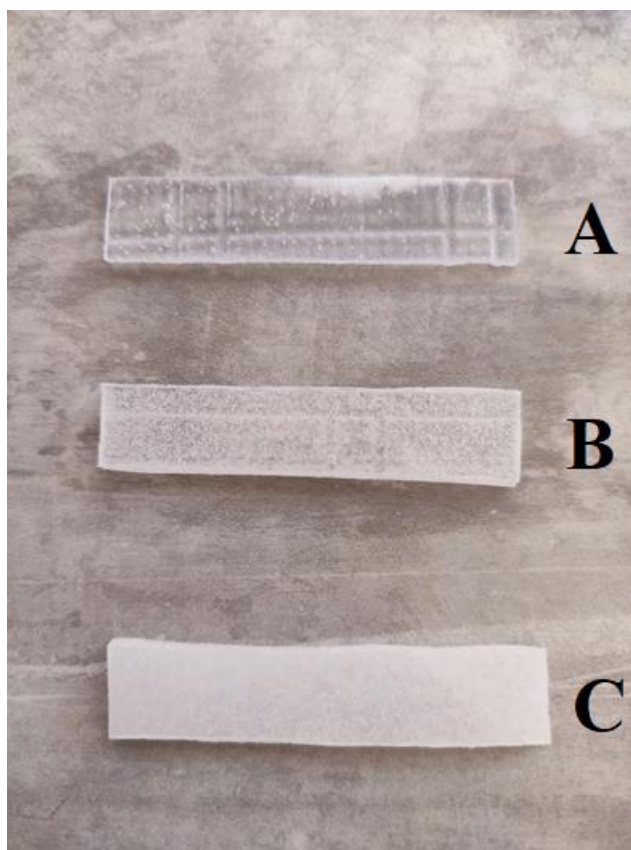
Group ID	NFC (%)	PMMA (%)	MMA (%)	BPO (%)
Control	-	-	-	-
A	1	0.05	0.05	0.005
B	3	0.05	0.05	0.005
C	5	0.05	0.05	0.005

In an ultrasonic homogenizer operating at 2000 rpm for 300 seconds, a 2:1 weight ratio of epoxy and hardener was mixed. NFC was subsequently added to the thoroughly blended epoxy and hardener liquid mixture at weight ratios of 1%, 3%, and 5% under the same homogenization conditions.

In another container, 0.005% BPO by weight of the epoxy mixture was added to 0.05% PMMA by weight of the epoxy mixture and mixed with a wooden stick until homogenized. Similarly, in a separate container, 0.05% MMA by weight of the epoxy mixture was added to 0.05% PMMA by weight of the epoxy mixture and mixed with a wooden stick until homogenous. The purpose of preparing the chemicals separately was to induce interaction and a reaction between them; on the other hand, the purpose of combining them later was to induce the process of polymerization by cross-linking.

The mixture containing BPO was homogeneously mixed with the epoxy prepared with NFC, and the mixture containing MMA was combined in a single container, and the reinforced-liquid mixture was poured onto a one-piece open-mold polytetrafluoroethylene (PTFE) panel. The specimens were then left to cure at room temperature. As a result of the crosslinking and polymerization reactions proceeding in the mold, transparent advanced nanocomposites were obtained by taking the shape of the mold. The samples were left to cure at room temperature for 72 h. At the end of three days, the composites produced were cut to the sample sizes specified in the relevant standard for each analysis. Three specimens were prepared for each group.

Figure 1 shows images of the NFC/PMMA/MMA/BPO-reinforced transparent advanced smart nanocomposites.



**Fig. 1.** Images of the NFC/PMMA/MMA/BPO-reinforced transparent advanced smart nanocomposites

## Characterization

### *Tensile test*

Tensile testing is used to determine a material's ability to withstand loaded tensile stresses before breaking. The tensile test was carried out according to the ASTM D-3039 (2014) standard. After the dog-bone-shaped composites had been prepared, a DVT Devotrans device (Istanbul, Türkiye) was used to carry out a tensile test at a speed of 10 mm/min. Three test specimens were used for each sample, and average results were obtained.

### *Modulus of elasticity*

Ultrasonic velocity testing was carried out to determine the modulus of elasticity of the transparent advanced nanocomposites with an ultrasonic flaw detector (General Electric, USM Go). The modulus of elasticity ( $E$ ) was calculated by the following equation,

$$E = \rho V_T^2 \frac{3V_L^2 - 4V_T^2}{V_L^2 - V_T^2} \quad (1)$$

where  $V_T$  and  $V_L$  are the ultrasonic longitudinal and transverse velocities, respectively, and  $\rho$  is the density.

### *Impact test*

The impact test measures the energy a material absorbs during a fracture. The amount of energy absorbed indicates the toughness of a certain material. The impact test was carried out according to the ASTM D1709-22 (2022) standard. The specimens for the impact test were determined using a Devotrans machine (Istanbul, Türkiye) weight drop impact testing machine. From a height of 1.5 m, loads ranging from 180 to 400 g were applied in 45-g increments. Three test specimens were used for each sample, and average results were obtained.

The impact energy of the nanocomposites was calculated with the following formula,

$$E_p = m \times g \times h \quad (2)$$

where  $E_p$  is potential energy (joule),  $m$  is mass (kg),  $g$  is gravity ( $m/s^2$ ), and  $h$  is height. The acceleration of gravity is equal to the number 9.8, which corresponds to approximately 10.

### *Hardness test*

A hardness test is used to determine a material's resistance to being penetrated by an indenter that resembles a spring-loaded needle. The range of a shore hardness value is 0 to 100. The hardness test was carried out with Shore D according to the ASTM D2240-15 (2021) standard. A device known as a durometer was used to determine the hardness. Durometers have an indenter loaded by a calibrated spring. The measured hardness was determined by the penetration depth of the indentation under load. Three measurements were taken of the upper and bottom surfaces of the produced specimens. Three test specimens were used for each sample, and average results were obtained.

### *Self-healing analysis*

After the nanocomposites were prepared, they were allowed to cure at room temperature, and self-healing analysis was carried out after 72 h.

The extrinsic approach method was used for the self-healing analysis. The extrinsic self-healing mechanism is based on the addition of different reinforcing components to the structure during the synthesis of the matrix resin. PMMA was used as a microcapsule, MMA as a monomer, and BPO as an initiator and a catalyst.

A scratch with a width of 1 mm and a length of 10 to 15 mm was made on the composites, and the closing (self-healing) behavior of the artificial defect (scratch/notch) for 24 hours was monitored with a thermal camera (IR imaging) device (Bosch GTC 400 C). The thermal imager is capable of measuring temperatures between -10 and 400 °C. The resolution of the thermal imager is 0.1 °C.

Sample dimensions for the self-healing analysis are shown in Fig. 2.

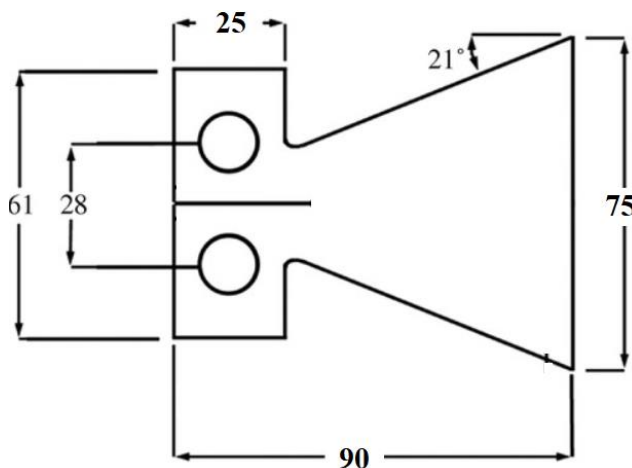


Fig. 2. Sample dimensions for self-healing analysis

## RESULTS AND DISCUSSION

The mechanical analysis results of the control group and NFC/PMMA/MMA/BPO-reinforced transparent advanced smart nanocomposites are presented in Table 2.

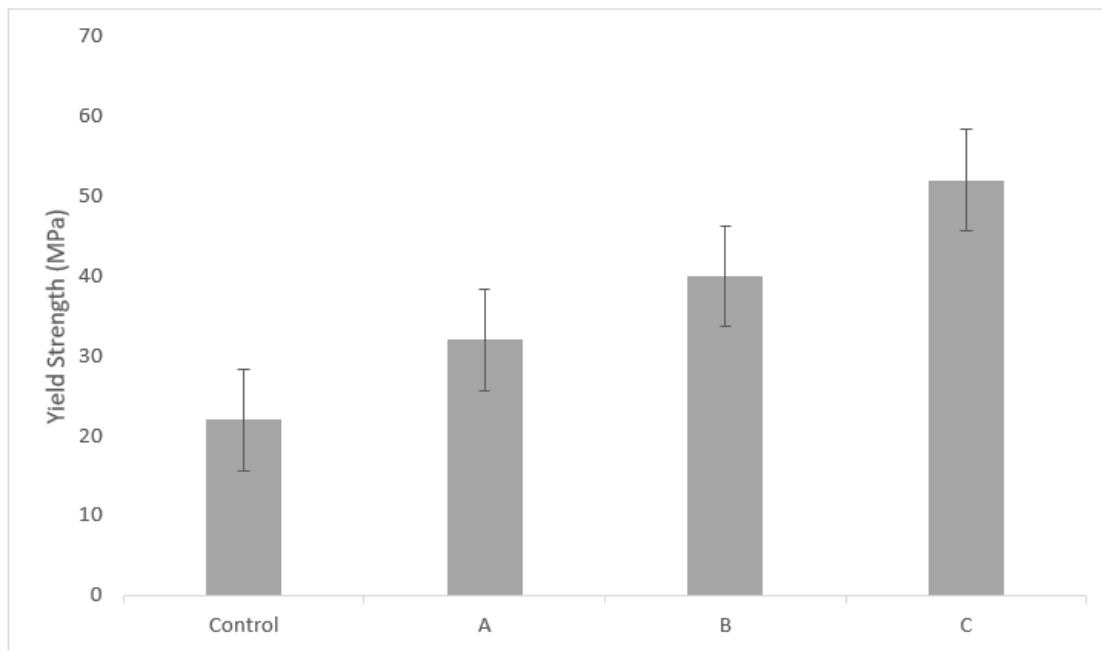
**Table 2.** Mechanical Properties of Control Group and NFC/PMMA/MMA/BPO-reinforced Transparent Advanced Smart Nanocomposites

Group ID	Yield Strength (MPa)	Modulus of Elasticity (GPa)	Hardness (Shore D)	Impact Energy (kJ/m <sup>2</sup> )
Control	22	2.0	60	28
A	32	4.1	62	33
B	40	5.5	69	41
C	52	7.2	77	49

### Yield Strength

Figure 3 shows the yield strength values of the control and reinforced nanocomposites graphically.

The yield strength of reinforced groups incorporating NFC/PMMA/MMA/BPO was found to be higher than that of the control group. The group C had the maximum yield strength at 52 MPa, whereas the control group had the lowest at 22 MPa.



**Fig. 3.** Graphical representation of yield strength values of the control group and NFC/PMMA/MMA/BPO reinforced groups

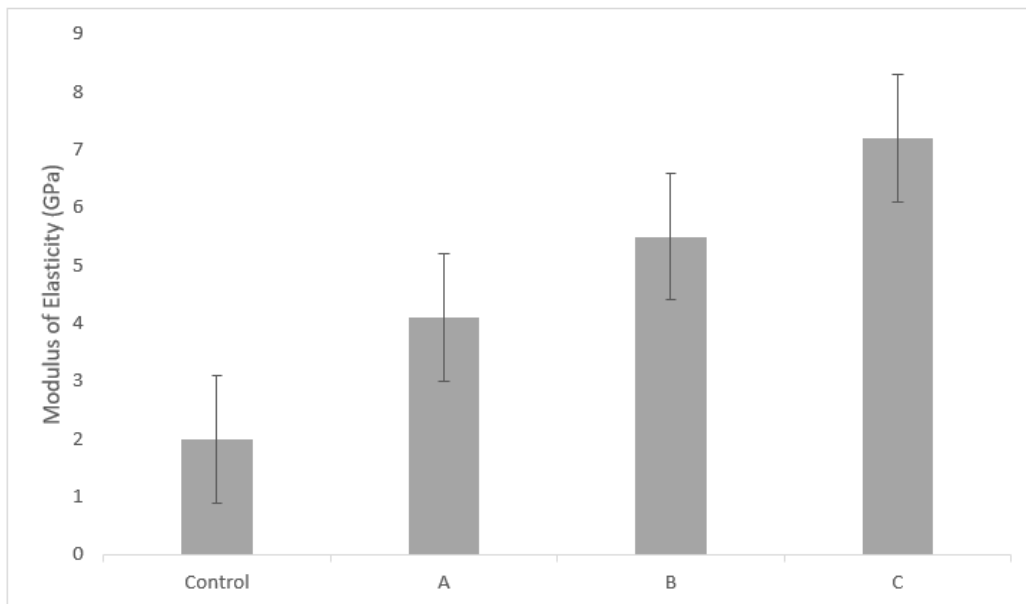
In comparison to the control group, yield strength values in groups A, B, and C increased by 45.5%, 81.8%, and 136.4%, respectively. Increasing the NFC loading amount from 1% to 5% additionally enhanced yield strength. The reinforced nanocomposites were stiffer and tougher than the control groups, as indicated by their higher yield strengths. The high surface area of the NFC provided more contact area, resulting in strong interfacial bonding between the NFC and epoxy matrix. This bonding inhibited fast crack formation and improved stress transfer between the two components. This interaction resulted in increased yield strength in the reinforced nanocomposites.

The results obtained are supported by the results of studies conducted by other scientists. Pruksawan *et al.* (2017) determined that epoxy resin incorporating cellulose nanocrystal (CNC) aggregates significantly increased adhesive strength and fracture toughness compared to the control group. Yeo (2017) investigated the effect of microfibril cellulose-reinforced epoxy composites on fracture toughness. It was reported that GPS-MFC/epoxy composites showed improved interfacial adhesion between the epoxy matrix and cellulosic filler and improved fracture toughness.

### Modulus of Elasticity

Figure 4 shows the modulus of elasticity values of the control and reinforced nanocomposites graphically.





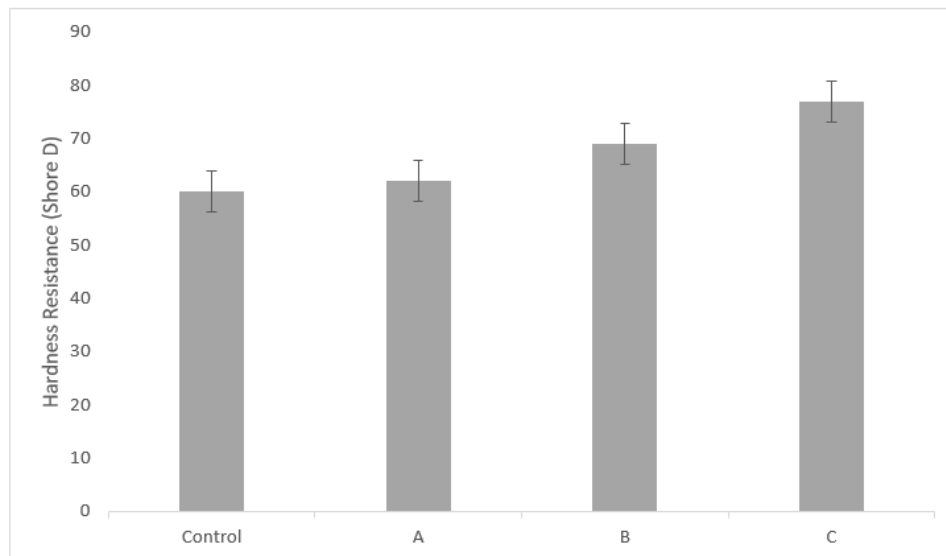
**Fig. 4.** Graphical representation of modulus of elasticity values of the control group and NFC/PMMA/MMA/BPO reinforced groups

The modulus of elasticity followed a similar trend to yield strength, increasing as the NFC loading increased from 1% to 5%. The modulus of elasticity values in groups A, B, and C increased by 105%, 175%, and 260%, respectively, when compared to the control groups. The addition of NFC increased the composites' modulus of elasticity, demonstrating that NFC can stiffen epoxy resins. This increase has been attributed to the nanoscale of the fibrils, which provided more surface area, as well as the good interaction and bonding between the NFC and epoxy matrix, which resulted in higher stress transmission; hence, the elastic deformation of the composites improved.

By incorporating NFC into the epoxy matrix, gaps in composites can be filled, and the void in the polymer fibril matrix can be closed (Svagan *et al.* 2007). As the quantity of empty space between particles decreases, so does the flexibility of the polymer chain, while the modulus of elasticity increases (Abdul Khalil *et al.* 2013). The results obtained are supported by the results of Wongjaiyen *et al.* (2017). The authors investigated the effect of cellulose nanofibrils on the mechanical properties of epoxy nanocomposites. The authors found that the modulus of elasticity and tensile strength increased with increasing NFC content up to 3 wt%.

### Hardness

Figure 5 shows the hardness values of the control and reinforced nanocomposites graphically.

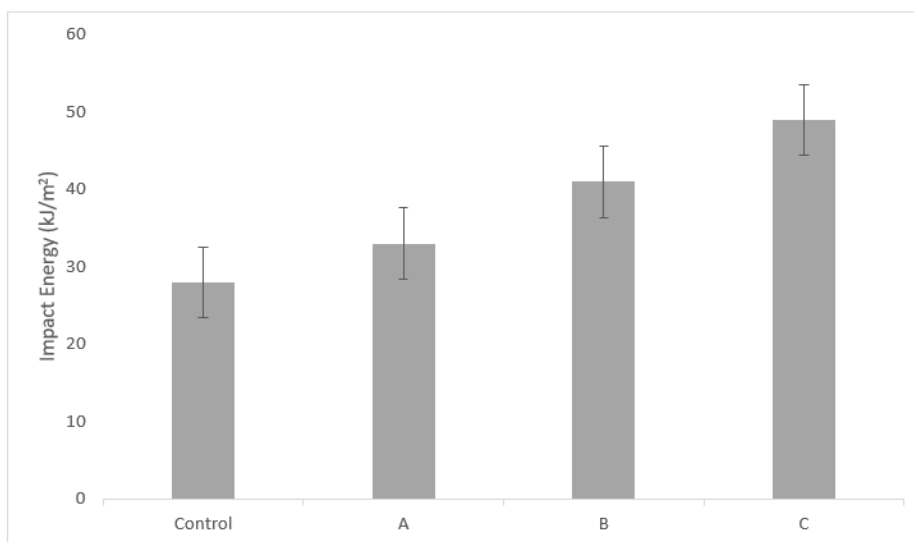


**Fig. 5.** Graphical representation hardness values of the control group and NFC/PMMA/MMA/BPO reinforced groups

When compared to the control group, hardness values in group A increased by 3.3%, 15% in group B, and 28.3% in group C. Composites' hardness increased as the NFC content increased from 1% to 5%. The NFC has high strength, stiffness, aspect ratio, surface area, and strong interactions with polymeric compounds, resulting in increased hardness. The results obtained are supported by the results of studies conducted by Véliz *et al.* (2023). The authors reported that adding nanocellulose to some epoxy resin samples improved their mechanical properties.

### Impact Energy

Figure 6 shows the impact energy values of the control and reinforced nanocomposites.



**Fig. 6.** Graphical representation impact energy values of the control group and NFC/PMMA/MMA/BPO reinforced groups

When compared to the control group, impact energy values in group A increased by 17.9%, whereas 46.4% in group B and 75% in group C. Rapid fracture propagation began when the composite was exposed to an impact. When the fracture propagated to the NFC in the composite, the NFC absorbed the impact energy and stopped it due to strong interfacial interaction between the NFC and the epoxy matrix. Because of the NFC's small size and higher surface area, increased NFC content results in an increase in impact strength (Seydibeyoglu *et al.* 2013). It is clear that the incorporation of NFC improves impact properties when compared to pure epoxy composites, suggesting the favorable effects of the reinforcement.

The results obtained are supported by the results of studies conducted by other scientists. Roszowska-Jarosz *et al.* (2021) investigated the mechanical properties of biocomposites produced using nanocellulose as a reinforcement material and epoxy resin as a matrix material. The authors reported that the impact resistance of the nanocomposites was doubled compared to the reinforced epoxy resin, and the highest breaking stress value was obtained at a 1% nanocellulose loading level, which was also 15% higher than the unreinforced epoxy resin. It has been reported that even with very low nanocellulose addition, the mechanical properties of nanocomposites are improved, while other studies have reported that much more nanocellulose addition is required.

### Self-healing

Table 2 shows the self-healing percentages of the control group and NFC/PMMA/MMA/BPO-reinforced transparent advanced smart nanocomposites.

The percentages of nanocomposites self-healing were obtained as 6% in Group A, 6% in Group B, and 7% in Group C. Self-healing consisted of four stages in total. In the first stage, damage was initiated as a result of a scratch or notch. In the second stage, the PMMA microcapsule was opened as a result of capsule destruction due to damage. In the third stage, the MMA monomer reacted with the BPO catalyst, and polymerization occurred. In the fourth stage, the cracked area was closed to a certain extent by the solidification of the polymerization, and the surface integrity of the transparent nanocomposites was maintained.

**Table 2.** Self-healing Percentages of the Control Group and NFC/PMMA/MMA/BPO-reinforced Transparent Advanced Smart Nanocomposites

Group ID	Self-Healing (%)
Control	0
A	6
B	6
C	7

### CONCLUSIONS

1. Due to their high performance qualities, nanofibrillated cellulose/polymethylmethacrylate/methylmethacrylate/benzoyl peroxide (NFC/PMMA/MMA/BPO)-reinforced transparent smart nanocomposites can be produced using the casting method and used in advanced material applications.

2. The smart properties of the composite, such as self-healing and crack propagation inhibition, are provided by PMMA, MMA, and BPO, while the high efficiency of the mechanical properties was ensured by NFC.
3. The increase in NFC loading levels from 1% to 5% significantly improved the mechanical properties of smart composites, such as yield strength, modulus of elasticity, impact resistance, and hardness. However, when the nanomaterial loading level exceeds 5% in polymer reinforcements, agglomeration and a decrease in strength values may occur.
4. Due to the synergistic effect of PMMA microcapsules, an MMA curing agent, and a BPO catalyst, the nanocomposites self-healed by approximately 7% after the notch/scratch defect.
5. The transparent smart nanocomposites developed in this study are lightweight and particularly impact resistant. These qualities may enable their use in interior and structural parts of the aerospace and automotive industries. This can lead to decreased maintenance costs and improved aircraft and automotive performance. It also has the potential to be used in a variety of applications, such as packaging, flexible screens, and lightweight transparent materials.

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