Research Article

Gülşah Alar Öner*

Flexural strength and thermal properties of carbon black nanoparticle reinforced epoxy composites obtained from waste tires

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Abstract: In this study, both mechanical and thermal properties of epoxy@carbon black nanocomposite (EP@CB-NC) produced by adding 0.3, 0.6, and 1% by weight carbon black nanoparticle obtained from waste automobile tires to epoxy were investigated. The chemical and structural composition of EP@CB-NC was characterized by Fourier transform infrared spectroscopy (FTIR) in scanning electron microscopy (SEM). In addition, simultaneous thermo-gravimetric analysis (TGA), differential scanning calorimetry (DSC) experiments, and thermal conductivity measurements were performed to determine the thermal stability of the prepared EP@CB-NC. Increasing the strength of modified epoxy composites by means of nanoparticles obtained with waste may pave the way for obtaining new materials with clean environment and superior properties. The mechanical and thermal properties were improved by adding carbon black to the bare samples.

Keywords: flexural strength, epoxy@carbon black nanocomposite, waste tire, thermal properties

1 Introduction

Every year, millions of tires are discarded or buried worldwide, posing a very serious threat to ecology. It is estimated that around 1,000 million tires worldwide end their service life each year and more than 50% are discarded without any treatment. By 2030, this number is expected to reach 1,200 million tires annually and 5,000 million tires to be disposed of regularly, including stocked tires [1].

Discarded tires often cause “black pollution” as they are not biodegradable and pose a potential threat to the environment [2]. For this reason, the methods of recycling end-of-life tires are becoming more and more widespread today. The pyrolysis method, which is used in the recovery of end-of-life tires, is one of the most interesting methods used in recent years. Pyrolysis can be defined as the thermal decomposition of organic materials as a result of heating them at high temperatures (500–1,000°C) in an oxygen-free environment [3]. The pyrolysis process is an energy and material recovery process and is recognized as an effective and sustainable process for solving the global problem of waste tires [4–6].

The basic material recovered by the pyrolysis process is carbon black. As a result of the recycling process, approximately 35–45% of the waste tires (depending on the type of tire processed) are recovered as carbon black. Today, carbon black is used as a basic raw material or additive in many industries. Depending on its carbon black structure and usage rate, it improves the durability, strength, color, and general performance of rubber-based materials. In addition, carbon black is used in different industries such as cables, conveyor belts, conveyor belts, hoses, mats, black bags, mixture with rubber paste, auto spare parts, heat insulation, dyestuff in rubber materials, base material, plastic, and fire extinguishing [7–9].

Carbon black, which has been used as a reinforcing element especially in recent years, is an important product that is widely used to change the mechanical, electrical, and other physical properties of the environment in which it is dispersed. It is the most widely used nanomaterial that gives superior properties to the composites of which it is a part, with particle sizes ranging from tens to several hundred nanometers [10,11].

In recent years, carbon materials have been widely used in the most basic industrial areas such as aluminum, steel, chemical materials and aerospace, electronics, recreation, and environmental protection [12].

With the advancement of technology, carbon products are in great demand on a global basis. High corrosion
resistance, high thermal conductivity, low porosity, dimensional stability, high strength properties, and high weight-to-volume ratio are the properties that make carbon attractive as a material. When these superior properties of carbon are combined with composite materials, it is used in many fields [12,13].

Epoxy resin is a widely used polymer matrix for advanced composites where good stiffness, dimensional stability, and chemical resistance are required [14].

When nanoparticles with different shapes and particle sizes are added to the epoxy matrix, it causes many changes in the microstructure and material properties of the polymer composites produced [15].

However, the mechanical properties of this polymer matrix, such as the strength, modulus, and toughness of the epoxy resins, may not be sufficient for some end-use applications. It is therefore desirable to modify the polymer matrix to achieve such purposes. The addition of fillers to polymer matrix is a fast and cheap method to modify the properties of the base materials [16].

Composite materials are widely used in automotive, construction, and packaging application due to their low density, excellent stiffness, and good thermal and mechanical properties [17].

Recently, conductive polymer composites obtained by filling polymer matrices with various carbon blacks [18–20] and also some other composite types studied for different purposes [21–25] were reported.

A detailed methodology has been obtained to fabricate and characterize modified epoxy resin composites with carbonaceous filler (in the form of nanocarbon black obtained from the pyrolysis of waste tires). Composites with varying carbon filler content (0, 5, 10, and 15 wt%) were produced using manual hand lay-up and compression molding techniques. It was found that 5% by weight carbon black in the epoxy resin exhibited the best mechanical properties [26].

The mechanical properties of the new carbon black obtained from agricultural wastes (wood apple peels) were investigated using the pyrolysis method at various carbonization temperatures (400, 600, and 800°C) and used as reinforcement in polymer composites. Results were observed to improve mechanical properties such as tensile strength, tensile modulus, flexural strength, and flexural modulus [27].

Different ratios (0, 5, 10, and 15% by weight) carbon black added carbon fiber–reinforced epoxy composite samples were subjected to tensile, bending, and impact tests produced according to ASTM test standards using the hand lay-up technique. Remarkable results were observed in the tensile strength, flexural strength, and impact strength of the hybrid composite (10% by weight) of 65.78, 32.07, and 36.11%, respectively [28].

In this study, it is aimed both to recycle waste tires that threaten the environment and to produce lower cost and more durable materials. Different from the literature, carbon black obtained from waste tires was added to the epoxy in more precise proportions (0.3, 0.6, and 1 wt%) to produce more durable materials. Characterization of EP@CB-NC was made and its bending strength was investigated.

2 Materials and test methods

2.1 Carbon black

The carbon black nanoparticles to be used in the experiments were obtained from ERA Environmental Technologies Company. Car, truck, bus, and truck tires that have completed their life in the company are mechanically shredded at room temperature, purified from the court and steel wire, subjected to heat treatment in the pyrolysis reactor, and carbon black is produced as a recycled product.

2.2 Production of the matrix

In this study, Epoxy (epoxy resin DTE-1200 and hardener DTS-1151) is used as the matrix material. The first step to fabricate the composites was to weigh the nanoparticles in three different ratios in the digital scale in Figure 1a, and added to the epoxy in appropriate proportions as shown in Figure 1b. The nanoparticle was added to the resin and mixed with an ultrasonic mixer at 80 W power for 10 min, as shown in Figure 1c. In the second step, the samples were prepared by adding the appropriate proportion of hardener to the resin, mixed mechanically with a mechanical mixer at 500 rpm for 5 min, as shown in Figure 1d, and poured into specially prepared silicon molds (Figure 1e).

In the production phase of nanocomposites, ultrasonic cavitation technique was used because it is difficult to ensure homogeneous dispersion of carbon black in the polymer matrix. In this study, the Hielscher UP400S ultrasonic processor (Ultrasonic Device UP400S 400 watts, frequency 24 Hz amplitude adjustable, 20–100%) was used, as shown in Figure 1c.

The preparation of the pure composite by pouring into silicone molds was done as in Figure 2a, and the
preparation of carbon-black added nanocomposites was done as in Figure 2b.

Plain epoxy composite is also seen in Figure 3a. In addition, nanocomposites produced with recycled carbon black added to the epoxy composite at different rates are shown in Figure 3b–d, respectively.

3 Results and discussion

3.1 Three-point bending test results

Three-point bending tests were carried out to determine the bending strength of nanocomposites. The tests were...
carried out on a universal mechanical testing device (AG-IS 100, Shimadzu Corp., Japan). Flexural properties of the six samples were measured by the ASTM D-790 standard test method at a crosshead speed of 1 mm min\(^{-1}\) at 23°C. In the tests using a 5 kN load cell, 12.5 mm × 5 mm × 60 mm samples were used. The photograph of the test setup is given in Figure 4a and b [28].

According to the three-point bending test results in Figure 5a and b, flexural strengths of 74.9, 72.6, and 77.5 MPa were determined for carbon black added samples for 0.3, 0.6, and 1 wt% additive ratios, respectively. This indicates that the 0.6% CB dispersion is not well done. Accordingly, while an increase of 7% occurred in the samples with 0.3 wt% CB added compared to the samples without additives, there was an increase of 4 and 11.6% in the samples with 0.6 and 1 wt% additives, respectively [10].

3.2 SEM, Fourier transform infrared spectrophotometer (FT-IR), TGA-DSC analyses

3.2.1 SEM analyses

Scanning electron microscope (SEM) images of carbon black doped composites, carbon powder, and epoxy

Figure 3: Different proportions of carbon black added samples and neat samples: (a) neat samples, (b) 0.3% carbon black added samples, (c) 0.6% carbon black added samples, and (d) 1% carbon black added samples.

Figure 4: Image of bending tester: (a) flexural strength tester and (b) flexural strength test.
composite neat (control sample) were made using Zeiss Sigma 300 VP operating at 5.00 kV. From all SEM images in Figure 6, the nano-size range was determined to be in the 25–65 nm size range. Especially when compared to the control sample, a homogeneous distribution was observed in the SEM images in Figure 6b. As can be seen from Figure 6c and d, carbon black added epoxy composite structures appear to have a large surface area with their rough surface properties. Large surface area is a desirable feature in carbon black. Thanks to its large surface area, it can integrate effectively with the structure and increase its strength. When the 0.3, 0.6, and 1 wt%, carbon black added epoxy composite structures in Figure 6b–d were examined, it was seen that the composite structures showed a significant structural difference compared to the control sample and there was a homogeneous distribution in all SEM images. The SEM image of the used tire powder is given in Figure 6e. In this image, it is seen that the dust has a rough structure because it consists of grains of different sizes and is obtained by shredding waste tires at room temperature. Thanks to the rough structure of the grains and the gaps on the surface, a stronger physical bond with the polymer chains is provided [10, 29].

3.2.2 FT-IR analyses

Chemical structure characterizations of carbon black powder and epoxy resin composites were performed by FT-IR analysis and are given in Figure 7. The peaks seen at 908–1,132 cm⁻¹ indicate the peaks of C–H bending. The peaks located around 2,109, 2,329, 2,489, and 2,669 cm⁻¹ indicate C–H stretching. While the peaks indicating C—C stretching belong to the peaks around 1,986 and 1,971 cm⁻¹, the peaks around 1,722 and 1,132 cm⁻¹ belong to C=O stretching. The broad peak around 3,100–3,500 cm⁻¹ belongs to O–H stretching. Vibrations around 1,918 and 1,606 cm⁻¹ indicate the epoxy resin ring and the aldehyde group. The vibrations around 2,919 cm⁻¹ show the vibration of the protons in the aromatic ring. These peaks show the characteristic peaks of the epoxy resin. As a result of the FT-IR analysis obtained, it is observed that the epoxy resin forms the composite structure with carbon black powder [30].

The most suitable and widely used spectroscopic method for polymers is the infrared method. New developments in FT-IR analysis have further increased the applicability of this method. In the infrared technique, chemical bonds in molecules are vibrating, bending, twisting, swinging, etc. The energy required for all its motions is absorbed from the electromagnetic energy of infrared rays. The IR spectra obtained as a result of these absorptions show the functional groups in the molecule. Here, the measured absorbances are expressed as peaks. Infrared spectra are usually identified by the wave number. The measured absorbance is directly dependent on the concentration and sample thickness. Chemical bonds do not absorb the same amount of energy as C–H C–C. Peaks are defined as strong, medium, and weak depending on their structure and wide, medium, and narrow depending on their shape. By examining the IR spectra according to the location of the peaks, their structures and shapes, the material type is determined in the samples. Quantification can also be made by measuring the peak length and peak area and comparing them with the standards. The most important issues in FT-IR studies on polymer samples are to prepare the appropriate sample and to interpret the obtained spectra. It is possible to make comments by looking at previously published IR spectrum atlases. Analyzes were made...
at the Atatürk University DAYTAM center. Plain and carbon black with 0.3, 0.6 and 1 wt% samples in Figure 7 were placed in the device and infrared spectra were taken in the range of 300–3,800 cm\(^{-1}\) with a resolution of 5 cm\(^{-1}\).

The carbon black powder sample in Figure 8 was placed in the device and infrared spectra were taken in the range of 400–4,000 cm\(^{-1}\) with a resolution of 5 cm\(^{-1}\).

FTIR responses at different scales are shown to further describe the functional groups present (Figure 8). Peaks resulting from vibrations and stretching of different bonds to corresponding functional groups can be observed at 3,500–2,500 cm\(^{-1}\), with vibrations and tensile bonds in the range of 2,000–600 cm\(^{-1}\) \cite{18–20}. Considering the reactions, the functional groups present in the film electrode correspond to carbon black and Nafion. This analysis shows that the chemical composition of the film is very diverse due to the presence of different functional groups which confer some degree of chemical reactivity. The carbon film was supported on glassy carbon (as current collector); Figure 8 shows images corresponding to the support material and film. The purpose of showing GC and carbon film is just to compare the surfaces before and after putting the black carbon film, the film shows spherical particles and agglomerates, which makes it porous.

### 3.2.3 TGA analyses

Thermal analyses were performed using the Thermal Gravimetric Analysis (TGA) and was conducted with the EXSTAR 7300 device at a heating rate of 10°C min\(^{-1}\) in a
The samples were analyzed between the temperature range of 30–500°C with the 10°C min\(^{-1}\) heating rate under the condition of 70 mL min\(^{-1}\) feeding rate of nitrogen. The decomposition temperature was determined by TGA analysis of the samples. TGA analysis shows the thermal behaviors of materials under the condition of

\[
\begin{array}{cccc}
3,388.57 & 2,919.92 & 2,323.98 & 2,104.11 \\
1,029.88 & 1,606.53 & 1,508.17 & 1,454.17 \\
827.37 & 555.44 & 0.6 & 0.65 \\

carbon powders
\end{array}
\]

**Figure 7:** FT-IR results of neat (control sample) and 0.3, 0.6, and 1 wt% carbon black added samples.

**Figure 8:** FT-IR results of carbon black powder.
high temperature. As can be seen from Figure 9, the resistance of the lean sample to thermal degradation is approximately 340°C, it was observed that it increased against degradation with the addition of carbon black additive, and the mass loss decreased positively with the increase in the CB additive ratio.

The effect of thermally stable CB particles on the thermal resistance of their epoxy composites was

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**Figure 9:** TGA results of Neat (control sample) and 0.3, 0.6 and 1 wt% carbon black added samples.

**Figure 10:** DSC results of Neat (control sample) and 0.3, 0.6 and 1 wt% carbon black added samples.
Table 1: DSC glass transition temperature and crystallizations onset temperatures of Neat and 0.3, 0.6 and 1 wt% carbon black added samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Glass transition temperature (°C)</th>
<th>Crystallizations onset temperature (mW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control sample (Neat)</td>
<td>59.5°C (~5,940 mW)</td>
<td></td>
</tr>
<tr>
<td>Carbon black 0.3 wt%</td>
<td>62.5°C (~7,999 mW)</td>
<td></td>
</tr>
<tr>
<td>Carbon black 0.6 wt%</td>
<td>63.2°C (~4,859 mW)</td>
<td></td>
</tr>
<tr>
<td>Carbon black 1 wt%</td>
<td>61.4°C (~6,218 mW)</td>
<td></td>
</tr>
</tbody>
</table>

characterized using thermogravimetric analysis. Figure 9 shows the mass loss curves (TGA) for neat and carbon black 0.3, 0.6 and 1 wt% composites. Particularly, the reduction in mass loss attracted attention on the basis of additive ratios [31,32].

3.2.4 DSC analyses

The glass transition temperature (TGA) is a key property of epoxy systems and is dependent on the extent of curing. Physically, glass transition temperature is the point at which polymer chains gain enough mobility within the polymer matrix and the material changes from a stiff glassy state to soft rubbery state. Understanding the TGA can, therefore, be critical for determining material suitability for specific applications. In order to determine the glass transition temperatures, the samples weighing 0.5 mg were analyzed with DSC at a heating rate of 10°C min⁻¹ between 30 and 500°C. DSC analysis is a useful tool for testing the crystallization temperature range of the nanocomposite sample. According to Figure 10 and Table 1, it was observed that the glass transition temperature shifted to higher values with the addition of carbon black at different rates to the neat sample.

Compared to the plain sample, it was observed that the glass transition temperatures increased with the addition of nano carbon black particles obtained from tire recycling to the epoxy resin at different rates. The highest crystallization value was −7,999 mW in 0.3 wt% CB added samples. In parallel with these results, it was observed that the crystallization temperatures decreased with the addition of carbon. The lowest decrease was −4,859 mW in samples with 0.6 wt% CB additives [31].

4 Conclusion

In this study, it is aimed both to recycle waste tires that threaten the environment and to produce lower cost and more durable materials. The characterization of EP@CB-NC produced by adding different ratios (0.3, 0.6, 1 wt%) of carbon black obtained from the recycling of waste tires to the epoxy composite was made and its bending strength was investigated.

According to the results of the research, an increase of 11.6% was achieved with 77.5 MPa in the samples with the highest flexural strength with 1 wt% additive ratio compared to the control sample. In addition, it appears to have a large surface area with its rough surface properties in SEM images with 1 wt% additive ratio. The large surface area is a desirable feature in carbon black. It has shown that it can increase the strength by integrating effectively with the structure, thanks to its large surface area. With the increase in the carbon black additive ratio, the mass loss and crystallization temperature decreased. The highest increase crystallization value was determined to be 34.6% CB with 0.3 wt% added sample. The results showed that the mechanical and thermal properties were improved by adding carbon black nanoparticles to the epoxy composite.

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Data availability statement: Data sharing is not applicable to this article as no new data were created or analyzed in this study.

References


