



Rheological and electrical properties of carbon black and carbon fiber filled cyclic olefin copolymer composites



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ARTICLE INFO

Article history:

Received 23 July 2013

Received in revised form 19 January 2014

Accepted 17 February 2014

Available online 28 February 2014

Keywords:

A. Polymer–matrix composites (PMCs)

B. Rheological properties

B. Electrical properties

E. Extrusion

ABSTRACT

In this study, morphological, rheological and electrical properties of cyclic olefin copolymer (COC)/carbon black (CB) and COC/carbon fiber (CF) composites were investigated. Rheological measurements indicated that the CB was more effective filler than the CF to improve the viscoelastic parameters such as melt elasticity and dynamic viscosity of samples because of relatively higher surface area and nano size of CB particles. Based on the improvement in melt elasticity of samples depending on the type and amount of filler, the first rheological percolation threshold, the critical filler amount to stepwise change the rheological behavior of composites, were determined to be 9.4 and 15 phr for the CB and CF, respectively. It was also found that the local and continuous agglomeration of CB particles predicted by the Kerner–Nielsen method began at the filler amount of 10 and 30 phr, respectively. The electrical conductivity measurement performed by an impedance spectroscopy exhibited that the electrical percolation was about 15 phr for both fillers. Maximum electrical conductivity values of 10^{-2} and 10^{-1} S/cm were obtained by introducing of 40 phr of CB and CF, respectively.

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1. Introduction

Carbon filled polymer composites have been attracted much technical attention in recent years because of their superior physical properties such as high electrical and thermal conductivity, enhanced mechanical performance, weight advantage and excellent resistance to corrosive environments and chemicals compared to metals and metal filled polymers. In literature, using of different forms of carbon fillers which are significantly varied in size, geometry and structural properties such as single and multiwalled carbon nanotubes (SWCNTs and MWCNTs) [1–3], fullerenes [4], carbon black [5,6], carbon fiber [7–9], graphite and graphite derivatives [10–12] (e.g. graphite oxide, graphene, surface modified graphenes etc.) have been reported to enhance the electrical and mechanical properties of polymers. Furthermore, possible using of conductive polymer composite (CPCs) in various technological applications, such as sensors [13], batteries [14], bipolar plates in fuel cell systems [15,16], electromagnetic interference (EMI) and radio frequency interference (RFI) shielding materials [17–19] have also been investigated. Especially, CNTs have generated great scientific attention since they provide superior physical performance and electrical conductivity at very low loadings compared to other

types of carbon fillers. However, lack of mass production and cost of carbon nanotubes are still serious drawbacks for their industrial usage in the production of low-cost conductive CPCs as well as fullerenes [10].

The CB, the amorphous form of carbon, is primarily used as commercial filler/additive of ultraviolet light stabilizer, antioxidant and antistatic agent in rubber industry, pigment or colorant in dye industry, conductive filler in polymer and composite industry for semi-conductive applications. Reported works about the CB filled polymer composites have mainly focused on the electrical and rheological behavior of such materials. Main challenge about the CB filled polymer composites is high melt viscosity due to the structural features of CBs. Thus, many works have investigated the rheological properties of such composites, in detail [20–23]. On the other hand, CF has become one of the most widely used reinforcements in engineering applications of polymer based composites due to its high temperature tolerance, elastic modulus and tensile strength, low weight and thermal expansion. Various grades of CF, as chopped fiber, prepreg or fabric, have been widely used to improve the mechanical performances of resin or thermoplastic based polymer composites especially in aircraft and aerospace industry [24,25]. Although both of CB and CF have the same chemical structure, there is significant difference in geometry and physical forms. Studies on the preparation and physical characterization of CPCs have mainly focused on the improving

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of electrical conductivity. On the other hand, effect of various forms of carbon based fillers on the rheological properties of CPCs is another important issue in terms of melt processing operations because sufficiently high conductivity values generally require high filler content which leads to increase melt viscosity significantly.

Cyclic olefin copolymers (COCs) are considered the new-generation olefin based amorphous thermoplastics obtained from the copolymerization of olefins, mainly ethylene, and cyclic olefins. COCs are characterized by their superior mechanical properties, excellent transparency, low moisture absorption and excellent resistance to solvents. Depending on the mole or weight ratio of the ethylene units in the structure, they also exhibit relatively high glass transition temperatures, ranged between 80 and 180 °C, compared to other polyolefin derivatives and thus long service life without a loss in physical properties [10]. Beside the excellent physical properties of the COCs, one of the most important advantageous of such polymers is their melt processability. There are many promising applications to use COCs in film and packaging, optical, medical in the industry. Although many works have been published on preparation and characterization of COC based nanocomposites with different inorganic fillers [26–30], only a few works have been reported about the physical properties of COC/carbon composites [10,31,32]. Motlagh et al. prepared CF and CB filled COC composites (by single and dual using of fillers) in a batch mixer and investigated the electrical and rheological properties of such composites [31]. In their study, they used high structured carbon black (surface area is 1250 m²/g) and chopped carbon fiber. They reported that the critical volume fraction for gaining the electrical conductivity was about 2.7% (v/v) for the CB and CF filled composites. They also remarked that better processability can be achieved when the carbon fiber (CF) was much higher than the carbon black (CB) in the matrix, for instance the volume ratio of CF:CB is about 3.

In this study, morphological, rheological and electrical properties of highly filled COC/carbon composites were investigated, in detail. Cheap, versatile and commercially available forms of carbon, CB and CF were used as filler by regarding the possible technical and commercial applications of materials. Structure-property relationships of composites depending on the type and amount of fillers were studied. Rheological and electrical percolation thresholds for the series of samples were determined and compared.

2. Experimental

2.1. Materials

The cyclic olefin copolymer used in this study was a commercial grade copolymer, Topas[®] 8007, kindly donated by Ticona. Commercial grades of carbon black (Ensaco[®] 250) and carbon fiber (AKSACA[®]) were also kindly supplied from the TIMCAL (Switzerland) and AKSA (Turkey), respectively. The CF used in the study was a chopped strand of the surface modified grade with a phenoxy-based resin. Some physical properties of the polymer and fillers employed in the study are listed in Table 1.

2.2. Sample preparation

Composites were prepared by melt processing in a lab. scale co-rotating, intermeshing twin screw extruder (Rondol Micro Lab., UK, D:10 mm, L/D: 20) with a screw speed of 75 rpm. The kneading segments of screws were configured as 3D of 4 × 60° followed by 2D of 4 × 90° blocks in the steady-state melt zone to provide an intensive mixing. A temperature profile of 120–200 °C was applied throughout the barrel from the feeding zone to die. Before the melt processing, all materials were dried in a vacuum oven overnight at 70 °C. The COC, Topas[®]8007 was also processed at the

Table 1

Some physical properties of the materials used in the study.

Commercial name	COC TOPAS [®] 8007	Carbon Black TIMCAL ENSACO [®] 250	Carbon fiber AKSACA [®]
Density (g/cm ³)	1.02	1.80	1.7–2.0
T _g ^a (°C)	78		
MVR ^b (ml/10 min)	32		
Surface area (m ² /g)		65	
Particle size (d ₉₀)		45 μm	D:8 μm L:3 mm
OAN ^c (ml/100 mg)		190	

^a Glass transition temperature measured with DSC method.

^b Melt volume flow index under the test conditions of 260 °C and 2.16 kg (ISO 1133).

^c Oil adsorption number (ASTM).

same conditions. Sample compositions are listed in Table 2. Sample compositions varied with the filler amount in the composition on the base of phr (part of filler per hundred of polymer). Volume fraction of the filler was determined with the given formula;

$$\phi_f = \frac{\rho_p W_f}{\rho_f W_p + \rho_p W_f} \quad (1)$$

where ρ_p and ρ_f are the densities of polymer and filler, W_p and W_f are the weight fractions of the polymer and filler, respectively.

2.3. Scanning electron microscopy (SEM) study

Filler morphology and microstructures of composite samples were investigated by a field emission scanning electron microscope (FE-SEM, FEI Quanta FEG 450) operated at 30 kV. Cryo-fractured surfaces of the extrudates were directly imaged in the electron microscope after a proper sample preparation.

2.4. Rheological measurements

Rheological behavior of the samples in the melt state was measured by a dynamic oscillatory rheometer. A controlled strain rheometer (AR-G2, TA Instruments, USA) equipped with 25 mm diameter parallel plate geometry was used in the rheology tests. Samples were directly loaded and molded between the plates and rheological tests were carried out at 200 °C with a gap distance of 1 mm. The thermal stability of COC during the rheological tests was monitored by a time sweep test conducted at the angular

Table 2

Sample composition.

Sample name	COC	phr	
		CB	CF
COC	100		
CB3		3	
CB5		5	
CB10		10	
CB15		15	
CB20		20	
CB25		25	
CB30		30	
CB35		35	
CB40		40	
CF3			3
CF5			5
CF10			10
CF15			15
CF20			20
CF25			25
CF30			30
CF40			40

frequency of 1 rad/s and the strain amplitude of 5% for 30 min. Then, the strain sweep test was performed in the strain range of 0.1–100% for the COC and 0.01–10% for the composites with the angular frequency of 1 rad/s to determine the linear viscoelastic (LVE) region of samples. Finally, the frequency sweep tests were carried out in the angular frequency range of 0.1–100 rad/s in the LVE region. (strain value of 5% for the COC and 0.1% for the composites).

2.5. Electrical conductivity measurements

The *ac*-conductivity measurements of the samples were carried out with an impedance spectroscopy analyzer (Solartron SI 1260 Impedance/gain-phase analyzer and Solartron dielectric interface 1296 devices) at 100 mV between the frequency ranges of 10^7 – 10^0 Hz. Test specimens for the conductivity measurements, a rectangular bar (2×1 cm) with the thickness of 0.2 cm, were prepared by compression molding method in a hot pres at 200 °C. The surfaces of specimens were directly contacted with electrodes by coating with a conductive silver paste to provide better surface contact. All measurements were carried out at the room temperature and moisture.

3. Results and discussion

3.1. Sample morphology

SEM micrographs of the carbon black and carbon fiber are given in Fig. 1. Fig. 1(a) and (b) show the sizes of CB particles and agglomerate, respectively. It is clearly shown that the average size of CB agglomerate is about 20–30 μm which consists of thousands of spherical CB particles having an average diameter of 40–50 nm. Fig. 1(c) shows the surface of a CF with the diameter of 8 μm . The length of the chopped carbon fiber is declared as 3 mm by the producer. The phenoxy-based resin onto the fiber surface (marked with a red circular) can also be clearly seen in Fig. 1(c). The amount of surface modification agent onto the CF was found to be about 2.5% (w/w) by a thermogravimetric analysis (not given here).

SEM images of cryo-fractured surfaces of the CB30 and CF30 samples taken at various magnifications were given in Fig. 2. Fig. 2(a) and (b) imply that the CB particles or agglomerates could be homogeneously dispersed into the polymer matrix without using a compatibilizer or chemical modification. It is seen that the average size of CB agglomerates into the composite structure are about 150–200 nm which indicates that the melt processing yielded formation of smaller CB agglomerates and effective dispersion into the matrix. Although a single CB particle is a nano-filler, micro-structure of COC/CB composites could be defined as a macro-composite as the average agglomerate size of filler is higher than 100 nm. Fig. 2(c) and (d) show that the CFs are dispersed well into the polymer matrix and oriented throughout the flow direction. In these figures, large gaps between filler and polymer phase, marked with the red circulars, can be seen which implies that interfacial interaction between the COC and CF is weak. This could be originated from the fact that incompatibility between the resin onto the CF surface and the COC melt and/or the shrinking ratio which is related to the thermal expansion coefficients of components. Moreover, it should be noticed that the surface modification of filler plays great role on the physical properties of composites and the phenoxy-based resin could be incompatible with the COC matrix. But, the main goal and motivation of the study was not only enhance the interfacial interaction between filler and matrix phases but also increase the electrical conductivity as the lowest loading as possible. It is also a well-known relationship that the surface modification processes or chemical treatments on the surfaces of carbon materials (especially for carbon fiber, graphene

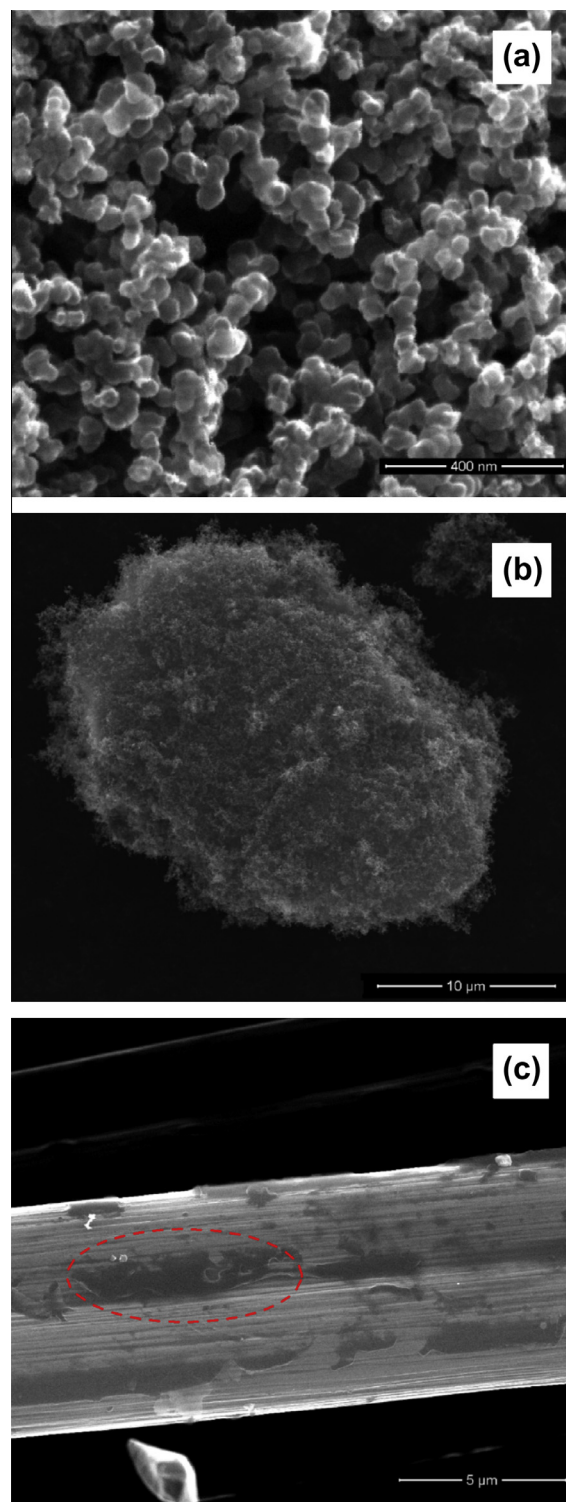


Fig. 1. SEM images of fillers. (a and b) carbon black and (c) carbon fiber.

and carbon nanotubes) can enhance the interfacial interactions between polymer matrix and fillers but dramatically reduce the electrical conductivity. The “processability”, “filler cost”, “mechanical performance depending on the interfacial interactions” and “conductivity requirements” are important parameters and such issue is kind an optimization work for the engineering application of carbon filled composites. Furthermore, single and multiple contacts between the carbon fibers, marked with the blue circulars, were also observed, as seen in Fig. 2(d). It can be assumed that such

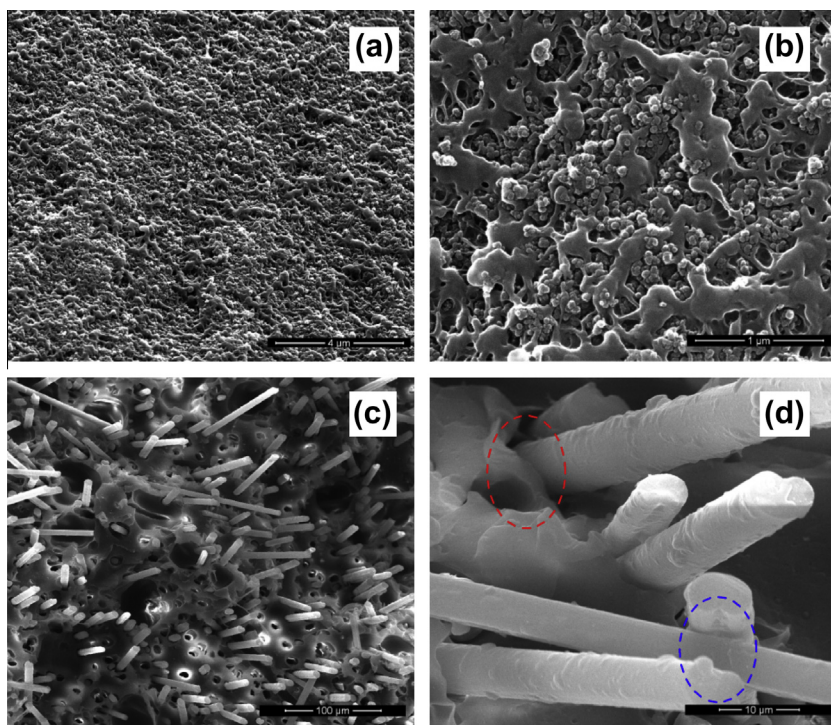


Fig. 2. SEM images of (a and b) CB30 and (c and d) CF30 samples at different magnifications.

contacts are mainly responsible for the electrical conductivity throughout the composite structure. As seen in the SEM image given in Fig. 1(c), small amount of phenoxy resin cannot cover the entire carbon fiber surface. It is located in some domains. It could be concluded that the effect of surface modification agent on the electrical conductivity can be ignored since the conductive pathways are formed by the multiple contacts between the carbon fibers.

3.2. Rheological behavior of samples

In the CPCs including macro-fillers are generally highly filled materials to provide sufficient electrical conductivity. High amount of filler can greatly affect the melt viscosity of polymer and disturb the processing conditions. Therefore, melt rheology measurements are important to understand the effects of type and amount of filler on the processing condition. Rheological behavior of polymer composites can be used to estimate some microstructural and physical properties of such materials.

Time sweep curves, given in Fig. 3, shows the change of storage (G') and loss (G'') modulus with time. In this test, the G' and G'' curves of a test sample sheared in a certain conditions is monitored for a period of time to practically see the possible effects of oxidative conditions on the molecular structure of polymer such as degradation, cross-linking and decomposition of volatile components at processing temperatures. Another benefit of the test is to check the thermal stability of polymer matrix during the rheological tests. In this study, time sweep test was only applied to the COC because of the high thermal stabilities of the carbon fillers. In Fig. 3, no change in the G' and G'' curves is observed during 30 min which implied that the polymer matrix provided the melt stability for, at least, 30 min. This result clearly indicates those cases of the processing conditions were quite safe for the possible thermo-oxidative degradation of COC which is a member of new-type polyolefin copolymers and thermally stable thermoplastics and the rheological tests can be safely run under the air

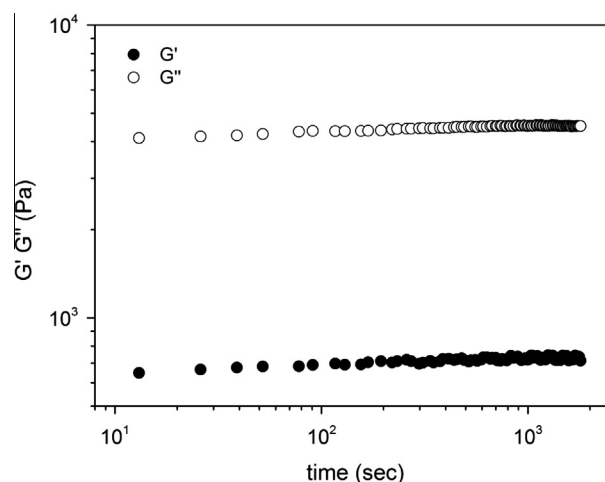


Fig. 3. Storage and loss modulus of COC as a function of time at 200 °C.

atmosphere for 30 min by neglecting the possible degradation effects of polymer matrix on the rheological properties of samples.

Secondly, strain sweep test was applied to the samples to determine the boundaries of LVE regime in which the G' and G'' are independent from the shear strain ($\gamma\%$). Dependence of storage modulus (G') on the shear strain is given in Fig. 4(a) and (b) for the sample series prepared with the various amounts of CB and CF, respectively. Since the G' is more sensitive rheological parameter than the G'' to the effects of filler on the structural changes, only the G' curves are presented here. In this figure, it is seen that the G' of the composite samples exhibits a linear region (Newtonian plateau, G'_{plt}) at low strains and non-linear region at high strain amplitudes. It is also clear that the melt elasticity of CB and CF series of composites enhances with increasing of filler amount. Increase in G'_{plt} can be analyzed more quantitatively by defining the reduced modulus (G'_R) which is the ratio of the plateau

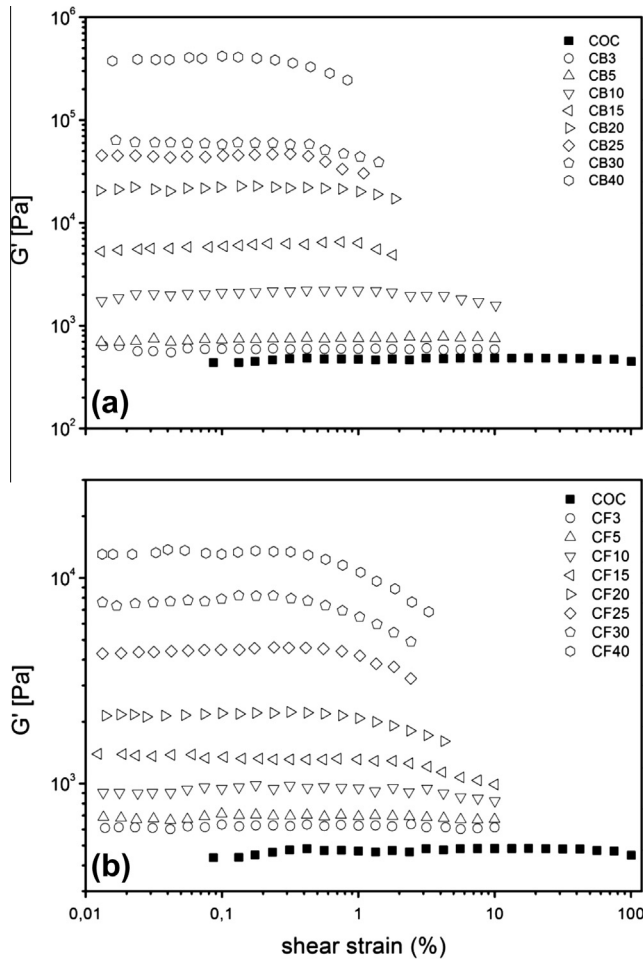


Fig. 4. Dependence of storage modulus (G') of sample series prepared with various amount of (a) CB and (b) CF on the shear strain ($\gamma\%$).

modulus of composite to that of polymer (G'_c/G'_p). Fig. 5 illustrates the dependence of G'_R values on the volume fraction of filler (ϕ_f). As seen in this figure, the G'_R increases slightly up to a particular volume fraction of filler. Above this volume fraction, the value of G'_R increases significantly for higher filler loadings. This critical volume (or weight) fraction of filler (ϕ_c) is called the rheological percolation threshold. It was found that the rheological percolation for the CB and CF filled sample series were 10 and 15 phr, respectively. Another important finding obtained from Fig. 5 is

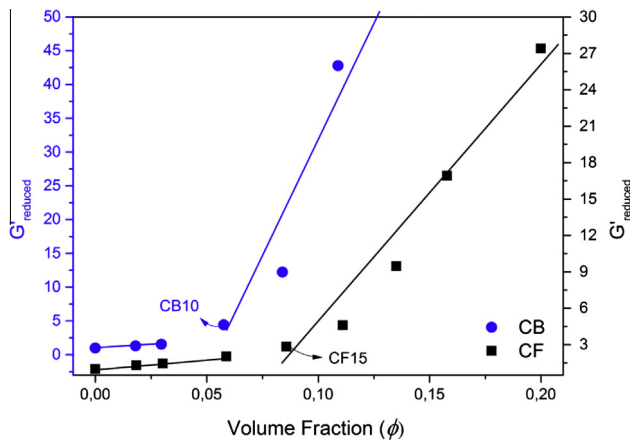


Fig. 5. Dependence of reduced modulus (G'_R) on the volume fraction of filler for the sample series prepared with the CB and CF.

the determination of reinforcement effect of fillers above the percolation threshold. To compare the reinforcement effect of fillers, improvement in melt viscosity with the amount of filler can be fit by the following power-law equation;

$$G'_R \propto (\phi - \phi_c)^n \quad (2)$$

In this equation, “ n ” is defined as the power-law index which shows the enhancement effect of filler. The n values were found to be 7.11 and 2.84 for the samples series prepared with the CB and CF, respectively. This result implies that the CB is more effective filler than the CF on the improvement of physical properties of polymer melt because of its relatively higher surface area and smaller size of dispersed agglomerates.

Dependences of G' of the samples on the angular frequency (ω) are given in Fig. 6 for the series of CB and CF filled composites as a function of filler amount into the composition. It is observed that the storage modulus values of composites increases with the increasing amount of filler in the entire range of frequency for the both series of samples. It is clearly seen that the increasing in G' is more pronounced at low frequency region. Moreover, the slope of $G'-\omega$ curve in the low frequency region decreases with the increasing amount of filler and becomes frequency independent ($G' \propto \omega^0$) above a particular filler amount. This phenomena is a well-known relationship for the polymer composites and nanocomposites, defined as solid-like (or pseudo solid-like) behavior, which points out the formation of physical network by fillers. In order to determine the solid-like behavior more precisely, increasing in G' at the lowest frequency, in the measurement range, could

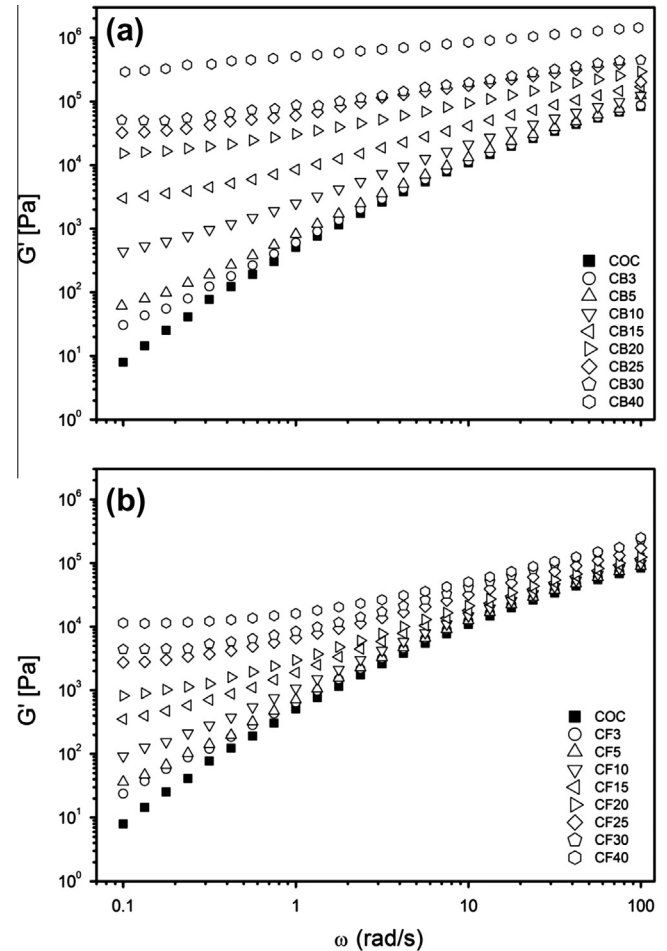


Fig. 6. Storage modulus (G') as a function of angular frequency (ω) for the samples series prepared with the (a) CB and (b) CF.

be used. Improvement in G' at the 0.1 rad/s depending on the filler amount is given in Fig. 7. It can be seen that the $G'_{0.1}$ increases dramatically above a critical volume fraction of the filler. This relation is similar to the enhancement of Newtonian or plateau modulus mentioned before. This critical volume fraction of filler is defined as the rheological percolation threshold (ϕ_p). The ϕ_p values were found to be 0.054 and 0.085 for the sample series prepared with the CB and CF, respectively, which correspond to 9.4 and 15 phr. The ϕ_p values obtained from the rheological measurements is generally considered the formation of fractal flocks for the composite systems [33–35]. It is known that the rheological percolation does not require the physical contact between filler particles and it is more related to the hydrodynamic effects of fillers into the polymer melt. Inset of Fig. 7 illustrates the change in $G'_{0.1}$ in entire composition range. It is seen that the $G'_{0.1}$ is significantly increased again about the filler amount of 30 phr for both fillers. This second increase in $G'_{0.1}$ corresponds to another microstructural threshold called “second rheological percolation” which represents the physical contact between filler particles and the formation of a continuous structural network of flocks [33–35]. Many studies have been reported on the determination and explanation of first and second rheological percolation thresholds for various polymer–filler systems [35–37].

To determine the effect of agglomeration formation on the percolation thresholds and the electrical conductivity, Kerner–Nielsen method [37–40] was used for the CB series of composites because of high agglomeration tendency of CB. The Kerner–Nielsen equation is defined as;

$$\frac{G'_f}{G'_p} = \frac{1 + KB\phi_f}{1 - B\phi\phi_f} \quad (3)$$

where G'_c , G'_p and G'_f are the dynamic storage modulus of composite, polymer and filler, respectively. The parameter K is a coefficient which is sensitive to the number of aggregate and the filler geometry and ϕ_f is the volume fraction of the filler. Parameters B and ϕ are defined with the following equations;

$$B = \frac{\left(\frac{G'_f}{G'_p} - 1\right)}{\left(\frac{G'_f}{G'_p} + K\right)} \quad (4)$$

$$\phi = 1 + \left(\frac{1 - \phi_m}{\phi_m^2}\right)\phi_f \quad (5)$$

where ϕ_m is the maximum packing fraction of filler which equals to 0.637 for random, compact packing of rigid circular particles. For rigid particles, B equals 1 because the modulus of filler is much

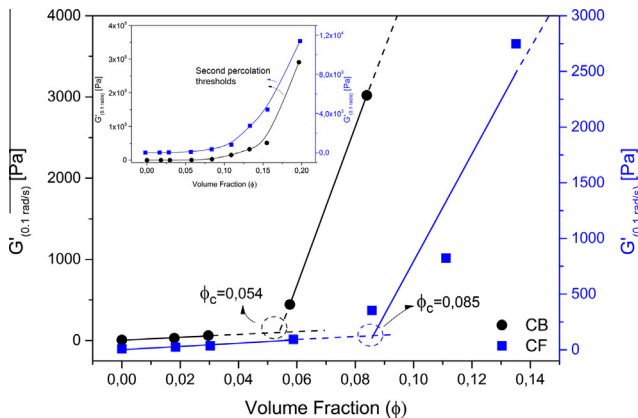


Fig. 7. Dependence of storage modulus values of samples at the angular frequency of 0.1 rad/s ($G'_{0.1}$) on the volume fraction of fillers for estimating the critical volume fraction (ϕ_p).

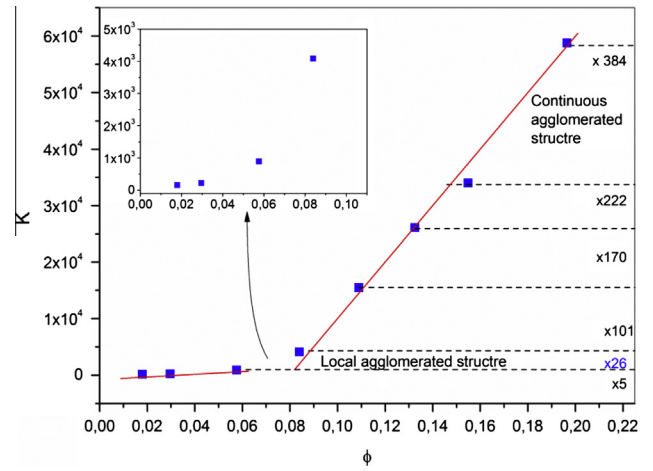


Fig. 8. Dependence of K parameter in the K–N model on the volume fraction of CB.

higher than that of polymer. Change in K with the volume fraction of filler is given in Fig. 8. It is seen that the value of K becomes five times higher than the initial value (3 phr) when the amount of filler reaches to the critical volume fraction which is 0.058 (10 phr). Above the critical volume fraction, the K begins to increase abruptly and becomes 26 times higher than the initial K value at the ϕ_f is 0.083 (15 phr). It can be concluded that significant number of CB agglomerates were formed at the filler amount of 15 phr which is slightly higher than the rheological percolation thresholds. Based on the Kerner–Nielsen calculations, formation of a continuous network among the filler agglomerates can be expected in the CB30 sample which also indicates the second percolation thresholds.

On the other hand, another important rheological parameter for polymer and/or composite processing is melt viscosity. Although low melt viscosity is desired in polymer processing due to the reducing of power consumption and many processing advantages in melt processing operations. But, the CPCs generally exhibit high melt viscosity because of introducing of high amount of filler. Therefore, studying the effects of compositional parameters on the melt viscosity of composites provides important knowledge. Dependence of complex viscosity (η^*) values of samples on the amount of filler and angular frequency is given in Fig. 9. It is seen that the viscosity values of samples increased with the increasing of filler loading amount. It was also found that the CB particles yielded higher melt viscosity than the CF for a given amount of filler. This can be originated from the facts of relatively higher surface area and agglomerated structure of CB particles.

3.3. Electrical conductivity of samples

Electrical properties of samples were characterized by the ac -conductivity measurements conducted with an impedance spectroscopy. It is known that the electrical properties of materials can be characterized in terms of complex quantities of impedance (Z^*), admittance (Y^*), permittivity (ϵ^*) and modulus (M^*). There are several ways to quantify the electrical behavior of a material by impedance spectroscopy such as plotting real and imaginary parts of such complex parameters. In this study, conductivity–frequency plots were used to analyze electrical behavior of the samples. The ac -conductivity of the samples was calculated by the following equation.

$$\sigma_{ac} = 2\pi f \epsilon_0 \epsilon'' \quad (6)$$

where f , ϵ_0 and ϵ'' are the natural frequency, dielectric constant of air and dielectric loss, respectively. Fig. 10 shows the behavior of the ac -conductivity (σ_{ac}) as a function of frequency for all samples. It was observed that the ac -conductivity of samples was enhanced

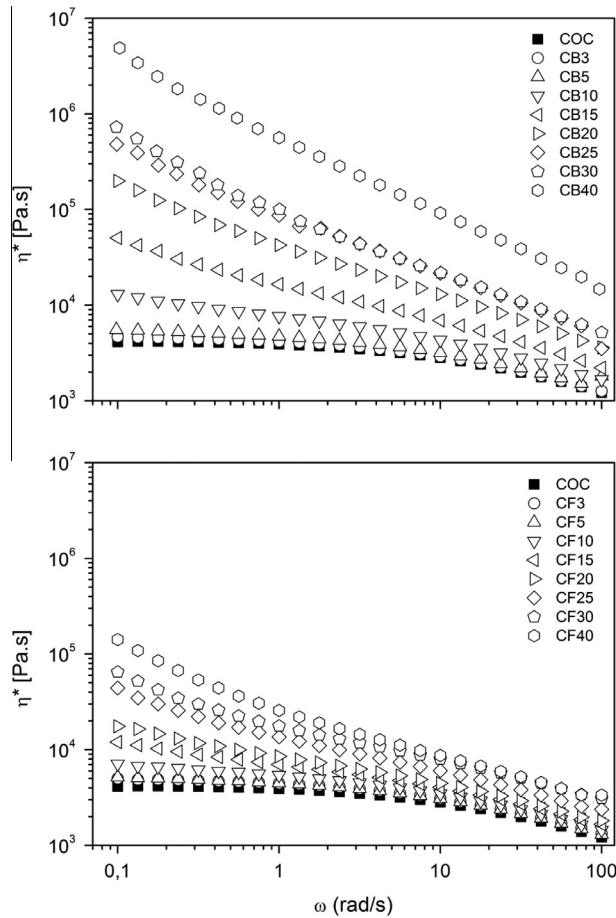


Fig. 9. Dependence of complex viscosity of sample series prepared with various amount of (a) CB and (b) CF on the angular frequency (ω).

with the increasing amount of filler, as expected. Similar to rheology curves, structural changes in the composite structure can be estimated with the ac -conductivity values of sample at the low frequency region. The conductivity at high frequency region is almost independent of composition and more related to the polarization effects. At low frequency region, the ac -conductivity of samples including low amount of filler were found to be slightly higher than that of COC because filler–filler contact was not formed yet and electric charge may flow only by means of hopping or tunneling through a non-conducting medium between the adjacent particles. When the filler loading reached to 15 phr, a dramatic increase in the ac -conductivity was observed for both the CB and CF series of samples. This improvement in the ac -conductivity is related to the decreasing of gaps between the conductive particles and the randomly formation of filler–filler contacts. This phenomenon is defined as the electrical percolation threshold. One can easily notice that the electrical and rheological percolations are the same (15 phr) for the series of samples filled with CF because of the macro size of the CF. On the other hand, electrical percolation for the series of samples filled with CB is higher than the rheological percolation. Another important point is to find that the electrical percolation of CB series of samples is related to the formation of agglomerated structure. It was found that the agglomerated filler amount obtained from the Kerner–Nielsen model and the electrical percolation obtained from the ac -conductivity measurements were the same for the CB series of samples as 30 phr. Experimental data showed that the formation of CB agglomerates positively affected the electrical conductivity of CB series of composites. This result is very consistent with the previously reported works [41,42].

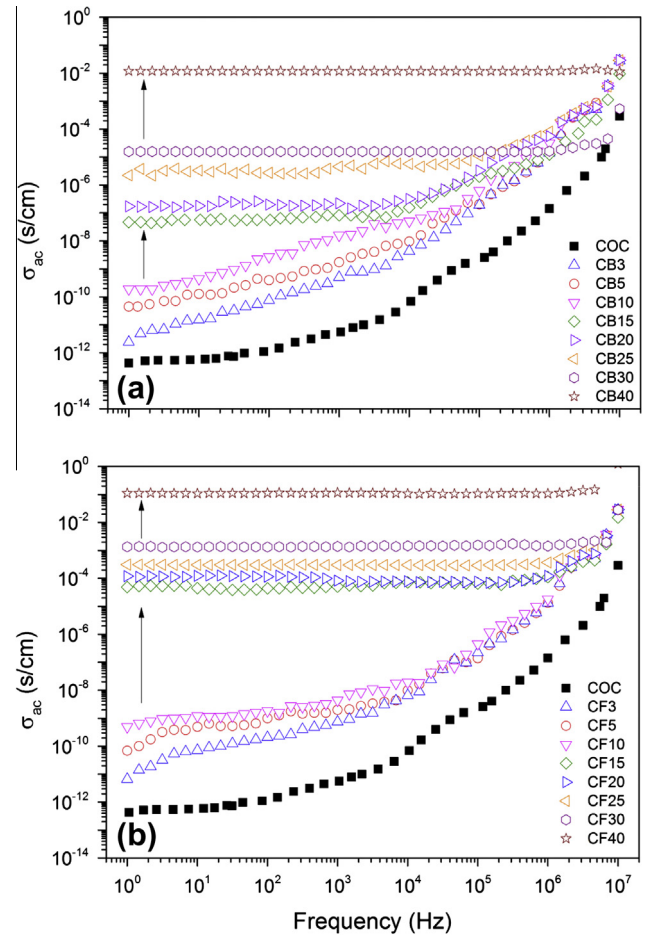


Fig. 10. Dependence of ac -conductivity of sample series prepared with various amount of (a) CB and (b) CF as a function of frequency.

Dependence of ac -conductivity of samples, at the measuring frequency of 1 Hz, on the filler amount is given in Fig. 11. In this figure, step-like increase in the ac -conductivity is clearly seen about the filler amount of 15 phr which is the first electrical percolation and the 30 phr which is the second electrical percolation for the both CB and CF series of samples. Multiple contacts between the carbon fibers (as seen in Fig. 2(d)) and the formation of agglomerated structure of CB particles due to the relatively high amount of filler (40 phr) are responsible for the second electrical percolation.

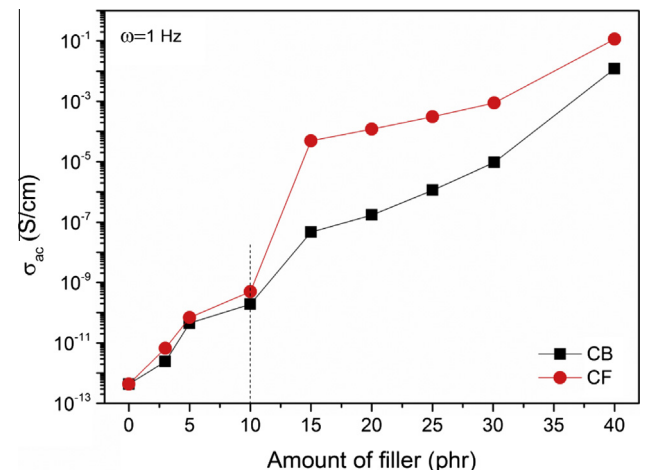


Fig. 11. Changing of ac -conductivity of the samples series as a function of filler amount.

The *ac*-conductivity of CF15 (4×10^{-5} S/cm) was higher than that of CB15 (5×10^{-8} S/cm). The maximum conductivity values of the COC/carbon composites were 0.01 and 0.1 S/cm by introducing of 40 phr of CB and CF, respectively.

4. Conclusion

In this study, morphological, rheological and electrical properties of COC/CB and COC/CF composites were investigated. Microstructural characterization of samples indicated that the CB and CF could be homogeneously dispersed into the COC phase in a twin screw extruder without a compatibilizer. Rheological measurements pointed out that the viscoelastic parameters of composites were more affected by the CB than the CF probably due to its higher surface area and nano size particles. Based on the *ac*-conductivity measurements, the CF provided higher electrical conductivity for a given amount of filler, especially at relatively high filler loadings. It can be concluded that the higher electrical conductivity of CF filled composites was probably due to the fact that the CFs as macro-filler yielded much less number of filler–filler contact resistance. The first rheological percolations were determined to be 9.4 and 15 phr for the CB and CF, respectively. The Kerner–Nielsen model proved that the CB agglomeration dramatically increased at filler amount of 15 phr which also induced the electrical conductivity throughout the composite structure.

Acknowledgement

This study was supported by TÜBİTAK, The Scientific and Technological Research Council of Turkey, with the project number of 110M671. Authors acknowledged to TOPAS (Germany), TIMCAL Graphite & Carbon Company (Switzerland) and AKSA (Turkey) for kindly supplying the polymer and fillers used in this work and Mr. Vedat Sariboga, from the Department of Chemical Engineering at Istanbul University (Turkey), for his efforts and helps in the SEM study.

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