Preparation and Properties of Multifunctional
Nylon 6 Composite Material

Chiu-Chun Lai¹, Chyi-Wen Jen², Yuh-Shyang Chang³, Kuo-Shien Huang².*

¹Department of Textile Engineering, Chinese Culture University, 55, Hwa Kang Road, Yang Ming Shan, Taipei, Taiwan

²Department of Polymer Materials, Kun Shan University, Yung Kang, Tainan, 71003 Taiwan

³Institute of Organic and Polymeric Materials, National Taipei University of Technology, Taipei, 10608 Taiwan

*E-mail: hks45421@ms42.hinet.net
Tel: 886-6-2050317, Fax: 886-6-2728944
Abstract

We considered polyamide 6 as a base material for a composite and added improved tourmaline and carbon fiber to manufacture a material that could release negative ions and resist electromagnetic waves. Through Fourier transform infrared spectroscopy and thermogravimetric analyses, we verified that the improved tourmaline could disperse homogeneously in the base material, whose thermal properties improved as the content of tourmaline increased. Scanning electron microscopy demonstrated that the added tourmaline and carbon fiber complemented the conductive network of the composite material. A negative ion detector and an infrared thermal imaging system both revealed that with an appropriate tourmaline content, the negative ion release properties of the composite material could reach 2020 units/cm$^3$ with a difference in temperature of up to 7.54°C. Analyses by a four-point probe low-resistance tester and electromagnetic wave shielding effectiveness tester demonstrated that the osmotic concentration was approximately 4%, and the surface resistivity was high, up to $1.04 \times 10^7 \Omega$/cm, reaching the range of static dissipative materials ($10^6$ – $10^{12} \Omega$/cm). The maximum electromagnetic wave shielding effectiveness was as high as 30 dB/MHz.

Keywords: polyamide; tourmaline; carbon fiber
1. Introduction

As a new industrial mineral, tourmaline can be used for environmental protection purposes, or it can be used in medicines, building materials, and the electronics or chemical industries. Due to the special characteristics of minerals and the high added value of the resulting products, tourmaline has attracted much attention from countries worldwide. As technological research and development has progressed, tourmaline has been widely considered for numerous prospective applications [1].

Past experiments have demonstrated that fine tourmaline powder has a large specific surface area. Therefore, it has better piezoelectric and thermoelectric properties. However, with high polarity and fine grains, the ultrafine powder is difficult to disperse in nonpolar substances. In addition, because tourmaline powder and high molecular polymer have quite different surface properties, it is difficult to combine them firmly. Direct filling negatively impacts some properties of the material and causes embrittlement, adversely influencing integration of the overall properties of the base material. Therefore, it is necessary to treat the surface of the tourmaline powder in order to resolve problems such as agglomeration, dispersibility, and compatibility with nonpolar substances [2].

As scientific technology and the electronics industry develop, the electromagnetic pollution caused by the wide use of various appliances and electrical equipment has become regarded as the fourth largest public nuisance following
atmospheric pollution, water pollution, and noise pollution. Electromagnetic compatibility (EMC) resulting from electromagnetic waves not only disturbs electrical equipment, but also seriously threatens the health of the human body [3]. For this reason, researchers have focused on how to reduce the strength of electromagnetic irradiation, avoid pollution of electromagnetic irradiation, protect the environment, and protect the health of the human body [4].

With high mechanical strength, good abrasion resistance, stable chemical characteristics, and fine self-lubrication, nylon 6 engineering plastic is widely used in automotive spare parts, electrical appliances, and the petrochemical industry. However, the application range of nylon 6 is limited because it has poor thermal and acid resistance, as well as a low impact resistance, high absorption rate, low transparency, and low solubility in a low temperature environment. To meet the requirements of different application fields, the properties of nylon 6 can be improved through blocking, blend grafting, and filling. Industry and academia have focused on nylon 6 nanocomposites due to their high strength, thermal resistance, high barrier, flame-retardant properties, ease of processability, and excellent overall characteristics [5].

Various inorganic conductive fillers are often added to the polymeric base material. The antistatic polymeric materials manufactured through this technology have a high application value and are mostly commercialized in foreign countries.
Commonly used raw materials include: 1) the carbon black series, such as graphite, carbon black, and carbon fiber; 2) metals, such as metal powder and fragments, and fibers, such as metallized glass fibers and mica plated with nickel, copper, chrome, and stainless steel; and 3) other series, such as inorganic salts or metal oxides [6].

The most notable disadvantages of carbon black filler are the large filling amount and poor adjustability, which limit its application in many fields. Although the copper, iron, and aluminum included in metal fillers are easily oxidized and reduce the conductivity rate of the system with time, it is difficult to use them on a large scale because the price of gold and silver is high. In addition, the metal particle content must reach 70% to make any substantial reduction in the surface resistivity coefficient. Such a high content will influence the mechanical and spinning properties of the polymer [7]. Therefore, we selected carbon fiber as the conductive filler for this study.

At present, common methods to manufacture polymeric composites include thermal pressure, injection molding, and high-temperature melting. Among them, injection molding is the most convenient and effective. Therefore, we used injection molding with tourmaline powder and carbon fiber and a nylon 6 polymer base material to manufacture a composite material in the hopes of improving the effects of heat preservation and thermal insulation and increasing the number of anions. This can reduce the resistivity and increase the conductivity of the material to improve the electromagnetic shielding effectiveness and antistatic effect. Such multifunctional
composite materials are expected to be used in the cases of electronic and electric machines and the antistatic cushions of clean rooms, as well as in underwear, elbow pads, waist pads, kneepads, gloves, scarves, and jackets.

2、Experimental

Materials

Polyamide 6 (Hualong Co., Ltd., Industrial), tourmaline powder (75 nm, Tianjin Hongyan Mineral Products Co., Ltd., Industrial), carbon fiber (TC-35, 12 K, Taiwan Plastic Industrial Company, Industrial), stearic acid (Japan Test Medicine Industry Co., Ltd., test medicine), and acetone (Daojiu Medicine Co., Ltd., test medicine) were used in this study.

Methods

Modification of Tourmaline

An appropriate amount of tourmaline powder and acetone were mixed and then vibrated for 15 minutes in a supersonic oscillator. Next, 5% (weight percentage of nylon) stearic acid was added and allowed to react for 2 hours at a fixed rpm in the reaction tank. The solution was dried, washed with acetone to remove the stearic acid, and then dried again.

Preparation of Polymer Composites
Nylon 6, tourmaline, and the carbon fiber were placed in a 1-liter ball mill and mixed and milled for 1 hour in a milling machine in order to improve the dispersion, increase the processing properties, and reduce the loss of powder. After this step, the tourmaline and carbon fiber composite was removed and then shaped with a tablet machine. After cooling, the composite was sent to a grinding machine to be ground into master batches.

The ground master batches were poured into the feeder of the injection molding machine, which then processed the master batches into the nylon6/carbon fiber/tourmaline composite. These composites were used as samples to test the amount of anions released and the physical characteristics of the anions.

Analysis and Measurement

Fourier transform infrared spectra in the attenuated total reflection mode (FTIR/ATR) of the finished fabrics were recorded with a Bio-Rad Digilab FTS-200 spectrometer using a mercury–cadmium–tellurium (MCT) detector. A diamond crystal was used as the internal reflectance element. Single-beam spectra resulted from 64 scans. The spectral resolution was 4 cm$^{-1}$. The thermal resistance of the samples was measured by a DuPont 2200 weight-loss analyzer. The 5 – 10 mg samples were placed in alumina crucibles and tested at a thermal ramp over a temperature range of 30 – 600ºC at a heating rate of 20ºC/min under a nitrogen flow speed of 20 cc/min, after which their initial decomposition temperature (IDT) was obtained. The surface
morphologies of the films were observed with a JEOL Model JSM 6400 scanning electron microscope. A gold coating was deposited onto the samples to avoid surface charging.

Air Anion Test

First, a controlled-environment room was operated for more than 2 hours with the temperature controlled to 20 ± 5ºC and the relative humidity controlled to 65 ± 5%. Then, the anion-test sample was placed in the center of an airtight acryl box, and the box was placed into the room with an anion tester (Andes, ITC-201A). The fan switch was turned on to blow air over the test sample and the anion tester was started. Each test lasted for 10 min. The maximum, minimum, and average number of anions tested were recorded at regular intervals by the anion tester.

Far Infrared Ray Thermal Image Temperature Test

As shown in Figure 1, to test the composite membrane sample, it was first placed on the sample mount, and a 500-W halogen lamp was installed at an angle of 45º and a distance of 100 cm. An infrared thermal imaging system (AGEMA, Thermovision 900) was placed over the test sample at a distance of 50 cm. During this period, pictures were taken at regular intervals to analyze the surface temperature of the sample, and the temperature difference before and after irradiation were compared to
determine the incremental temperature of the sample. When the temperature
difference of the test sample and of the raw sample for 0.5°C above, we could assume
that the composite membrane provided heat preservation and thermal insulation from
the far infrared rays.

Four-point Probe Low-resistance Test

This experiment utilized the LASESTA-GP MCP-T600 low-resistance
coefficient tester manufactured by Mitsubishi Chemical Corporation. The sample was
placed in a controlled environment for more than 24 hours to reach a standard
temperature and humidity. Then, the surface resistance, volume resistance, and
conductive rate were determined. The length, width, and thickness of the membrane
were measured first. These values were inputted into the low-resistance tester and
the distance of the measuring coordinate point was provided. The tester then gave the
point coordinates where tests were required. Finally, the surface resistance, volume
resistance, and conductive rate were measured at the point coordinates.

Electromagnetic Wave Shielding Effectiveness Test

This experiment utilized an HP8722 Vector Network Analyzer, whose
measurable frequency ranged from 50 MHz to 40 GHz. Coaxial clamps were used to
test the wave shielding effectiveness according to ASTM D4935-99. The scanning
frequency of this experiment ranged from 144 MHz to 3 GHz. The electromagnetic absorption loss of the material was determined from the energy consumption of the electromagnetic wave shown on the test plate.

3、Results and Discussions

FTIR

From Figure 2A, the main functional group of pure nylon 6 had an absorption peak at 1638 cm\(^{-1}\), which corresponded to the stretching vibration absorption peak of >C=O. There was also an absorption peak at 1541 cm\(^{-1}\), which corresponded to the vibration absorption peak of the inside of amide N-H. Figure 2B shows a graph of stearic acid. An absorption peak of >C=O at 1737 cm\(^{-1}\) appeared on the main functional group. Figure 2C shows a plot for the composite material. Two absorption peaks appeared at 1637 and 1544 cm\(^{-1}\) on the main functional group with no great difference from those of pure nylon 6, but there was an additional absorption peak at 1703 cm\(^{-1}\). According to the above plots, the absorption peak of >C=O was displaced because after stearic acid CH\(_3\)(CH\(_2\))\(_{16}\)COOH was decomposed to CH\(_3\)(CH\(_2\))\(_{16}\)COO\(^-\), CH\(_3\)(CH\(_2\))\(_{16}\)COO\(^-\) combined with Ca\(^{2+}\), Fe\(^{2+}\), Mg\(^{2+}\), etc., ions at the surface activity center of tourmaline[2].

Through an FTIR analysis, it was possible to fabricate an improved tourmaline powder that had a good interface for combination and could effectively infiltrate into
the base material in order to improve its dispersibility.

TGA

From Figure 3, as the nylon 6/tourmaline/carbon fiber composite was heated to 500°C, the residual and initial decomposition temperature of the composite increased with the tourmaline content while the decomposition rate decreased, indicating that increasing the tourmaline content could effectively improve the thermal resistance of nylon 6 and slow down the rate of decomposition.

The TGA graph of the composite is shown in Figure 3. The initial decomposition temperature of nylon 6 was 394.83°C, and the decomposition speed of –1.767%/°C indicated quick decomposition. When the temperature reached 500°C, 5.589% of the composite material still remained. The initial decomposition temperature in Figure 3-B, 3-C, and 3-D were 404.95°C, 406.76°C, and 408.56°C, and the decomposition speeds were –1.628%/°C, –1.383%/°C, and –1.342%/°C, respectively. When heated to 500°C, the residuals of the composite material were 23.731%, 24.124%, and 29.049%. From the above data, the initial decomposition temperature, decomposition speed, and residuals were all better than those for pure nylon 6, indicating that adding tourmaline could improve the thermal stability of nylon 6.

When the tourmaline content was 16%, the thermal resistance, decomposition speed, and initial decomposition temperature reached optimal values because the
improved tourmaline actually served as a crosslinking point for nylon 6 that was good for entwisting the nylon 6 chains and physical crosslinking. A good interface for the combination of the filling particle and the base material was available such that it could serve as a chemical crosslinking point. Tourmaline itself, however, affected the heat preservation and thermal insulation; thus, more energy was required to decompose the composite material. As the tourmaline content increased, the thermal resistance, decomposition speed, and initial decomposition temperature of the composite material tended to increase [8,9].

SEM

As shown in Figures 4-A and 4-A’, the base material (nylon 6) without tourmaline or carbon fiber (CF) had a smooth surface with a few lines in its cross-section that were caused by the cutting stress. Figures 4-B and 4-C show the surface of the composite material containing 4% and 16% carbon fiber, respectively. Figures 4-B’ and 4-C’ show cross-sections of the composite. After adding 4% tourmaline and 10% carbon fiber, shown in Figures 4-B and 4-B’, respectively, the tourmaline was evenly dispersed and the carbon fiber formed an interwoven conducting net. When the tourmaline content increased to 16% (the carbon fiber content was fixed at 10%), the carbon fiber still formed an interwoven conducting net, but the tourmaline agglomerated because the surface energy of nanotourmaline was high, as shown Figures 4-C and 4-C’. Therefore, with an excessive amount of
tourmaline, the powder particles became less free and agglomerated.

An appropriate amount of tourmaline could disperse homogeneously throughout the base material, as shown by the SEM analysis, and thus mix with the carbon fiber and impose its spatial structure. The piezoelectric and thermoelectric effects [10-12] of tourmaline could complement the conducting net of the composite material.

Dynamic anions

From Table 2, as the tourmaline content increased, the amount of dynamic anions also tended to increase. As the tourmaline content increased to 8%, the number of anions decreased. The concentration of the released anions did not have a linear relationship with the increasing tourmaline powder content because after the powder content increased, its dispersibility in nylon 6 decreased. Since the nanotourmaline powder had a large specific surface area and a certain electronegativity, the anion particles were fine relative to the nylon 6 and thus agglomerated easily, influencing the performance of the tourmaline powder in releasing anions [13].

Heat preservation and thermal insulation

After irradiation, the surface temperature of the nylon 6 base material without tourmaline powder was lower than the nylon 6 composite with added tourmaline powder, as shown in Table 3. Also, the temperature tended to increase with the
tourmaline powder content. When the tourmaline powder content increased to 8%, the rising temperature reached a maximum value, possibly due to saturation of the heat preservation effect.

According to the irradiation principle of far infrared rays, after absorbing energy, the far infrared radioactive tourmaline powder emits far infrared rays and produces a thermal effect [13]. Therefore, the tourmaline powder in the composite material produced a thermal effect after absorbing the far infrared ray energy, and thus made the surface temperature of the composite material higher than the nylon 6 base material without tourmaline powder.

A continuous increase in the amount of filling provided little help in improving the heat preservation thermal insulation effects. As the tourmaline powder content increased to 16%, there was no substantial change in the heat preservation effect, possibly due to the heat preservation reaching saturation, and the large specific surface area and high specific surface energy of nano-tourmaline powder causing the agglomeration phenomenon, thus influencing the heat preservation and thermal insulation effects.

Surface resistance coefficient

As shown in Figure 5, the surface resistance of pure nylon 6 was approximately $10^{14} \, \Omega/cm$, and the surface resistance coefficient tended to decrease as the tourmaline
content increased, mainly because a conductive net was formed as the content of the conductive fillers increased.

When the tourmaline content increased by 2%, the surface resistance coefficient of the composite material decreased to $1.47 \times 10^8 \, \Omega/cm$. When the tourmaline content increased to 4 wt%, the surface resistance coefficient of the composite material decreased to $1.04 \times 10^7 \, \Omega/cm$, forming a steep curve, which indicates that a sound and close conductive net with the carbon fiber in the nylon 6 material formed at this tourmaline content, *i.e.*, the percolation region of percolation theory [14]. As the tourmaline content increased to 8% and 16%, the surface resistance coefficient of nylon 6 decreased to $2.50 \times 10^7$ and $2.47 \times 10^7 \, \Omega/cm$, respectively, and the curvature tended to be mild. From this curve, the critical concentration of added tourmaline to nylon 6 was approximately 4 wt%; when the tourmaline content increased to 8%, no dramatic change in the surface resistance coefficient was observed.

The resistance of electrostatic eliminating materials falls between the resistance values of conductive materials and insulating materials, approximately $10^6$ – $10^{12} \, \Omega/cm$. Static is mainly caused by the accumulation of inflow charges, and thus a reduction of the surface resistance can effectively release the charge accumulated on the material surface. Like conductive materials, electrostatic eliminating materials can transmit electrons, but at a speed between conductive and insulating materials [15]. As indicated by the above results, the surface resistance of
the tourmaline/carbon fiber/nylon 6 composite material prepared in this study had a minimum value of $10^7 \, \Omega/cm$. For this reason, it could be used as a material to eliminate static.

Electromagnetic Wave Shielding Effect (SE)

As shown in Figure 6-A, the electromagnetic wave shielding effect of nylon 6 was close to 0. With the appropriate tourmaline content (2% or 4%), as shown in Figures 6-C and 6-D, the electromagnetic wave shielding effect increased with the tourmaline content because the carbon fibers served as a bridge between tourmaline and the particles and help made the conductive net structure more complete such that the channel was wider for the electrons to transmit and move. A less obstructed electron flow improved the conductive effect, and thus also the electromagnetic wave shielding effect [16]. When the tourmaline content was 2%, the electromagnetic wave shielding effect was not obvious; when the tourmaline content was 4%, the electromagnetic wave shielding effect increased to 4 – 10 dB, with a maximum value of up to 30 dB. When the tourmaline content increased to 8% and 16%, as shown in Figures 6-E and 6-F, respectively, the electromagnetic wave shielding effect decreased because the uneven dispersion of tourmaline triggered the agglomeration phenomenon and adversely affected the shielding.

The combination of the piezoelectric effect and the conductivity produced an
electric effect [17]. For this reason, the application of substances containing tourmaline powder for outer casing applications could effectively produce an electromagnetic wave shielding effect [18].

Table 4 shows the influence of different tourmaline contents with carbon fiber content (10%) on the frequency shielding effect for common household appliances and cell phones. When the SE value was 10 dB, the shielding rate was 90%; when the SE value was 20 dB, the shielding rate was 99%; and when the SE value was 30 dB, the shielding rate was 99.9%. When the tourmaline content increased to 16%, the electromagnetic wave shielding effect only reached 10 – 20 dB at the frequency of common household appliances and cell phones. Therefore, the filling amount must be 4% to achieve an electromagnetic wave shielding effect of more than 20 dB. Generally, when the tourmaline content was at least 4%, a high electromagnetic wave shielding effect was attainable, over 25 dB, with a shielding rate of over 99%. Therefore, we believe that this material could be applied as a shielding material for household appliances and computers, such as an anti-electromagnetic wave liner. Better effects could be achieved in cell phone protection applications, such as using this material in leather cell phone cases.

4. Conclusions

We fabricated a nylon 6/tourmaline/carbon fiber composite material through the
injection molding method. The following conclusions can be drawn from our experiments.

1) FTIR testing and analysis demonstrated that the improved tourmaline powder had a good interface for combination and could effectively penetrate into the base material, improving its dispersion.

2) TGA testing and analysis indicated that the initial decomposition temperature and composite material residual content increased as the tourmaline content increased. This caused decomposition speed to decrease.

3) SEM showed that an appropriate amount of tourmaline could evenly disperse throughout the base material and mix with the carbon fiber, thus acting in a complementary manner with the conductive network of the composite material.

4) From the results of the anion tester, the nylon/tourmaline/CF composite material with added tourmaline powder improved with stearic acid and had a good anion release performance. The number of dynamic anions tended to increase with the tourmaline content. When the tourmaline increased to 8%, the number of anions decreased.

5) Testing the heat preservation and thermal insulation properties of the composite material with an infrared thermal imaging system indicated that the surface temperature of the nylon 6 composite material with added tourmaline powder increased by 5.1°C – 7.6°C, and the incremental temperature tended to increase.
with the tourmaline content. When the tourmaline powder content increased to 8%, the increasing temperature reached a maximum value. Further increases in the filling content did not improve the heat preservation thermal insulation effects.

6) The data from the four-point probe low-resistance tester and the electromagnetic wave shielding effect tester indicated that with the tourmaline appropriate content, the surface resistance coefficient could reach a maximum value of \(1.04 \times 10^7 \, \Omega/cm\) when the percolation concentration was approximately 4%. This is within the range of \(10^6 - 10^{12} \, \Omega/cm\) for electrostatic eliminating materials. The maximum electromagnetic wave shielding effect was 30 dB/MHz.

5. Acknowledgement

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