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Karbon Esaslı Polimer Kompozitlerde Elektriksel İletkenliğin Geliştirilmesi

Metin YURDDASKAL[a], Mustafa EROL[*,a], Erdal CELIK[a,b]

[a,*] *Dokuz Eylül Üniversitesi, Metalurji ve Malzeme Mühendisliği Bölümü, İZMİR 35390, TÜRKİYE*
[b] *Dokuz Eylül Üniversitesi, Nanobilim ve Nanomühendislik, İZMİR 35390, TÜRKİYE*

MAKALE BİLGİSİ

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[*]*Sorumlu Yazar:*
e-posta: m.erol@deu.edu.tr

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ÖZET

Günümüzde teknolojik uygulamalarda kullanılan iletken polimer kompozitler birçok önemli uygulamada fonksiyonel malzemelerin bileşenlerini oluşturmaktadır. Polimerlerin yüksek elektrik direnç seviyesini azaltmak büyük önem taşımaktadır. Karbon türevi katkı maddeleri, polimerlerin elektriksel iletkenliğini arttırmak için yaygın olarak kullanılmaktadır. Bu bağlamda, grafit ve karbon karası kullanarak elektrik iletkenliği için iletken perkolasyon yapıları geliştirilmektedir. Üretilen iletken polimer kompozitlerin yapılarını, elektriksel ve termo direnç özelliklerini göstermek için karakterize edilmiştir. Karbon siyahı ve grafit dahil olmak üzere kompozit filmlerin perkolasyon eşiği araştırılmıştır. Grafit ile birlikte az miktarda karbon siyahı eklenmesi sayesinde, tek bileşenli kompozitlerle karşılaştırıldığında daha düşük direnç seviyeleri elde edilmiştir. Sıcaklık sensörleri için aday olarak düşünülen grafit ve karbon siyahı katkılı iletken polimer kompozitlerin, sıcaklık değişimlerine karşı dirençlerinde meydana gelen değişikliklere iyi tepki verdiği görülmüştür.

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Development Of The Electrical Conductivity In Carbon Based Polymer Composites

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[*]***Corresponding Author:***
e-mail: m.erol@deu.edu.tr

ABSTRACT

Conductive polymer composites are nowadays used in technological applications and they constitute components of functional materials in many important applications. It is of great importance to reduce the high electrical resistance level of the polymers. Carbon containing additives are widely used to increase the electrical conductivity of polymers. In this context, some percolated networks were created to improve the level of electrical conductivity using graphite and carbon black. The produced conductive polymer composites were characterized to show their structures, electrical and thermo-resistive properties. We investigated percolation threshold values of composite films including both carbon black and graphite. Thanks to adding small amounts of carbon black together with graphite, it was achieved to be lower levels of resistance if compared to the individually filled composites. Graphite and carbon black filled conductive polymer composites to be considered as the candidates for temperature sensors exhibited good responses to temperature changes by the changes in their resistances.

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1. INTRODUCTION *(GİRİŞ)*

Conductive Polymer Composites (CPCs) are mostly produced by combining electrically insulating polymeric matrixes with various types and compositions of conductive fillers [1]. Fine metallic fillers (Ag, Cu, and etc.) and carbon derivate (carbon black, carbon nanotube, graphite, graphene) in micro or nano scale are the fillers which are mostly employed in the formation of CPCs [2]. At a critical fraction of the filler in matrix, a conductive three dimensional network, percolation, is created. Composites having filler compositions over the percolation threshold are called as the CPCs. In addition to desired electrical conductivities, CPCs have some remarkable properties such as; high electrical conductivity, lightweight, corrosion resistant and good mechanical properties performance [3]. However, the geometry, type, morphology and the structure of the filler are critical parameters on the formation of a conductive network [4].

CPCs have been evaluated in many applications such as, chemical detecting sensors [5], biosensors [6], strain sensors [7], self-regulating heaters [1] and temperature sensors [2]. CPCs in film or coating form have been mostly produced through melt mixing, solution casting or spin coating and spray coating [8]. When a material or a design is thought to be a candidate for a device or an application, it should be suitable for bulk (scale-up) production. Among the production techniques for CPCs, spray coating is a viable technique, which allows precise control over layer thickness and deposition on large and uneven surfaces [4].

As mentioned before, a wide range list of fillers are employed for the production of CPCs. The carbon based fillers; carbon black, carbon nanotube, graphite, graphene are standing one-step ahead against the fine metallic fillers due to their compatibility in polymeric matrix and ease in production [4]. In addition, if the bulk production is considered, carbon black and graphite can be chosen as the fillers thanks to their low cost and abundance. In literature there are many studies focusing on the CPCs made up of individual carbon black and graphite but a limited number of researches are dealt with their synergetic effects. In our previous studies, carbon black and graphite filled CPCs were evaluated as plane heaters [1] and temperature sensors [2] by means of the synergetic effect of the fillers. This phenomenon was discussed by Aneli et al with some theoretical calculations on the formation of conductive paths [9]. So as to show this phenomenon experimentally; electrical conductivities, particle size distribution, microstructures and the thermo-resistive properties of the CPCs with individual graphite flake and dual carbon black - graphite will be evaluated in details in the present study.

2. MATERIALS AND METHOD *(MATERYAL VE METOT)*

In this study composites were produced by using; graphite flake (Selen Chemistry, Turkey), carbon black (Tupras, Turkey) and styrene acrylic copolymer emulsion (Ata Chemistry Inc., Turkey) as fillers and the matrix respectively. Three groups of samples were designated, G-series, 5G series and 10G series, as individual graphite containing samples with varying graphite flake composition (0 to 20 % wt.), fixed graphite flake (5 % wt.) - varying carbon black (1, 3 and 5 % wt.) and fixed graphite (10% wt.) varying carbon black (1, 3, 5 and 7 % wt.) respectively. Regarding to the each series, the fillers were dispersed homogeneously in styrene acrylic copolymer emulsion by using a mechanical mixer for 30 minutes. As dispersed emulsions of each series were deposited on soda lime glass substrates using a compressed air driven spray coating apparatus in a fume hood. Deposited films were dried at 80 °C in order to provide polymerization and adhesion to substrates for an hour.

The conductivity measurements of the films were obtained by using Hall measurement system with a permanent magnet of 0.5 T (ECOPIA, HMS-3000). By using the data obtained from electrical measurements the change in conductivity versus filler content were plotted to determine the percolation thresholds of the samples. In order to determine particle size distribution of carbon black and graphite powders, a dynamic light scattering equipment (Malvern Zeta Sizer Nano ZS90) was employed. In this study, the surfaces of composites coatings were examined by using JEOL JSM-6060 instrument operating at an accelerating voltage of 20 kV with several magnifications. Thermoresistive measurements were applied to the samples by heating up to 90 °C and the changes in resistance and temperature were recorded simultaneously by using electrometer (Keithley 2400) and a digital multimeter equipped with thermocouple (UNI-T, UT71D), respectively, to represent the effect of heating on the resistance changes.

3. RESULTS AND DISCUSSION *(SONUÇLAR VE TARTIŞMA)*

3.1. Electrical Properties *(Elektriksel Özellikler)*

In Fig. 1, the changes electrical conductivity were plotted as a function of filler content for G, 5G and 10G series. The electrical conductivity of the composites sudden rose by many order of magnitude when the filler content outreached the threshold concentration. According to Fig. 1, the percolation threshold values of G, 5G and 10G series were determined as 20, 6 and 11, respectively. In addition, it can be expressed that the electrical conductivity increased approximately 5 orders of magnitude for all sample groups. It can be understood from Fig. 1 that the composites including small amounts of carbon black together with graphite are of newly co-supporting conductive paths. The obtained decrease in the thresholds of 5G and 10G series indicates that the filler amount can be used less than the individually filled composites (G series).

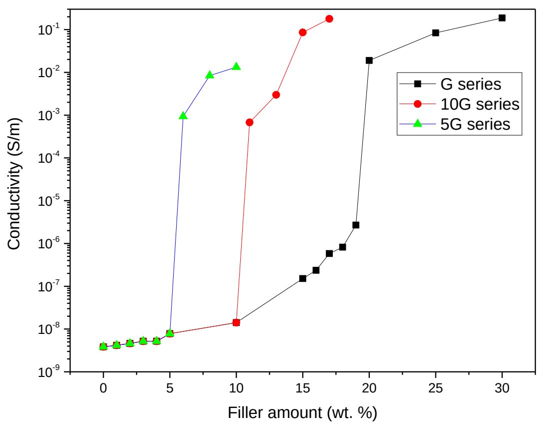

Figure 1. Electrical conductivity of polymer composites *(Polimer kompozitlerin elektriksel iletkenlikleri)*

3.2. Particle Size Distribution *(Partikül Boyut Dağılımı)*

In Fig. 2a and 2b particle size distribution curves were given for graphite and carbon black powders, respectively. Particle size of graphite powders exhibits a distribution in a wide range between 60 nm to 2.7 µm. Distributions over 1 µm were thought to be agglomerated particles which will be supported using micrographs. According to the carbon black particle size distributions, it can be successfully expressed that a monodisperse particle size distribution is obtained with a narrow range between 20 nm to 45 nm.

3.3. SEM Analysis *(SEM Analizi)*

Fig. 3 shows the microstructure of conductive polymer composites containing graphite 10 wt.% and 20 wt.% with general and detail views, respectively. The micrographs exhibits a good dispersion of graphite fillers with lower concentrations. Thus, the sample containing graphite 10 wt. % is of smoother surface than the 20 wt.% reinforced one. The obtained results are in a good agreement with the literature on conducting polymer composites based on graphite fillers [10, 11].

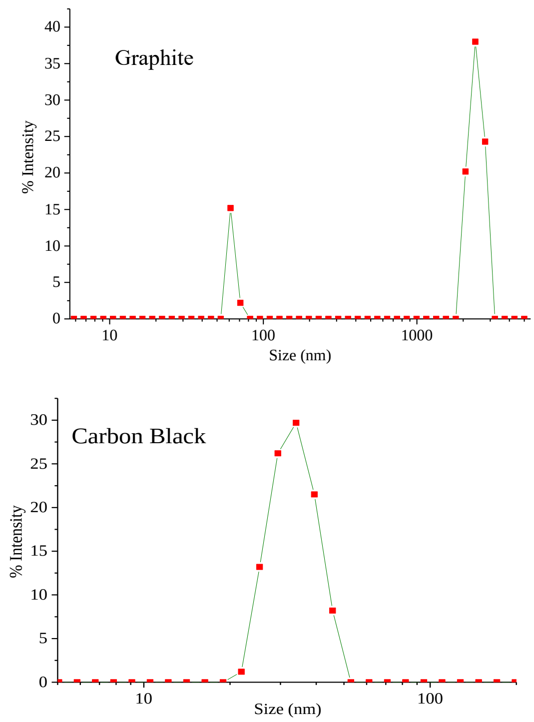

Figure 2. Particle size distributions of graphite and carbon black powders *(Grafit ve karbon karası tozlarının partikül boyut dağılımları)*

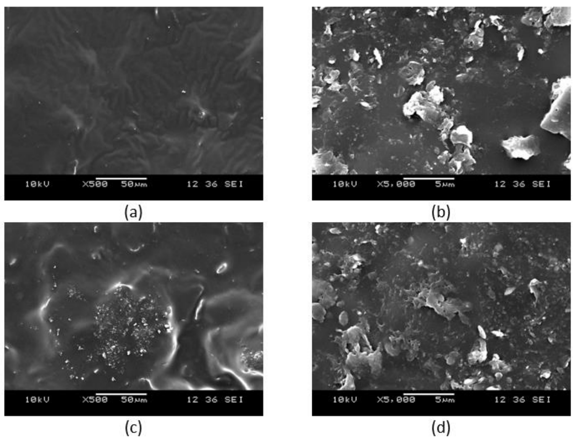

Figure 3. SEM micrographs of samples G10 (a, b) and G20 (c, d) *(G10 (a, b) ve G20 (c, d) numunelerinin SEM mikrogörüntüleri)*

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Micrographs of samples including both graphite and carbon black fillers were represented in Fig. 4 and 5, respectively. Thanks to adding small amounts of carbon black together with graphite, it can be found to the formation of new co-supporting conductive paths. The formation of conductive paths in polymer composites with binary fillers and its theory was revealed by Aneli et al [9]. In addition, it is observed from the SEM results that the conductive paths in the carbon black and graphite filled composites were formed as shown in the study of Fan et al [12]. Depending on this theory and our electrical conductivity results (Fig. 1), it can be understood from the Fig. 4 and 5, conductive paths have been achieved by surrounding the graphite around the carbon black. Thus, carbon black fillers with small aggregates or graphite powders in the polymer matrix had a sharp increase in conductivity compared to the individually filled composites, resulting in the conversion from insulation to conduction of the nanocomposites. It is also called as percolation threshold and if the carbon black content increased further, a dense and saturated conductive network was constructed with slowly increasing conductivity [13]. Finally, it can be expressed that the microstructure of the composites including both graphite and carbon black fillers are convenient to previous studies in literature [14].

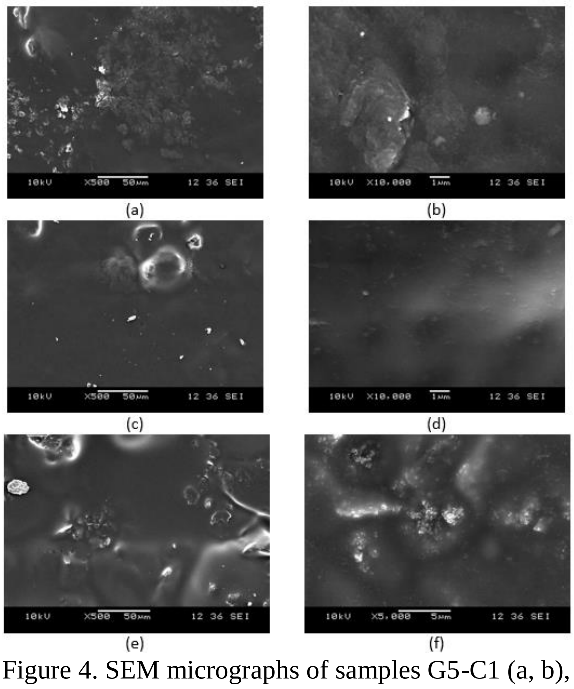

Figure 4. SEM micrographs of samples G5-C1 (a, b), G5-C3 (c, d) and G5-C5 (e, f) *(G5-C1 (a, b), G5-C3 (c, d) ve G5-C5 (e, f) numunelerinin SEM mikrogörüntüleri)*

3.4. Thermoresistive Results *(Termorezistif Sonuçlar)*

Thermoresistive results for composite including only graphite were depicted in Fig. 6. According to the results of thermoresistivity, it is obviously seen that temperature was increased and decreased with resistance simultaneously. The sample was heated to a range of 80 to 100 °C by applying an amount of current then were allowed to cool slowly. Thermoresistive results of the samples including both graphite and carbon black fillers illustrated in Fig. 7 and 8. It can be seen from the Fig. 6 and 7 that the composites with co-supporting conductive paths have more than 10 times compared to those with individually filled composites. The thermoresistive results seem to be stable when the temperature of the samples is heating up and cooling down. In this context, the obtained results indicate that the produced composites can be used as a temperature sensor as the electrical resistance of samples changes with varying temperature.

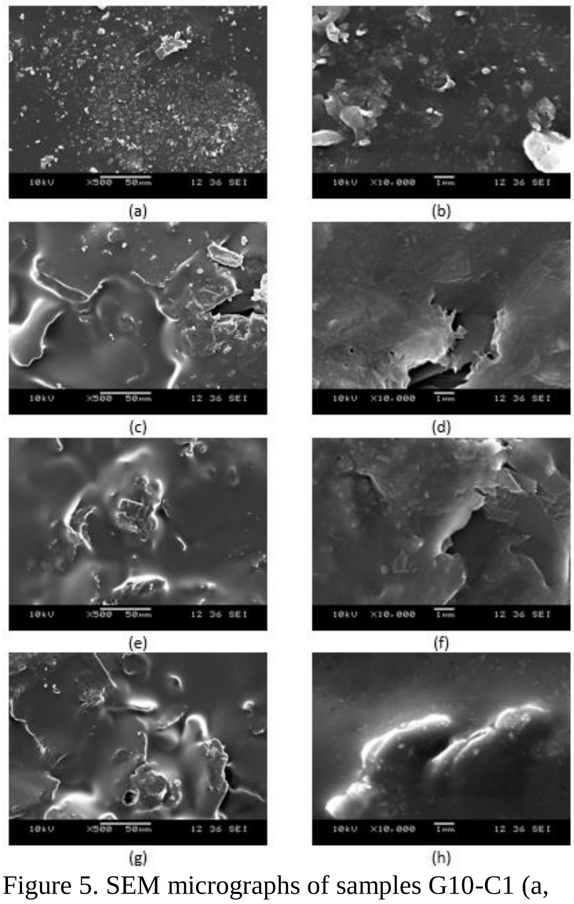

Figure 5. SEM micrographs of samples G10-C1 (a, b), G10-C3 (c, d), G10-C5 (e, f), G10-C7 (g,h) *(G10-C1 (a, b), G10-C3 (c, d), G10-C5 (e, f) ve G10-C7 (g, h) numunelerinin SEM mikrogörüntüleri)*

As discussed in previous sections, we can further summarize that the electrical properties, microstructures and thermoresistive results of the composites with carbon black and graphite in the same structure were investigated. It is proved in our previous studies [1,2] that the composites could be used as plane heaters and temperature sensors. Some results about electrical, morphological and thermoresistive properties which support our previous publications are obtained. The conductive composites are suitable for the production of sensors with lower cost and good electrical properties in accordance with studies in the literature [15–18]. Another important thing is that the composites including both graphite and carbon black in the same structure have better electrical properties unexpectedly [19].

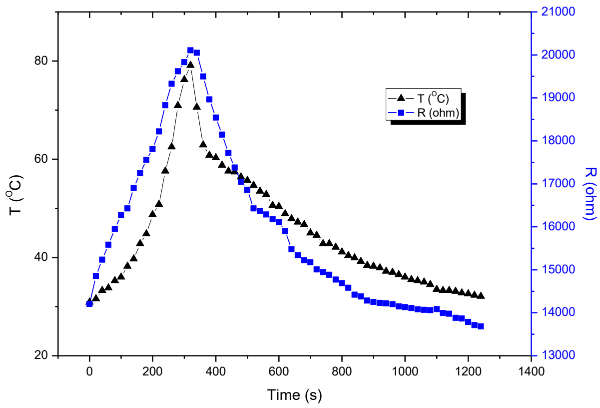

Figure 6. Thermoresistive results of 20G *(20G numunesinin termorezistif sonuçları)*

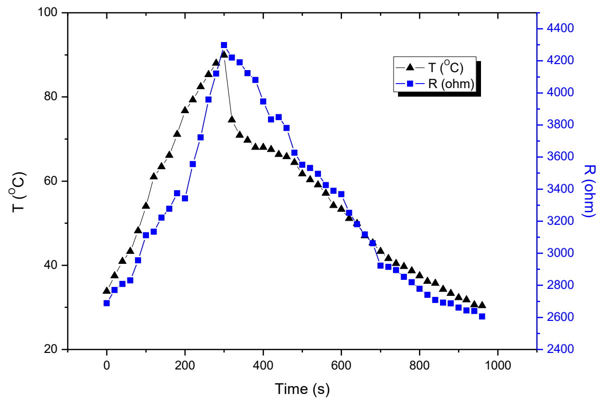

Figure 7. Thermoresistive results of G5-C5 *(G5-C5 numunesinin termorezistif sonuçları)*

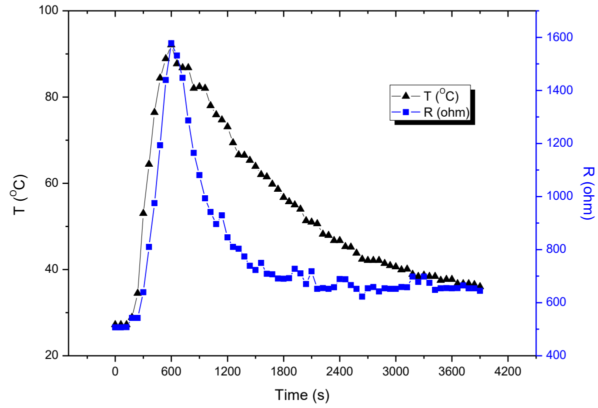

Figure 8. Thermoresistive results of G10-C7 *(G10-C7 numunesinin termorezistif sonuçları)*

4. CONCLUSION *(SONUÇ)*

Carbon based composites with relatively low cost fillers; graphite, carbon black and a combination of both were produced successfully. In contrast to our previous studies, we investigated the effects of presence of both carbon black and graphite fillers on the electrical conductivity and microstructures. The percolation thresholds decreased from 20 to 6 and 11 successfully thanks to synergistic effect for 5 and 10 series, respectively. The resistance values of the samples with concentrations over the percolation threshold exhibited a good response to temperature changes. All in all, electrical conductivity of the carbon based polymer composites with thermoresistive properties were developed successfully.

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Metin YURDDASKAL

Dr. Metin Yurddaskal was born in Izmir, Turkey on March 14, 1989. He graduated from Dokuz Eylul University in 2011 with a first degree in Metallurgical and Materials Engineering. He completed his Master of Science Thesis and his PhD thesis at the Department of Metallurgical and Materials Engineering in 2014 and 2017, respectively. He has been working as an assistant professor in the Department of Metallurgical and Materials Engineering at Dokuz Eylul University in Izmir. He works on composite materials, nanoparticles, thin films and materials characterization.

Mustafa EROL*

Dr. Mustafa Erol was born in Ankara, Turkey on April 25, 1983. He graduated from Dokuz Eylul University in 2007 with a bachelor degree in Metallurgical and Materials Engineering. He get MSc and PhD degrees from Dokuz Eylul University on Metallurgical and Materials Engineering in 2009 and 2014, respectively. He has been working as an assistant professor in the Department of Metallurgical and Materials Engineering at Dokuz Eylul University in Izmir. His area of research is as follows: heat releasing materials, semiconducting and functional materials, photocatalysis, and nanomaterials.

Erdal CELIK

Prof. Dr. Erdal Celik was born in Sivas, Turkey on November 23, 1967. He graduated from Istanbul Technical University in 1993 with a degree in Metallurgical and Materials Engineering. He is now director of the Center for Fabrication and Applications of Electronic Materials and works as a professor at Dokuz Eylul University. He also works on nanotechnology, production techniques, electronic materials, materials characterization and thin films.

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