

# Effect of Temperature on Composite Films Made with Activated Carbon, Graphite, or Graphene Oxide (GO) in a Gelatin Matrix

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Activated carbon, graphite, and GO/gelatin composite films were prepared by the blending method. The properties of composites were characterized by tensile strength (TS), elongation at break (EB), water vapour permeability (WVP), water-absorption ability, contact angle, scanning electron microscopy (SEM), and moisture at different temperatures. The properties of GO/gelatin composite films were better when each of three kinds of carbon materials were used as reinforcement phases and added into the matrix gelatin. The results showed that EB and TS of GO/gelatin composite films were both excellent. The moisture of GO/gelatin composite films was greater than the others. SEM micrographs showed that GO had better compatibility and dispersibility with gelatin than activated carbon and graphite. The water absorption of GO/gelatin composite films were low, at 15 °C and 25 °C, and the WVP was low at 35 °C. The WVP of GO/gelatin composite films was lower than the others at different temperatures. The contact angle of GO/gelatin composite films was larger than the others.

*Keywords:* Composites film; Carbon; Gelatin; Temperatures

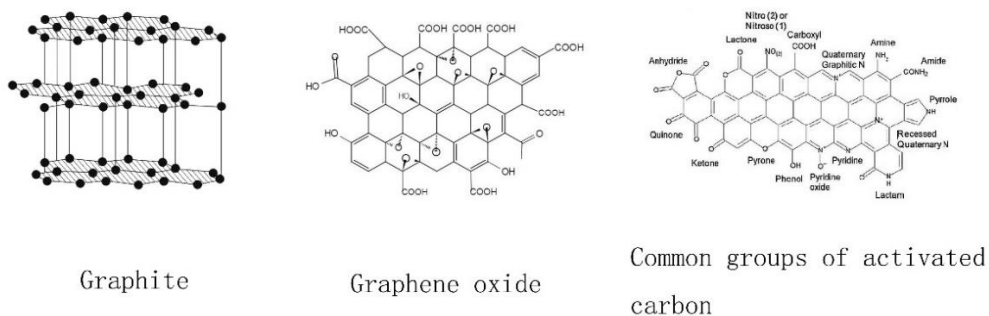
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## INTRODUCTION

Energy depletion and environmental pollution are caused by overusing petroleum-based synthetic packaging materials (Moreno *et al.* 2017; Zhuang *et al.* 2017; Kumar *et al.* 2019). Thus, it is important to find alternative renewable resources (Choo *et al.* 2016; Zhang *et al.* 2018; Yao *et al.* 2019). Polysaccharide-, protein-, and cellulose-based films have been widely applied in food packaging. The single biomacromolecule materials have many disadvantages, such as poor mechanical properties and thermal stability, which could be changed by adding plasticizers and a reinforcing phase.

Gelatin is a natural biomacromolecule polymer. It is a polypeptide composed of 18 types of amino acids and mainly obtained from hydrolysis of collagen in animals' bones, skin, and connective tissue (Gómez-Guillén *et al.* 2009). Gelatin dissolves into random chains in water upon heating, and it reassembles into a partial collagen-like triple helix structure during cooling (Hanani *et al.* 2012). Gelatin exhibits reversible gelling, such that in low temperature it is condensed, and at high temperature it dissolves (Su *et al.* 2015). Gelatins contain the amino (-NH<sub>2</sub>), carboxyl (-COOH), and hydroxyl(-OH) groups, which form hydrogen bonds with other hydrophilic functional groups (Guo *et al.* 2012; Haghghi *et al.* 2019). Gelatins show good film-forming ability, and they are widely used in food and edible pharmaceutical films (El-Sakhawy *et al.* 2018).



**Fig. 1.** Molecular structure of activated carbon, graphite, and graphene oxide

Graphite (Fig. 1) has a one-layered structure. Each carbon atom is attached to three other carbon atoms by covalent bonds, and layers are held together by van der Waals forces (Chen *et al.* 2019). It has many advantages, such as high-temperature resistance, small thermal expansion coefficient, lubricity, plasticity, chemical stability, electrical conductivity, and antistatic wire (Hokao *et al.* 2000; Park *et al.* 2015; Huang *et al.* 2016; Ramanujam *et al.* 2017). Graphene oxide (GO; Fig. 1) is an important derivative of graphite, with many characteristics similar to graphite (Gan *et al.* 2016). GO has many oxygen-containing groups, such as hydroxyl, epoxide, and carboxyl groups (Dong *et al.* 2017). Most of the oxygen-containing groups are at the edge of GO, and the electronegativity of edges is large. It has many advantages, such as hydrophilicity (good dispersion in aqueous media), adsorption, biocompatibility, and improved polymer hydrogel of mechanical strength (Gan *et al.* 2018; Pei *et al.* 2018; Kancharla and Sasaki 2019). Graphene oxide/hydroxyapatite/gold nanocomposites (GO/HAP/Au) have been utilized in medical fields including surgical sutures, drug delivery devices, tissue supports, and implants for interior bone fixation. This biomaterial can be used for bone regeneration application and shows high inhibition zones against bacteria (Prakash *et al.* 2020). Activated carbon is mainly based on physical adsorption, and it contains some hydrophilic (polar) functional groups (Fig. 1) (Lasindrang *et al.* 2015; DiamondWhites 2016). The interior of activated carbon contains many pores of different sizes. The structures of graphite, graphene oxide, and activated carbon were found to be similar, and their frameworks were all connected by carbon elements. However, there was a big gap between the frameworks structure and performance of the three.

The chitosan/GO combination exhibited a significant improvement in mechanical strength compared to a neat CS film; the composite film also had denser structure (Lyn *et al.* 2019). Graphene oxide (GO) particles were evenly distributed throughout the furcellaran films surface. Such nanofillers are expected to affect the structural, thermal, mechanical, and antimicrobial properties of furcellaran films (Jamróz *et al.* 2020). The tensile strength (TS) of 50.2%-chitin nanofiber (ChNF)/gelatin composite films was 5192 MPa, which is 2576 MPa higher than pure gelatin film in Young's modulus (Chuchu *et al.* 2018). The TS of graphite/gelatin composite films was good, at 35 °C and -10 °C. The elongation at break (EB) of graphite/gelatin composite films was good, at 0 °C and 10 °C (Yang *et al.* 2019). After adding 1% to 5% phenolic compounds, the TS of the film is enhanced, whereas its EB decreases (Thuy *et al.* 2018).

This research investigated activated carbon/gelatin composite films (ACGCF), graphite/gelatin composite films (GGCF), and graphene oxide (GO)/gelatin composite films (GOCF). Their performance was measured by testing TS, EB, water vapour

permeability (WVP), contact angle, and water-adsorption at different temperatures. The differences of three carbon materials were compared in matrix gelatin. This study provides a basis for future research on carbon materials in the field of packaging.

## EXPERIMENTAL

### Materials

Gelatin and glycerol were purchased from Aladdin (Shanghai, China). Activated carbon (coconut shell activated carbon, 50 nm) was purchased from Green Forest activated carbon company (Henan, China). Graphite (50 nm) was purchased from Tianjin Dingshi New Chemical Co. Ltd. (Tianjin, China). Graphene oxide was prepared as previously described (Yang *et al.* 2019). Gelatin and glycerol were of analytical grade.

### Preparation of Films

Gelatin (5 g) was dissolved in ultrapure water (70 mL) for 30 min ( $22 \pm 2$  °C) and left under magnetic stirring for 30 min at 60 °C. Glycerol (2 mL) was added to the solutions as a plasticizer after continuous stirring for 30 min. The activated carbon, graphite, or GO/gelatin solution was added to the film-forming solutions (activated carbon or graphite (0.5, 1, 3, 5, 7, and 10 %, w/w solid) or GO (0.5, 1, 5, 10, 15, and 20 %, w/w solids)) in quantities proportional to the gelatin. The film-forming solutions were poured into a PVC board (16 cm × 21 cm) and dried at  $22 \pm 2$  °C for 24 h. The dried films were peeled from the casting surfaces and stored at different temperatures and  $35 \pm 5\%$  relative humidity (RH).

### Tensile Strength and Elongation at Break

The TS and EB were tested according to GB/T 1040.1 (2018) and ISO 527 (2012). An XLW Intelligent Electronic Tensile Testing Machine (Shandong, China) was used to measure the tested film samples (100 mm × 30 mm), which were stored at -10, 0, 10, 25 and 35 °C and  $35 \pm 5$  % RH for 24 h. The speed was set at 50 mm/s. A total of ten replicates for each formulation were evaluated, and the average was recorded. The TS and EB were calculated as shown in Eqs. 1 and 2, respectively,

$$TS \text{ (MPa)} = \frac{F}{b \times d} \quad (1)$$

$$EB \text{ (\%)} = \frac{l_1}{l_0} \quad (2)$$

where  $F$  is maximum load (N),  $b$  is sample width (mm),  $d$  is sample thickness (mm),  $l_1$  is sample elongation at the moment of rupture (mm), and  $l_0$  is the initial grip length of each sample (mm).

### Scanning Electron Microscopy (SEM)

The samples were sputtered with gold and photographed using a JCM-6000 BENCHTOP SEM (Tokyo, Japan). The accelerating voltage was adjusted to 15 kV.

### Moisture

The moisture of the films was determined according to Nur and Nur (2016). The films were dried in an oven at 35 and 105 °C for 24 h until a constant weight was reached

(dry sample weight), and the moisture content (MC) was calculated as follows,

$$MC(\%) = \frac{M_0 - M_1}{M_0} \quad (3)$$

where  $M_0$  is the initial weight of samples (g) and  $M_1$  is the weight of samples after drying at 105 °C and 35 °C for 24 h (g).

### Water Vapour Permeability

The WVP of the sample was measured as reported (Shiku *et al.* 2004; Wu *et al.* 2017; Yang *et al.* 2019). Silica gel (30 g) was placed into a beaker of 50 mL, which was sealed by the sample. The WVP values were determined with RH of 80 ± 5% at 5, 20, and 35 °C, as shown in Eq. 4,

$$WVP/(g/(m \times h \times Pa)) = \frac{\Delta m \times d}{A \times t \times \Delta p} \quad (4)$$

where  $\Delta m$  is the mass increase of beaker at intervals (g),  $D$  is the thick bottom of the film (m),  $A$  is the area of beaker mouth (m<sup>2</sup>),  $T$  is the measurement time interval (h), and  $\Delta p$  is the pressure difference between the inside and outside of the film (Pa).

### Water Adsorption

The water adsorption ability of the sample was measured as described by Yang *et al.* (2019). Samples of 20 mm × 20 mm were placed in drying oven (35 °C) to free moisture of surface. The sample was immersed in water at 5, 15, 25, or 35 °C. The weight change of a sample was measured every hour,

$$WA(\%) = \frac{M_a - M_f}{M_f} \quad (5)$$

where  $m_a$  is the initial weight of the sample (g), and  $m_f$  is the dried after weigh of the sample (g).

### Contact Angle Measurements

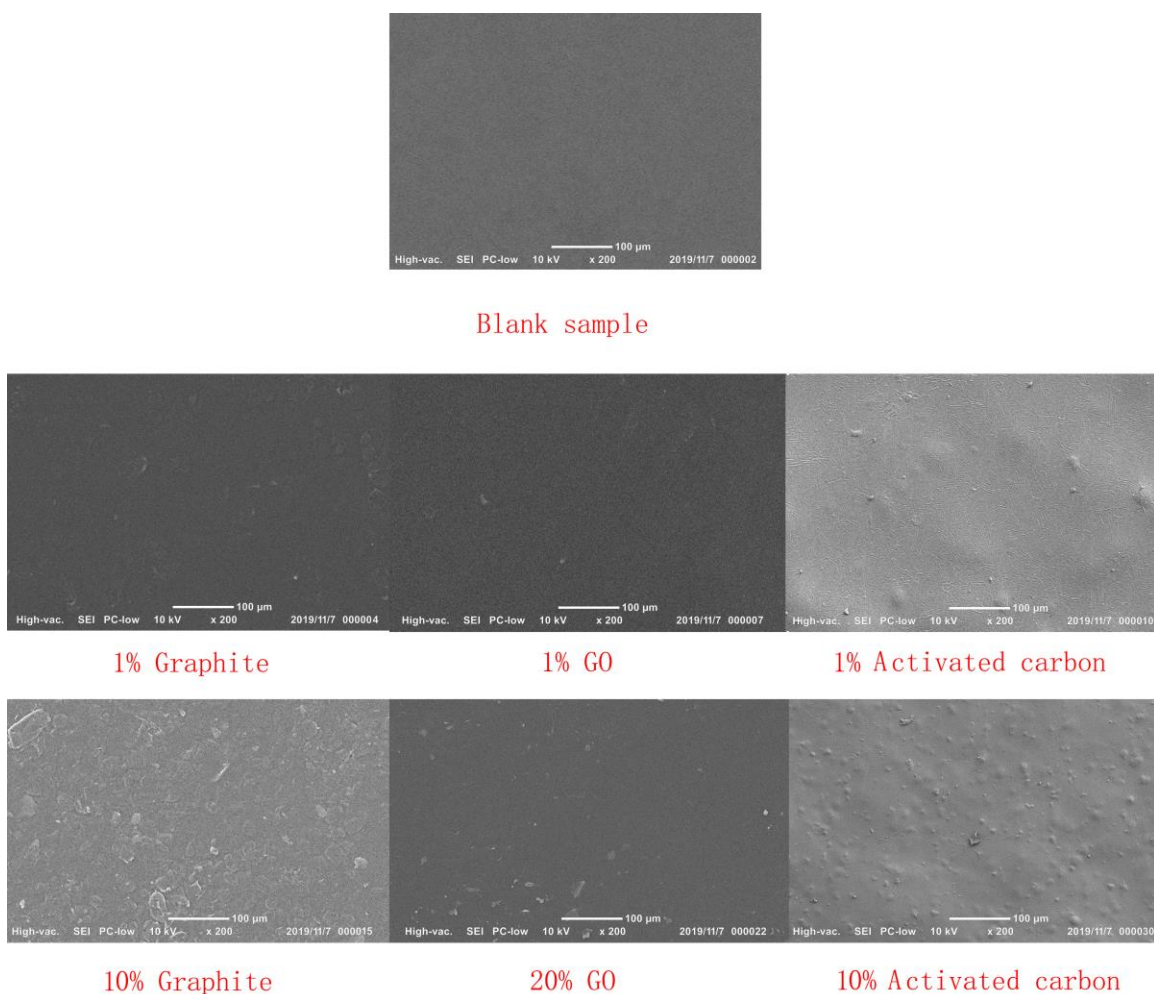
According to the method was reported by Manrich *et al.* (2017), 5 μL of distilled water was dropped vertically on the horizontal film surface with a syringe. The contact angle was determined by using a Kruss-DSA25 device.

## RESULTS AND DISCUSSION

### Scanning Electron Microscopy (SEM)

As shown in Fig. 2, the SEM of the blank sample showed no impurities. The surface was flat, and the structure of the molecular was stable. The surfaces of GOCF and GGCF were similar. Only some small particles adhered, and ACGCF had some circular salient when reinforced phases contents were less on composite films. The surfaces of GOCF, GGCF, and ACGCF differed greatly when reinforced phases contents were large in the composite films. For example, the particles on the surface of 20% GOCF were increased, but particles were still less than that of 20% GGCF. The surface of 20% ACGCF had a lot of circular salient. The compatibility and dispersibility of GO were better than activated carbon and graphite in the gelatin matrix. The GO was a single layer of graphite, and it contained more polar functional groups. Its surface area was larger than graphite and

activated carbon, so the hydroxyl, epoxide, and carboxyl groups of GO can bond with the hydroxyl, amino, and carboxyl groups in gelatin. The structure of graphite is stable; it is hydrophobic and cannot bond well with the hydrophilic surface of gelatin. Thus, the most of the graphite is gathered on the outer surface of the matrix gelatin, and the smaller part of the graphite is mixed in gelatin. The activated carbon contained a small number of polar groups and many pores of different sizes. After the gelatin molecules enter the pores, some of its molecular chains remain outside, which can be combined with the activated carbon or entangled with other gelatin molecular chains to form circular salient inside the gelatin.



**Fig. 2.** SEM of ACGCF, GGCF, and GOCF (100  $\mu\text{m}$ )

### Mechanical Properties

Temperature influences the EB and TS of composite films. The TS reflects the maximum tensile stress, while the EB reflects the maximum change in length of material before breaking. At the same content and temperature, the trend of TS from large to small was GGCF, GOCF, and ACGCF; the trend of EB from large to small was GOCF, GGCF, and ACGCF. Figure 3 shows higher TS and smaller EB at 35 and  $-10\text{ }^{\circ}\text{C}$ , and higher EB and smaller TS at 0 and  $10\text{ }^{\circ}\text{C}$ . The TS of composite films increased at first and then decreased with the content of the reinforced phase.

Gelatin forms a gel at low temperature and dissolves at high temperature. Gelatin

contains many functional groups such as amino, hydroxyl, and carboxyl. Those functional groups are beneficial to the production of polarity and hydrogen bonding (Parani *et al.* 2018; Krupa *et al.* 2004).

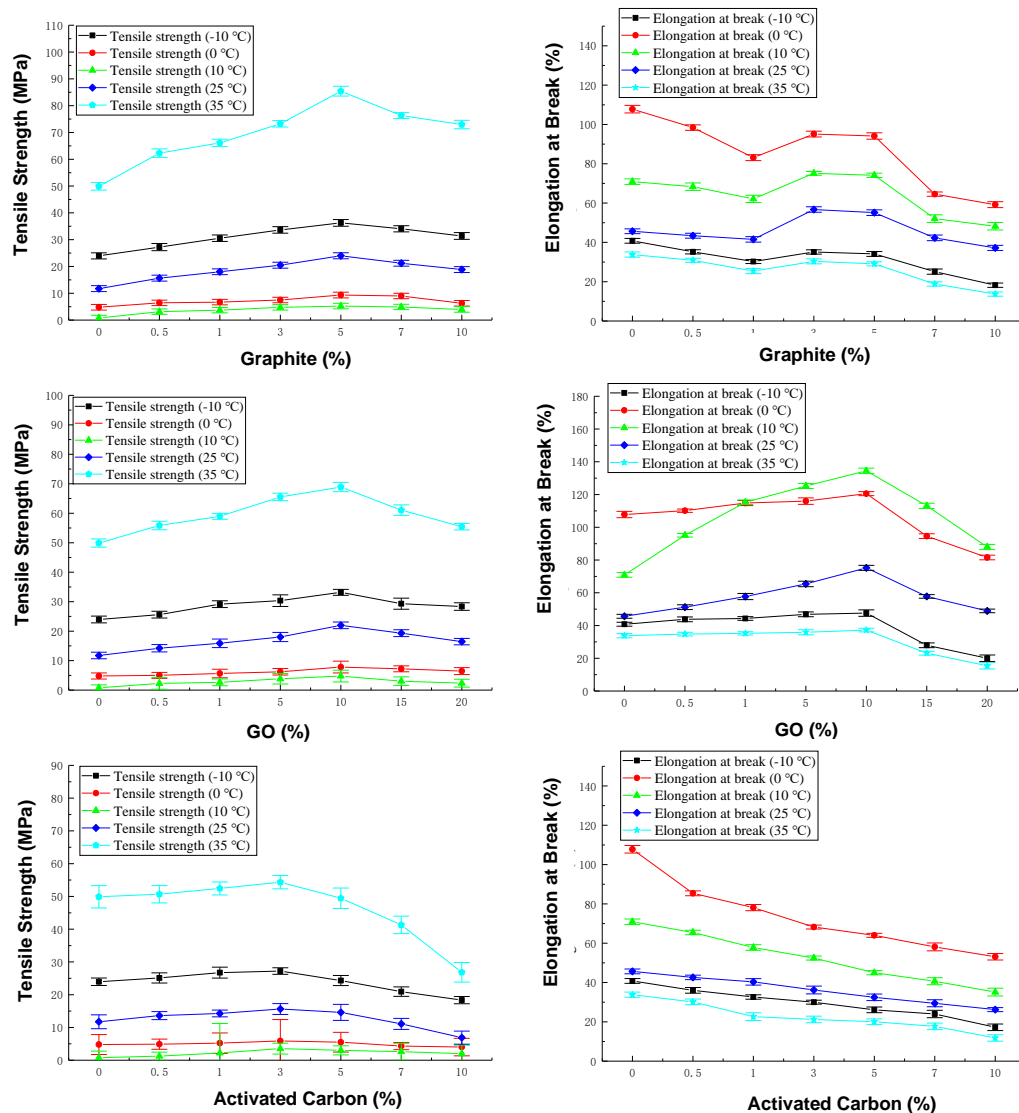


Fig. 3. EB and TS of ACGCF, GGCF, and GOCF at different temperatures

Figure 1 shows the structure of graphite molecules as a stable and strong interaction between sheets; it is hydrophobic and nonpolar. The addition of graphite increased the hydrophobicity of composite films, leading to composite films in which water molecule content decreased with increased graphite. The GGCF contained more glycerin and water molecules, which can be combined with the gelatin macro-molecules to alleviate and buffer the strong forces among the macro-molecules. The alleviation and buffering effect of glycerol and water molecules resisting the attractive force between macromolecules was reduced when the water molecule contents of composite films were decreased. This enhanced the forces between macro-molecules in the composite film, such that its TS was increased. Graphite has a high density (Huang *et al.* 2018). Graphite sheets are closely packed, leading to friction between the sheets. Graphite (a non-polar hydrophobic

substance) was blended with gelatin (a polar hydrophilic substance), because the polarities of two substances are different, so many graphite sheets were attached to the surface of gelatin, with little effect on the structure of gelatin. The graphite sheets prevent the loss of water molecules in composite films, when applied at 3% to 5% graphite content. When the graphite content was too low, the adhesion area of graphite sheets on the surface was small and not sufficient to block moisture. The aggregation and superposition of graphite sheets was able to decrease the mechanical properties of composite films when the content of graphite was too large. The graphite sheets attached to the surface will overlap each other. The overlap graphite sheets were separated, such that friction forces and friction distances between graphite sheets with others were generated, when GGCF was subjected to the tensile force. Yang *et al.* (2019) reported that when GGCF is subjected to tensile force, graphite sheets are separated. The above reasons lead to the trend of TS first increasing and then decreasing. The trend of EB first decreased and then increased (at 3 %-5 % content of graphite). The molecular structure of graphene oxide contains many oxygen-containing functional groups, which have characteristics of electronegativity (Wang 2015). The gelatin molecule contains hydroxyl, carboxyl, amino groups, the last of which provide a non-uniform distribution of positively charged groups in the molecular chain of the polypeptide (Thongjun *et al.* 2012). Gelatin molecules and GO exhibit both polarity and charge attraction. With the addition of GO, the polarity of composite films increases, and the GOCF contained a lot of water molecules, which can buffer the intermolecular force. The polar groups of GO and gelatin are bonded to each other, which can make the amount of bonding increase in composite films. The aggregation and superposition of GO can make the mechanical properties of composite films decrease when the content of GO becomes too large. Therefore, the EB and TS of GOCF were first increased and then decreased.

Activated carbon is a superior adsorbent (Salleh *et al.* 2014). The addition of activated carbon increased the TS of composite films. The experimental results were similar to Ziani *et al.* (2008). The molecular structure of activated carbon contains few active groups that can bond with gelatin. Figure 3 shows that the activated carbon can form circular salient in gelatin; the activated carbon contact sites with gelatin molecules were decreased. The interfacial effects were reduced, which broke the molecular structure of collagen. Therefore, the TS of composite films was first increased slightly and then decreased, and EB was always decreased.

The glycerol and water molecules can buffer interaction between macromolecules. The proportion of glycerol of composite films decreased when the reinforced phase increased. The difference in temperature and reinforcing phase can cause water molecules to change in composite films. The contents of water molecules and glycerol can affect the elasticity and flexibility of composite films. The elasticity between molecular chains was increased, and rigidity was reduced. The TS of composite films was larger than others, at 35 °C and -10 °C. The water molecules of composite films became crystals at low temperatures, so they could not act as a buffer. The inter-molecular activity was increased, and the evaporation of water molecules was increased, leading to a decrease in the water content of the composite films. Thus, intermolecular forces were increased after exposure to high temperature. The EB of composite films was larger than others at 10 and 0 °C. The intermolecular activity was low and the water content was greater (less affected by evaporation and crystallization) on composite films at this temperature. Water molecules can buffer the strong force between molecules, and the elasticity of the molecular chain was increased. Comparing the TS of GGCF and GOCF, it was concluded that hydrophobic materials can be added as reinforcement phase (graphite) to improve the TS of composite

film. This was because the effect of water molecules on TS of the composite film was greater than the bonding force between GO and gelatin.

## Moisture

For a gelatin composite film, differential scanning calorimetry shows peak moisture loss between 70 °C and 100 °C (Maria *et al.* 2017; Song *et al.* 2018). The water loss of the composite film was equal to the total water content of the composite film at 105 °C, and compared with the water loss rate at 35 °C. This difference value (Fig. 4's gap) was the water content of composite films, at 35 °C (This temperature was the higher temperature in the human living environment. This temperature's water content of composite film will provide the basis for the practical application of the materials in the future.). The purpose of this test was to test the water content of the composite film at 35 °C, and to simulate performances of dehydration and water retention on different composite films above room temperature (35 °C). The trend of water loss rate was ACGCF, GOCF, and GGCF from small to large at 35 °C. The trend of water loss rate was ACGCF, GGCF, and GOCF from small to large at 105 °C. The molecular chain of composite films can shrink, which leads to defects in the inner and surface of composite films at high temperatures.

Gelatin contains a large proportion of hydrophilic amino acids, and its water absorption capacity is strong (Cazón *et al.* 2018). A large number of water molecules in the blank sample was lost at 35 °C. This result showed that the bonding between gelatin and water molecules was not strong at 35 °C.

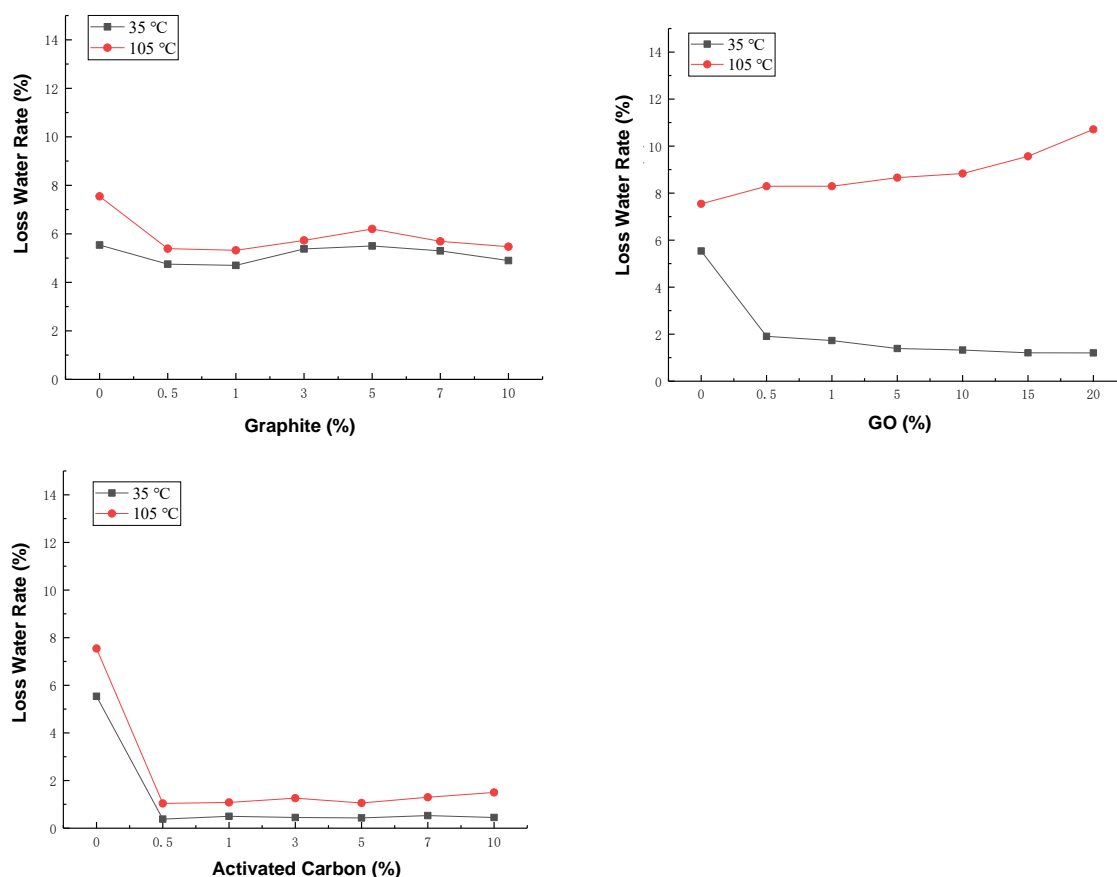


Fig. 4. Moisture of ACGCF, GGCF, and GOCF at different temperatures



The moisture of ACGCF was lower than the others at 35 °C and 105 °C. The addition of activated carbon destroyed the original stable structure of gelatin on composite film. The hydrophobicity of graphite reduced the moisture of composite film. The moisture of GGCF was little changed with the increase of graphite. Because the hydrophilicity of graphite and gelatin was different, the influence of graphite on the gelatin structure was small. The water loss rate of the composite films was increased when the graphite content was 3% to 5%. The results showed that the water content of those composite films was larger than that of other graphite content composite films. GO can be regarded as a single layer of graphite, and it contains many hydrophilic groups at the edges. The hydrophilicity of GO was larger than activated carbon and graphite. The moisture of GOCF was increased with GO. The moisture of GOCF was more than others, and the mechanical properties and flexibility of GOCF were good at 35 °C. The water content of GOCF was larger than that of other composite films, at 35 °C. Thus, the water retention (35 °C) of GOCF was greater than the other composite films.

## WVP

The WVP of composite films was affected by many factors, such as molecular structure, the interaction between the main polymeric chains and reinforced phase, plasticizers, or other additives (Bedane *et al.* 2015). The WVP refers to the permeability of sample film water vapor. It can evaluate the performance of a sample film for food preservation. A smaller WVP indicates better performance.

Gelatin, GO, and glycerin are hydrophilic substances. The WVP of composite films was increased with temperature. Due to the reversible gelling of gelatin, which is greatly affected by temperature, it was dissolved at high temperatures. Therefore, the many functional groups were exposed, such as amino groups, carboxyl groups, and hydroxyl groups, and it was easy to attract a lot of water molecules, on gelatin. The original structure of gelatin was destroyed. The intermolecular activity of composite films was increased with temperature. Water molecules entered and passed through the composite film, changing the pressure of the internal system, and the WVP of the composite film changed. The number of water molecules passing through the composite with temperature was increased.

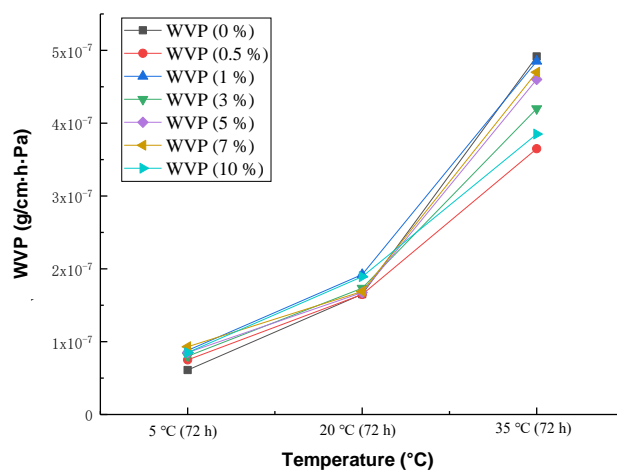


Fig. 5. WVP of GGCF at different temperatures

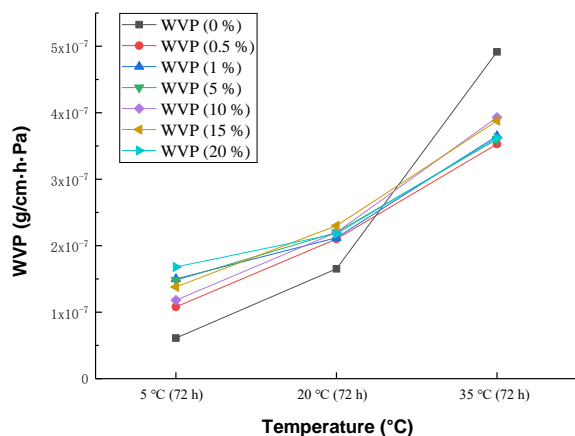


Fig. 6. WVP of GOCF at different temperatures

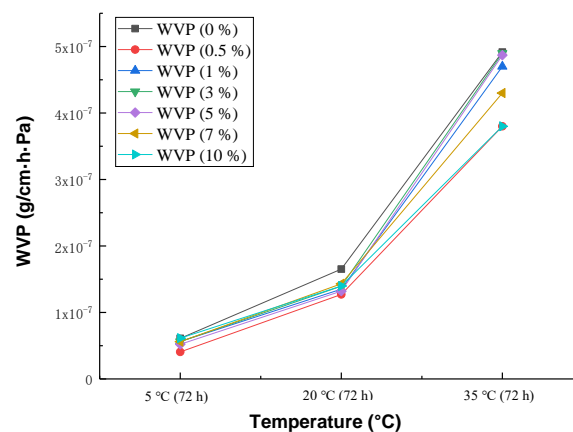


Fig. 7. WVP of ACGCF at different temperatures

The trend of WVP from small to large was ACGCF, blank sample, GGCF, and GOCF at 5 °C. The WVP values of ACGCF, blank sample, and GGCF showed little difference. The activity between molecules was low in composite films, and the speed of water molecules entering the composite films was slow at low temperature. Hydrophobic graphite can hinder and slow down the entry of water molecules into composite films. As shown in Fig. 2, the activated carbon within the gelatin formed many circular salient agglomerations inside ACGCF, and there were no obvious defects on the surface. The circular salient aggregation resulted in aggregation of gelatin molecules, and the number of polar and hydrophilic sites in the composite film decreased. As a consequence, the water molecules had difficulty in passing through ACGCF. The WVP of GOCF was increased with GO of content. The hydrophilicity and polarity of GOCF were increased with GO, leading to the GOCF being able to attract many water molecules, which entered the interior of the composite film. At the same time, the bonding degree of GO with gelatin and glycerol was not large at low temperature. The trend of WVP from small to large was ACGCF, blank sample, GGCF, and GOCF at 20 °C. The WVP of 20 °C was similar to that of 5 °C; because the trend was the same, the reasons were assumed to be similar. The trend of WVP from small to large was GOCF, GGCF, ACGCF, and blank sample at 35 °C. The intermolecular activity and molecular chain of shrinking were increased with temperature, leading to defects in composite films. The hydrophobic reinforcing phase was added into the composite films, and the entry of water molecules into composite films was hindered. At the same time, the bonding of GO with gelatin and glycerol was large at 35 °C. The molecular chains were shrunk, the activity of molecules increased, and the distance between the hydrophilic and polar sites was become shortened, and they were also likely mutual attraction with each other form bonds, at high temperatures. Therefore, the number of polar and hydrophilic was decreased, the number of bonds increased and its structural stability increased in GOCF.

Thus, the bonding degree of GO with gelatin and glycerol was affected by temperature. The water molecules were decreased, intermolecular activity was increased, and the degree of bond synthesis increased at high temperature. However, they were opposite, at low temperature. The range of changes in WVP was smaller for GOCF than for the others at different temperatures. This was attributed to the fact that the bonding degree of GO with gelatin and glycerol were changing with temperatures, and the amount of bonding was always greater than that of others. Therefore, it was difficult for water molecules to cross through GOCF.

### Water Adsorption

In 35 °C water, the GGCF and GOCF were completely dissolved at 50 min, and ACGCF was dissolved in 30 min. The water absorption ability of composite films was increased with temperature. However, the composite films dissolved in water when the temperature was too high. The water absorption of composite films was increased at 0 h to 5 h, and they were gradually stabilized at 6 h to 12 h. The water absorption of composite films was gradually stabilized with increased time. The hydrophilic sites of composite films were combined with water molecules, decreasing the hydrophilic sites in the composite film. The molecular polar attraction of composite films decreased and the diffusion rate of water molecules in the composite film was reduced.

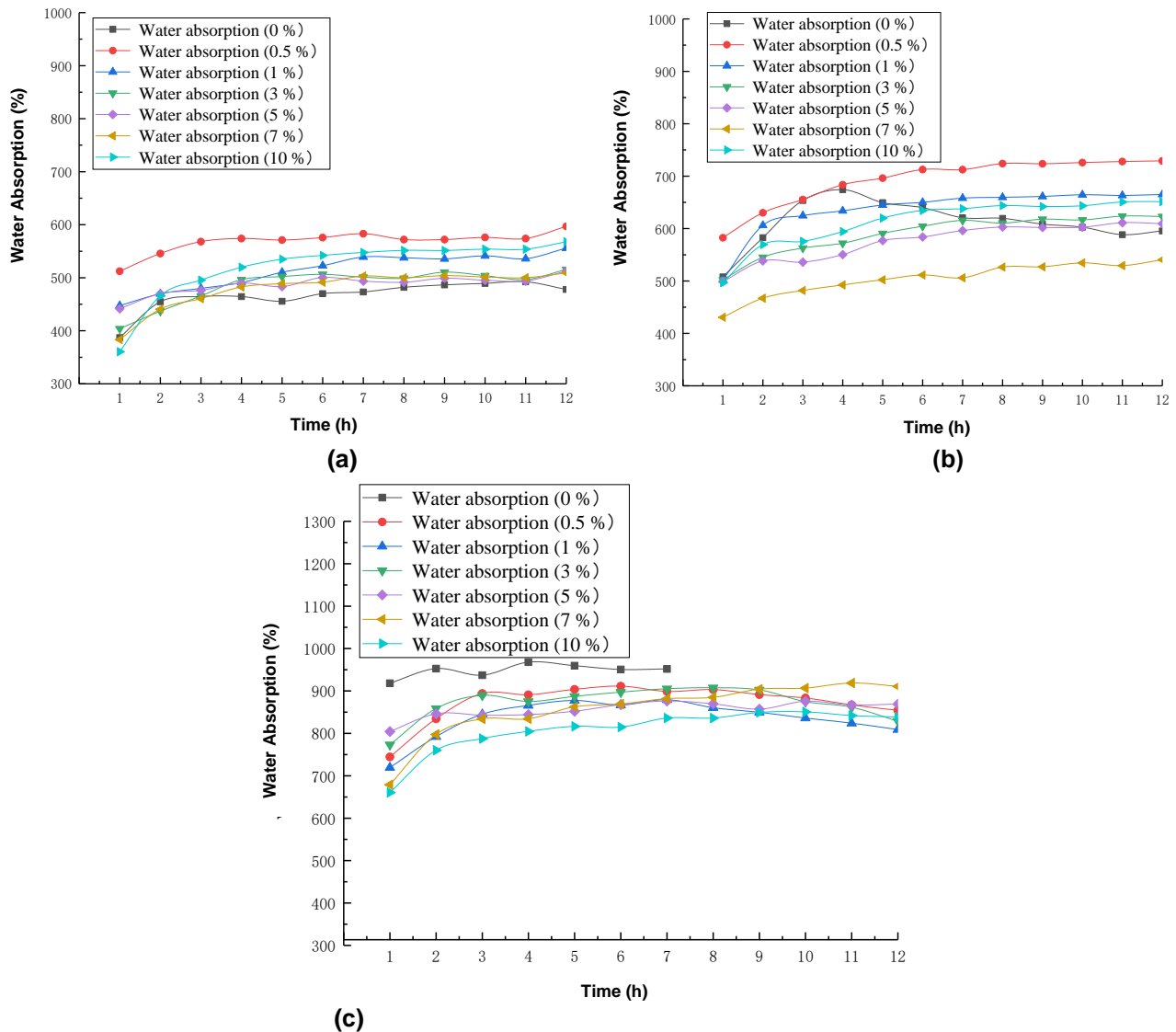
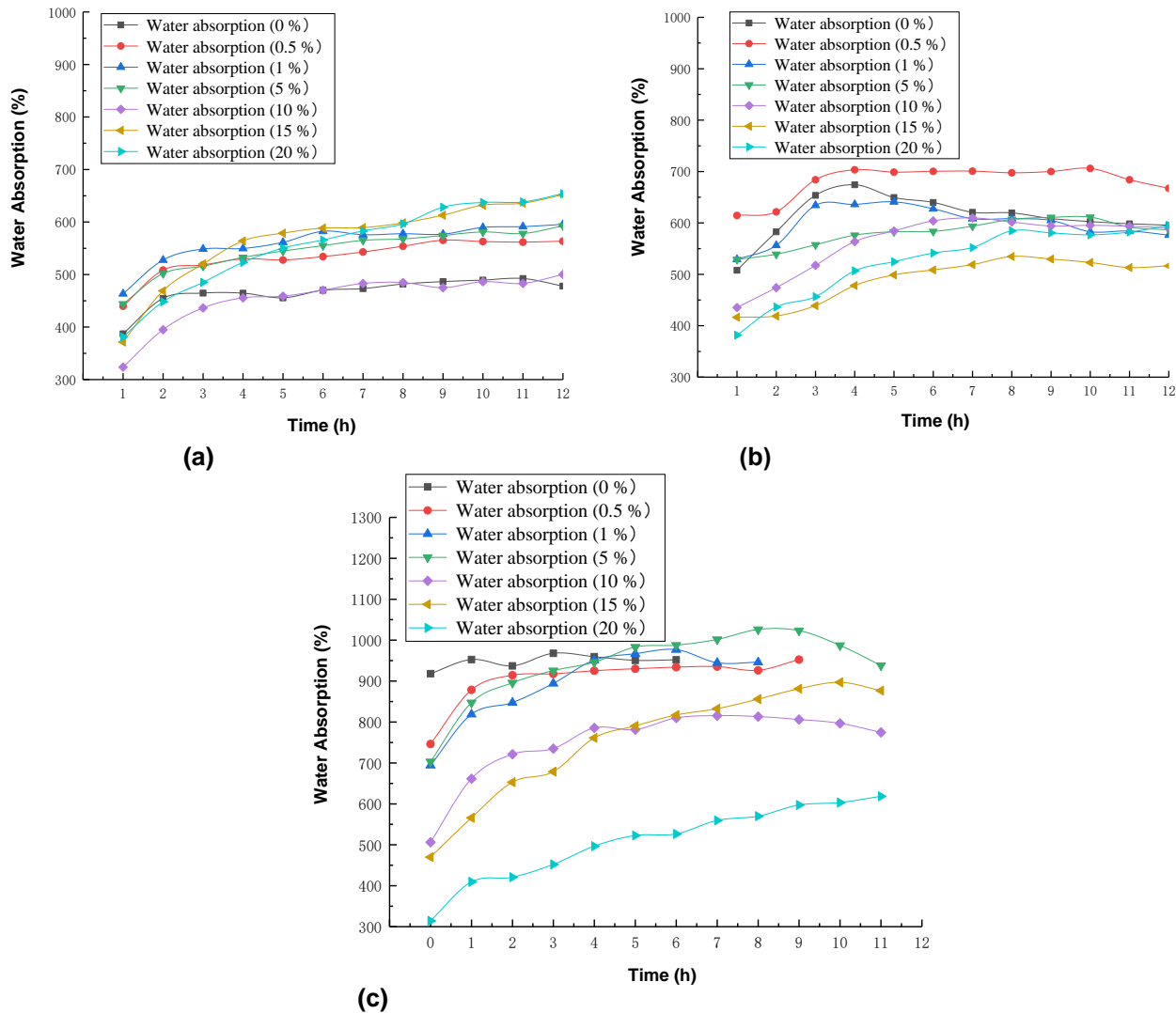
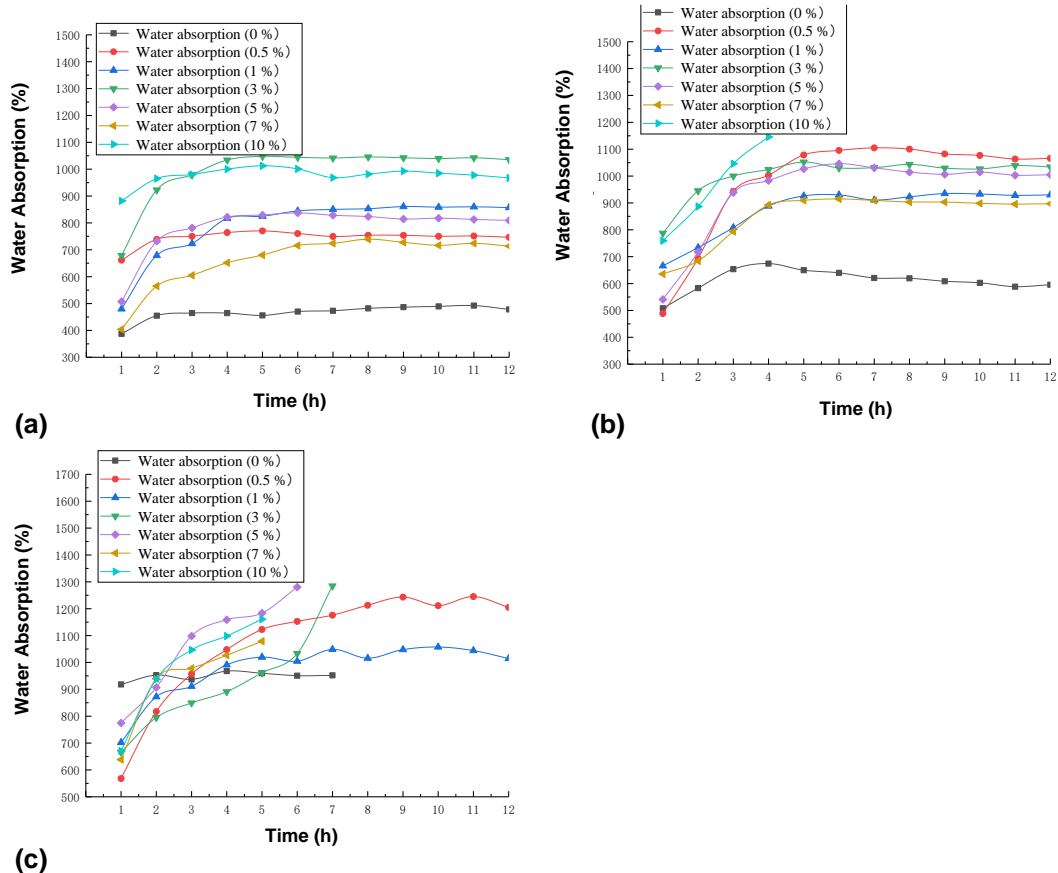


Fig. 8. Water adsorption of GGCF at different temperatures (a-5 °C; b-15 °C; c-25 °C)



**Fig. 9.** Water adsorption of GOCF at different temperatures (a-5 °C; b-15 °C; c-25 °C)

The water absorption values of ACGCF, GGCF, and GOCF were larger than the blank sample at 5 °C. The gelatin was in the form of a gel at low temperature and it was easy to dissolve at high temperature. The original structure of gelatin was stable at low temperature. The addition of reinforcing phases can make up some of the shortcomings of gelatin but they destroyed the original stable structure of gelatin (there were some defects on the surface of the composite film). The molecular activity was low, and the number of bonds was less in the composite film at low temperatures. The defects and hydrophilicity sites were exposed to composite films and water molecules easily entered and diffused inside of composite films. The water absorption of the blank sample increased with the temperature. The water absorption of many composite films with reinforced phases was lower than that of the blank sample at 15 and 25 °C. The gelatin was easy to dissolve at high temperature, and there were contents of many hydrophilic of functional groups and amino acids. When the blank sample was immersed in water, water molecules entered the interior of composite films, and the molecular structure of composite films was destroyed.



**Fig. 10.** Water adsorption of ACGCF at different temperatures (a-5 °C; b-15 °C; c-25 °C)

The GO contained many polar hydrophilicity groups. The activity of molecules increased with the temperature. As the probability of collision between molecules was increased, the bonding between molecules was increased. Therefore, gelatin, glycerol, and GO were bonded to each other, the water absorption of GOCF was become lower with GO content increased. Graphite is a hydrophobic substance. The graphite sheets attached to the surface of GGCF can prevent and slow down the water molecules from entering the composite films. The activated carbon contained few polar hydrophilic groups. There were many circular salients on ACGCF, and the compatibility of gelatin with activated carbon was low. As a result, the stability of ACGCF in water was low, and the diffusion speed of water molecules was fast. The 3% to 10% content of activated carbon composite films were ruptured at 25 °C. Therefore, the trend of water absorption of composite films from small to large was GOCF, GGCF, and ACGCF. The composite films had big water absorption capacity at low temperature and had a certain relatively water-hating at high temperature, with the addition of carbon materials.

### Contact Angle

Contact angle is an indicator used to measure hydrophilicity or hydrophobicity degree of a film surface. A film surface can be regarded as hydrophilic when the contact angle is small ( $\theta < 90^\circ$ ), while large contact angle ( $\theta > 90^\circ$ ) implies a hydrophobic surface (Dou *et al.* 2018). The blank sample had a low contact angle value, which can be attributed to the hydrophilic properties of gelatin and glycerol in it (Fig. 11). The contact angle of three composite films showed different trends, after the addition of three medium carbon

materials. The contact angle of ACGCF was decreased as the content of activated carbon increased, because there were many circular salients on ACGCF, and the compatibility of gelatin with activated carbon was low. The ACGCF was prone to defects, leading to increased hydrophilicity and polarity as the content was increased. Most of the graphite adhered to the surface of GGCF, since the graphite did not bond well with gelatin. Thus, the graphite had less influence on matrix gelatin than activated carbon. At the same time, the hydrophobicity of graphite can increase the hydrophobicity of the composite film. The contact angle of GGCF was increased. The polar and hydrophilic groups of GO and gelatin were combined with each other, resulting in the GOCF hydrophilic sites was reduced. The polar and hydrophilic groups of GO are decreased, since it can be regarded as a single-layer graphite, which also had a certain water resistance. Therefore, its hydrophobicity was higher than GGCF.

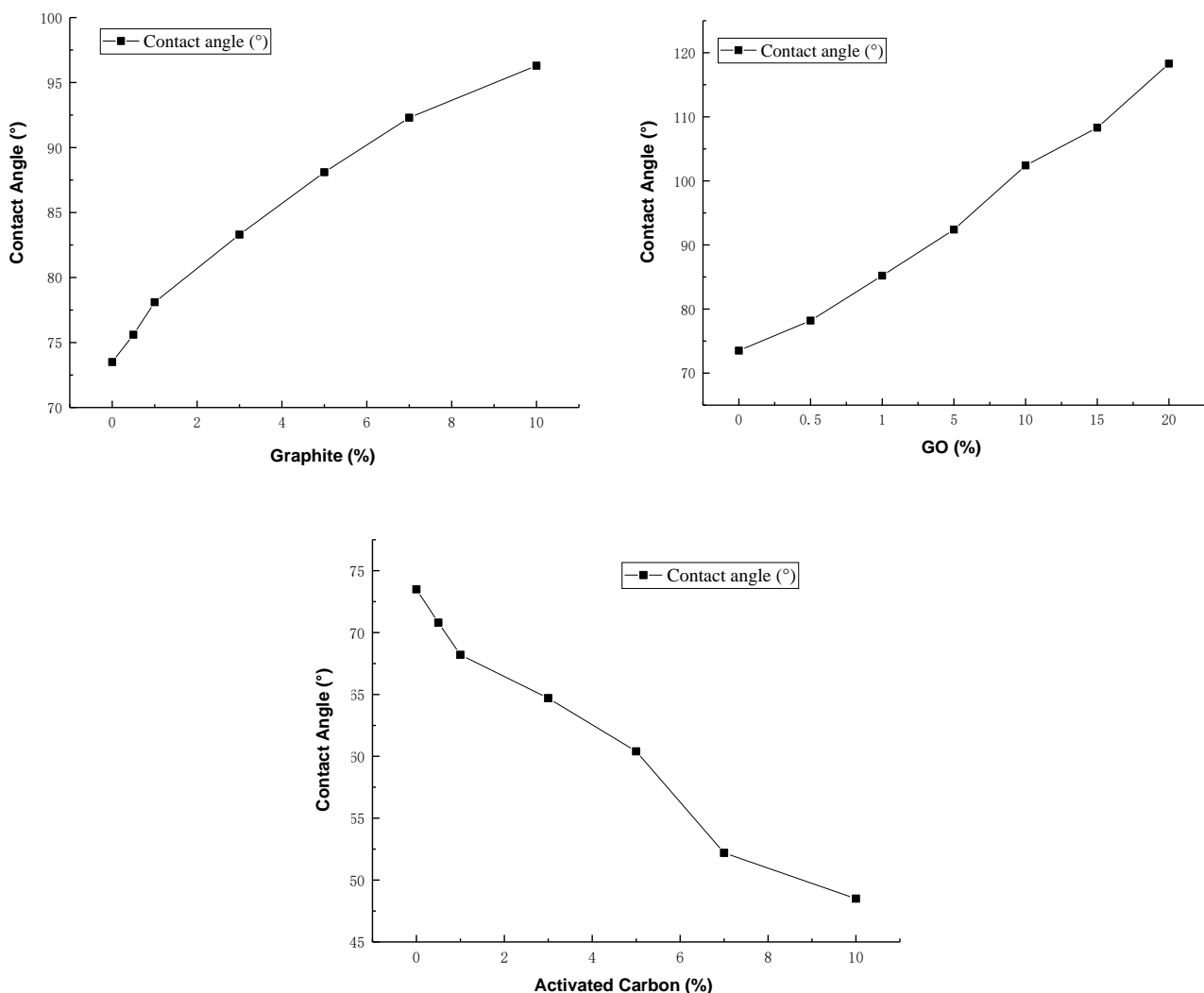


Fig. 11. Contact angle of ACGCF, GGCF, and GOCF at different temperatures

## CONCLUSIONS

1. The properties of composite films prepared with gelatin and three kinds of carbon were compared at different temperatures. The performance of composite films showed some improved and impacts, with the addition of the reinforcing phases (three carbon materials). Thus, changes were observed in tensile strength (TS), elongation at breakage (EB), water-resistance, moisture, and water vapor permeability (WVP). The three reinforcing phases all were carbon materials, but their activity, stability, and structure were different. Different performance of composite films were interpreted based on the addition of different reinforcing phases.
2. The properties of the matrix (gelatin) played a major role in the composite film at low temperatures. The gelatin had a condensed character at low temperature, whereas it became a solution at high temperature. Therefore, both the water absorption and the WVP corresponding to the blank sample were low. The interaction between the reinforcing phase with matrix (gelatin) played a major role, at high temperatures. The reason was that the stability of the matrix gelatin was reduced, and the gelatin was protected by different reinforcing phases, at high temperatures. For example, graphene oxide (GO) increased the intermolecular interaction by bonding with the matrix gelatin and glycerol. Graphene oxide composite films (GOCF) had higher TS, EB, and moisture, and their WVP and water absorption were lower at high temperature. Due to the different polarities of graphite, it was mainly attached to the surface of gelatin to protect the gelatin. GGCF had better TS and EB (when graphite contents were 3% to 5%), other properties were slightly poorer than GOCF. Activated carbon has a highly porous structure, and it was easy to form many circular salients inside the composite film when it was mixed with the matrix gelatin. The performances of ACGCF was much lower than that of GOCF and GGCF. The different composite films can be prepared accorded to the environment. The used composite films were immersed in water of 35 °C, can are dissolved completely, in a short time. The trend of hydrophobicity was GOCF, GGCF, ACGCF, in the contact angle test.

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## Declaration of Conflicting Interests

The author(s) declare no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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