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# Excellent Adhesion of Carbon Fibers to Polyurethane Matrix and Substantial Improvement of the Mechanical Properties of Polyurethane

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## ABSTRACT

In this study, polyurethane-carbon fiber composites were prepared with excellent interface with perfect adhesion of carbon fibers with the polyurethane matrix. The polyurethane was thermoplastic polyurethane and the carbon fiber was polyacrylonitrile based with 7 micron meter thickness. The composites were prepared with solvent casting technique. The composite materials were characterized with tensile testing, dynamic mechanical analysis, scanning electron microscope, and thermogravimetric analysis. The excellent adhesion of the carbon fibers in the polyurethane matrix was observed with scanning electron microscopy investigations. This adhesion creates huge improvements in the mechanical properties of the polyurethane. 300 % improvement in tensile strength was achieved with very low percentages of the carbon fiber such as 3 wt %. The hydrophilicity of the polyurethane matrix was confirmed with water contact angle measurements that led to better interaction.

**Key Words**: *Polyurethane, carbon fiber, mechanical properties, interphase..*

## 1. INTRODUCTION

Polyurethane (PU) is very important family of polymers which has a wide range of applications including construction, automotive and sports materials [1-3]. They are available in the form of bulk, films or foams. Their properties can be tailored with various polyols and isocyanates [4]. Isocyanates are the hard rigid segments giving the strength and polyols are the soft segments providing elasticity and toughness [5]. These versatile properties and applications make the PU a very valuable polymer.

The properties of the polymers and polyurethane are further improved in the form of composite materials [6]. The polymer composites have been developed since 1950s. Within the composite materials, glass fibers have been used widely in industry. Recently, carbon fibers (CFs) have attracted much attention in the composite industry due to high elastic modulus [7]. High performance CF can be combined with thermoset and thermoplastic resins. Polyacrylonitrile-based CFs are used for composite preparation in order to produce materials of lower density and greater strength. They are widely used for weaving, braiding, filament winding

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applications, unidirectional tapes and as prepreg tow for fiber placement having excellent creep, fatigue resistance, high tensile strength and stiffness characteristics [8-10]. The decrease in the price of the CF will enable more widespread use of them in the polymer industry [11].

The application fields of PU and CF are intersecting in many areas, especially sporting goods, textiles and automotive. This makes the PU-CF composites more important for industrial applications. The PU-CF composites have been prepared by different researchers [12-14]. Sanchez-Adsuar et al. [12] suggested that the surface polarity of the CF is critical parameter for the PU-CF composites. They could achieve nearly 100% improvement in the tensile strength by using short CF. Borda et al [13] determined that the PU matrix could be mechanically reinforced up to certain limit by using short fibers. On the other hand, Correa et al. [14] prepared short CF composites by extrusion method and they compared the performance with that of the aramid fiber composites. They found that the aramid fibers had better mechanical properties than CF reinforcement and they could not obtain improvement in the tensile strength of the PU with CF.

Since the usage of short CF is very critical for the industrial applications, PU composites were prepared with short carbon fibers. The materials were prepared with solvent casting method. The mechanical properties of the neat PU increased enormously (300 % increase in the tensile strength) due to the excellent interaction of the PU and CF. The excellent interaction was clearly shown by the scanning electron microscopy studies. Further analysis were conducted with Fourier transform infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA) and water contact angle. With the reduction in the prices of the CF, this PU-CF composite technology will be very important for many different applications.

## 2. EXPERIMENTAL

### 2.1. Materials

Polyurethane was obtained from Flokser Polychem Co. from Turkey. It was prepared with polyester polyol and diphenylmethane diisocyanate (MDI). The molecular weight and $T_g$ value of PU were 30,000 Dalton and -52.4°C, respectively. 35 wt % PU solution in dimethylformamide (DMF) was used in composite preparation. Polyacrylonitrile-based CF (SGL SIGRAFIL C 320 B, SGL Carbon Group) was used. The thickness of CF was 7 µm and the length of carbon fiber was a few milimeters.

### 2.2. Composite Preparation

PU-CF composite materials were prepared by solvent casting method. CF was added into PU solution at different weight percentages, 0.5, 1, 2 and 3 wt %. The composites were coded as PUCar05, PUCar1, PUCar2 and PUCar3. The short CFs were dispersed in the PU-DMF solution with magnetic stirrer overnight at ambient temperature. The magnet was removed from the solution and let to settle down at least 1 day in order to avoid bubble formation in the final film. The solution was cast on a special release paper with a special casting knife by which the thickness of the wet film and the final dry film can be easily adjusted. The DMF was evaporated in the oven at 150°C and the final composite film was obtained. The film with a thickness of 100 µm was easily peeled off from the release paper.

### 2.3. Characterization

Shimadzu AG-S was used for tensile testing. The measurements were done with the speed of 50 mm/min. The dimensions of samples were 10x100x0.1 mm. The Perkin Elmer DMAII was used for determination of viscoelastic properties. The sample with 0.1x10x40 mm dimensions was heated from -100°C to +100°C with a heating rate of 3°C/min and tested using tensile mode at a frequency of 1 Hz. Perkin Elmer FT-IR Spectrometer was used to evaluate the structure of the PU and the composites. The spectra were recorded with ATR attachment. Perkin Elmer Diamond TG/DTA was used for TGA analysis. The heating was done from +50°C to +1200°C with a heating rate of 10°C /min. Leica DS 480 optical microscopy was used at x100 magnification. JEOL 5410 model scanning electron microscopy was used for obtaining SEM images. The operating voltage was 5 kV. Water contact angle measurement was done using a KSV CAM200.

## 3. RESULTS AND DISCUSSION

### 3.1. Mechanical Properties

The mechanical properties of the neat PU and the composites were measured with tensile testing and dynamic mechanical analysis (section 3.2). Tensile testing has been a powerful tool to understand the load that material can carry and the strength values under tensile load. In this study, the tensile measurements show that incorporation of the CF in the polyurethane matrix increased the tensile strength values significantly (Figure 1). The tensile strength increased 128% at 0.5 wt% loading of CF. At 1 wt % of CF, the loading of increase was 217% which corresponds to a tensile strength of more than three times than the pristine polymer. The increase was 264 and 293 % in the case of 2 and 3% CF loading, respectively. Beyond 3 wt % addition of CF in PU matrix was not tested as the tensile strength was leveling off.

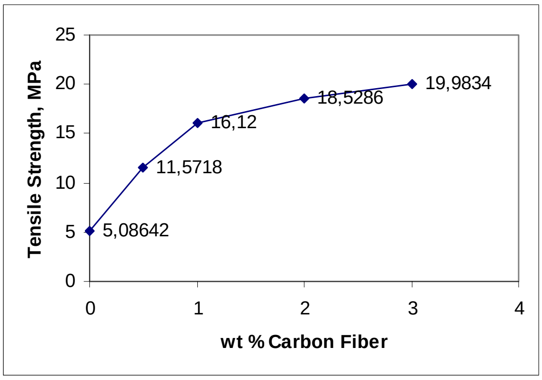

Figure 1. The tensile strength of PU and PU-carbon fiber composites.

PU has a copolymer structure with soft segment (polyol part) and hard segments (isocyanate part). This copolymer structure enables to have a variety of mechanical properties of the PU materials depending on the stoichiometric ratio of the PU. The interaction of the CFs with the PU was mainly at the soft segment part with the higher amount of the hydrophilic parts of the PU. The surface of the CF was also hydrophilic enabling the better interaction with the PU.

Sanchez-Adsuar et al. [12] demonstrated the importance of the polarity in order to obtain reinforcement for the PU matrix. They prepared different PU-CF composites with different lengths, diameters and polarities of CF. They emphasized the importance of the bond between the PU and CF. They concluded that the fibers should be short, thin and polar in order to increase the mechanical properties. They obtained the improvement of PU matrix at high percentages (up to 30 wt%) of the CF, whereas in our study very low concentration of the CF could be enough to obtain superior improvement in the mechanical properties.

Borda et al. [13] prepared PU-long CF composites. They have stated that using long CF could increase the tensile strength of the material because of the orientation of the fibers. On the other hand Sanchez-Adsuar et al [12] stated that the long fibers hinder the motion of the PU chains. In our study, short fiber was chosen due to the applicability at the industrial scale. This study showed that similar reinforcement could be achieved with short fiber reinforcement contrary to the long fiber reinforcement [13]. Long fibers are always better in reinforcing the polymer phases creating stiff long enhancement of the neat polymers. Correa et al [14] could not succeed to increase the mechanical properties of PU by using CF. They stated that this was due to the short fiber reinforcement. But in this study, due to the excellent interaction of the CF and the PU structure, the reinforcement was achieved with short fibers with low levels of loading.

Borda et al. [13] pointed out that the bond between the PU and the CF was very important to obtain good mechanical reinforcement. They stated the importance of the polarity of the CF. Moreover when they used long fibers, the results deviated from the theoretical calculated values. This result was explained that the fiber could not be ideally bounded to the PU matrix because of the fiber slippage. They also stated that the fiber breakage was very important as well. In literature, there are a few studies emphasized the importance of certain surface treatments for CF [15-17]. In our study, very successful results were obtained with short fibers. The distribution of the CF in the PU matrix is shown in the optical microscopy photographs (Figures 2-4). Since short fibers used, the fiber breakage was not a problem. Additionally, very strong bond was formed between PU matrix and CF (Figures 5-8). PU surrounded the CF at the joining point and covered the CF up to certain part. Since the CF was very well adhered to the PU matrix and no fiber slippage, improved mechanical properties were obtained for the composites.

One of the reasons for good bonding was the polarities of both CF and PU matrix. PU used for preparation of composites is hydrophilic. The contact angle of PU film was measured 63.7° (Figure 9). The composite materials were not characterized with water contact angle measurement as it was only used to determine the hydrophilicity of the PU matrix. The polarity of the CF is known from the company specifications. Normally for polyolefins and other thermoplastic materials, the adhesion between carbon fiber and the polymer matrix is poor due to polarity and hydrophilicity difference and this significant improvement cannot be obtained. In this study, the polyurethane and carbon fiber shows excellent interaction due to the urethane linkages in the polyurethane structure that can connect with carbon fiber.

Figure 2. Optical microscope photo of PUCar3.

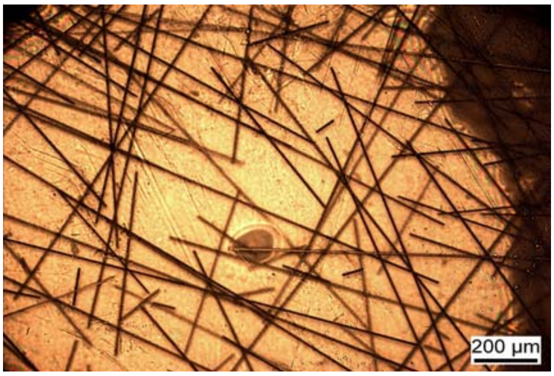

Figure 3. Optical microscope photo of PUCar3.

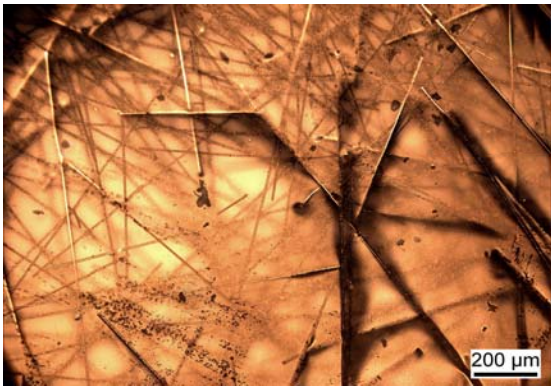

Figure 4. Optical microscope photo of PUCar3.

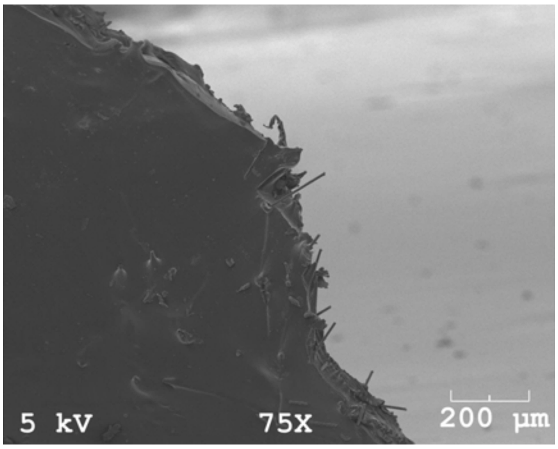

Figure 5. SEM image of the cross-section of PUCar3.

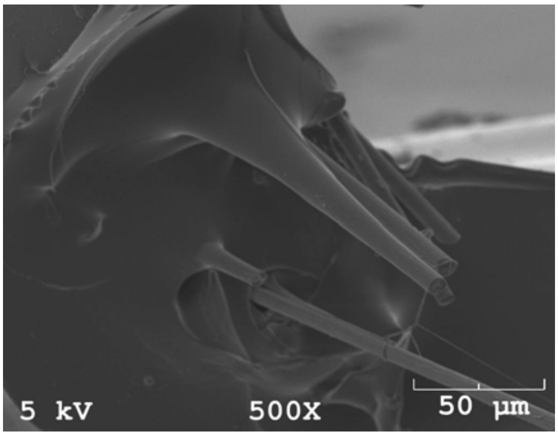

Figure 6. SEM image of the surface of PUCar3.

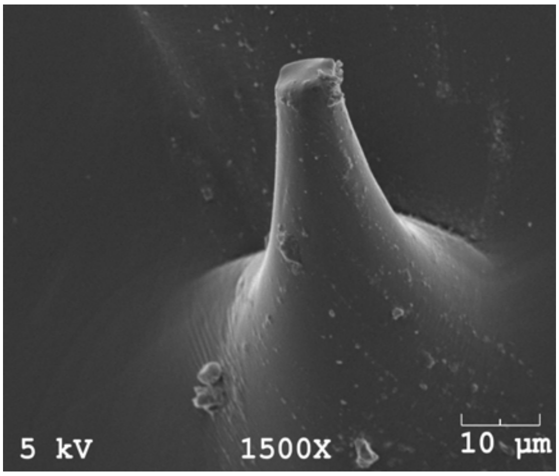

Figure 7. SEM image of the surface of PUCar3.

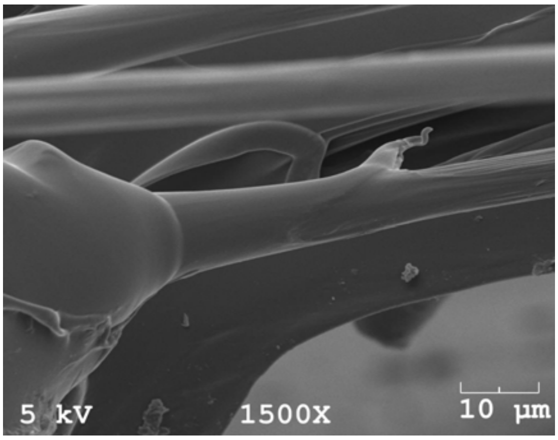

Figure 8. SEM image of the surface of PUCar3.

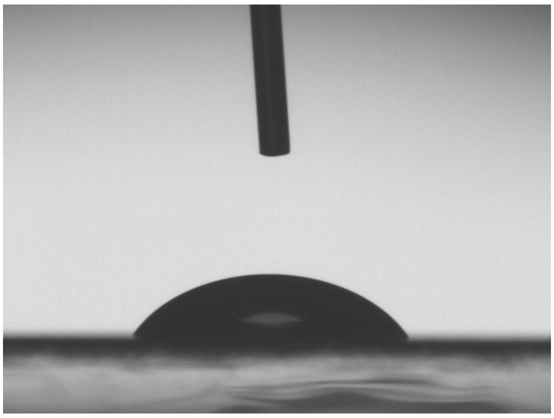

Figure 9. The water contact angle measurement.

### 3.2. Dynamic Mechanical Analysis

Dynamic mechanical analysis were conducted to understand the modulus values at elevated temperatures, chain restrictions and to measure the glass transition temperature of the neat PU and the composites. The modulus values (E') were measured and it was understood that the modulus values of the CF reinforced PU composites are higher than the neat PU. The reinforcement is more prominent above the Tg temperatures (Tg values were determined from the onset of E' vs. temperature graphs, shown in Figure 10. The Tg values do not change with the addition of the CF). The higher modulus values is consistent with the previous PU nanocomposites published [18]. This reinforcement above Tg values is consistent with the CF interactions with the soft segment of the PU. Above Tg values, the soft segments are more effective for the material behavior of the PU. The CFs are much more effective. The modulus values of the PU-CF composites are higher as the CF content increases. These results are also consistent with the tensile test results.

The chain restrictions in the neat PU and composites are measured with tan D curves. The reduction in the height of the curve represents stiffer chains and stronger materials [19]. This is reflected in the measurements as well (Figure 11). Also the chain restriction increases as the weight percentage of the CF increases. This is consistent with E' values and tensile tests. This measurement is also critical part for the evaluation of the materials.

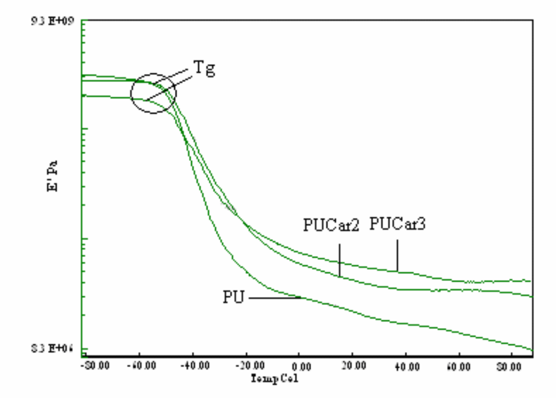

Figure 10. The storage modulus of PU and the PU-carbon fiber composites.

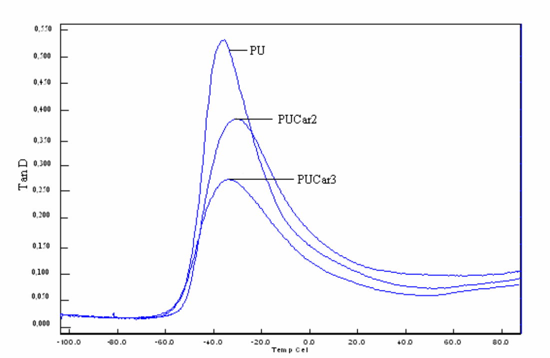

Figure 11. The tan D curves of PU and PU-carbon fiber composites.

### 3.4. TGA

The thermal stability of the composite materials was determined by using TGA. It was clearly shown that the final residue increased with the addition of CF (Figure 12). There is no significant difference between PU and composites in terms of thermal stability and onset temperature.

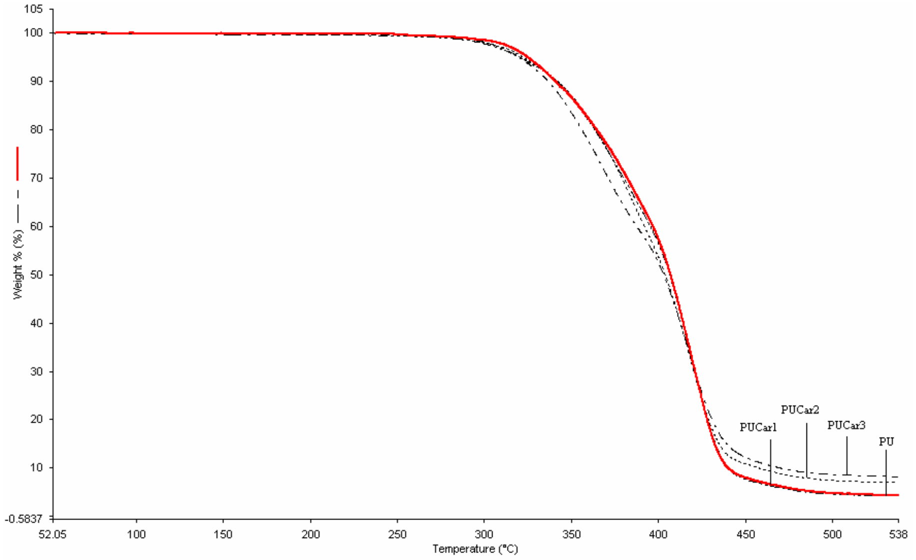

Figure 12. TGA thermogram of PU and PU-carbon fiber composites.

## 4. CONCLUSION

Short CF was used to increase the mechanical properties of PU. The mechanical properties of the PU-CF composites increased with increasing CF content.. The most important reason for the improvement was the adhesion of CF to PU matrix due to the surface polarity and hydrophilicity of PU. This study will help further understand composite materials with improved surface properties with matching surface polarity and hydrophilicity. This study will expand the usage of the PU material for different applications such as structural materials, automotive parts and sporting goods.

## ACKNOWLEDGMENTS

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