EFFICIENT DESIGN OF PIEZORESISTIVE SENSORS BASED ON CARBON BLACK CONDUCTIVE COMPOSITES

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EXTENDED ABSTRACT

Flexible and stretchable sensors are widely investigated taking into account their potential for wearable electronics, such as electronic skin, healthcare monitoring, human-machine interfaces, and soft robotics. In this contribution, highly sensitive conductive polymer composites (CPCs) for piezoresistive sensing are summarized, considering a straightforward manufacturing process based on extrusion of thermoplastic polyurethane (TPU) and/or olefin block copolymer (OBC), carbon black (CB), and additionally polyethylene-octene elastomer (POE) grafted with maleic anhydride (POE-g-MA). The design of the formulation variables is successfully performed to enable both low and high strain sensing, as highlighted by both static and dynamic testing.

Key Words: piezoresistive sensor, formulation variables, sensitivity, hysteresis minimization

1. INTRODUCTION

Stretchable strain sensors, which transduce mechanical excitation into a readable electrical signal, have attracted increasing attention in the emerging area of wearable electronics [1]. In order to be viably employ them in these applications, the sensors must exhibit excellent performance in two crucial parameters within appropriate workable range: sensitivity and cyclic durability (without pronounced hysteresis). In particular, sensitivity is of extreme importance, as it allows accurate diagnose, thus providing exhaustive information and achieving practical implementation. The sensitivity of resistive stretchable sensors is defined by gauge factor $GF = (\Delta R/R_0)/\varepsilon$, in which $\Delta R/R_0$ refers to relative resistance change and ε refers to tensile strain [1].

Conductive polymer composites (CPCs) in the field of strain sensing have gained broad interest with the superior characteristics of easy processing and high cost-effectiveness. However, it still remains a challenge to further increase the sensitivity of CPC based strain sensors with a good initial conductivity. Herein, this work covers a summary of the systematic study regarding the effect of formulation variables (filler content/type, blend ratio, annealing treatment or incorporation of POE-g-MA) on the improvement of piezoresistive sensing performance and initial conductivity by adopting TPU and/or OBC as composite matrix and two kinds of CB (CB₁ and CB₂) as conductive filler [2, 3].

2. EXPERIMENTAL

TPU (Desmopan 9395AU, Covestro CO., Ltd., Germany) and OBC (INFUSE 9530, Dow Chemical Co., Belgium) were used as polymer matrix. CB₁ (ENSACO 250G, IMERYS

Graphite & Carbon, Belgium) and CB₂ (Printex XE 2B, NECARBO BV, Belgium) were employed as conductive filler types. The sample preparation procedure and characterizations are referred in [2, 3]. A binary composite is denoted as OBC-CB_x-y or TPU-CB_x-y, in which x and y represent the type of CB (1 or 2) and the mass fraction of CB. The conventional ternary composites are denoted as OBC_z-CB_x/TPU_w-y, in which x and y represent the CB type and content, and z/w indicates the mass ratio of OBC and TPU. In addition, 5 m% of POE-g-MA (Acti-Tech 16MA13, NGC, Hellerup, Denmark), which is a Vistamaxx-based compatibilizer, was also blended with an OBC-CB₂ masterbatch and TPU to include POE-g-MA containing ternary composites for comparison.

3. RESULTS

3.1 Comparison of optimal binary and ternary composites under static tensile testing

Figure 1a gives the static electro-mechanical response for a selected number of CB_2 binary and ternary composites with comparable initial electrical conductivity. It is indicated that higher sensitivity of annealed ternary composites with filler amount below 10 m% is achieved. Figure 1b exhibits the sensitivity tunable range with focus on GF_{max} (GF at ε_{max}) for the formulation variables investigated.

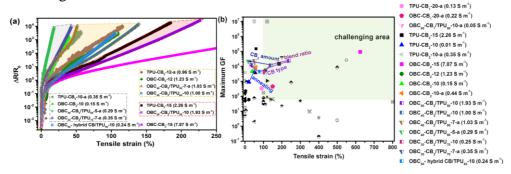


Figure 1. (a) $\Delta R/R_0$ (in log scale)-strain variation for selected CB₂ binary and ternary composites; (b) Further comparison based on GF_{max}. Also given are literature values (black symbols).

3.2 Comparison of optimal binary and ternary composites under dynamic tensile testing

Figure 2a-b display the resistance change during dynamic testing for a selected number of CB₂ based binary and ternary composites under different strain ranges with detailed sensing performance evaluation parameters listed in Table 1. It is indicated that both CB₂ based binary and ternary composites with relatively low filler content provide negligible hysteresis.

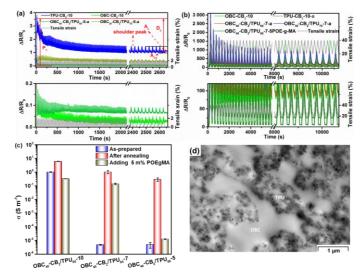


Figure 2. Δ*R*/*R*₀ variation for selected CB₂ binary and ternary composites under cyclic stretching/releasing testing for a strain range of (a) 0 - 2% (100 cycles) and (b) 20 - 40% (40 cycles). (c) Effect of annealing or incorporating POE-g-MA on (c) initial conductivity and (d) TEM image for OBC₄₀-CB₂/TPU₆₀-7-a.

Figure 2c shows the initial conductivity comparison for OBC_{40} - CB_2 / TPU_{60} after annealing or incorporating POE-g-MA. It is demonstrated that both annealing treatment and incorporating of POE-g-MA can promote the increase of initial conductivity for composites with lower filler content (< 10 m%). The incorporation of POE-g-MA is an alternative for conductivity and sensor property regulation thus avoiding post-annealing treatment and its possible deterioration of other properties. The morphological analysis in Figure 2d interprets that control of the microscale phase morphology (phase continuity/size) and distribution of CB_2 , so as to obtain a desired tunnelling effect, is responsive to the sensitivity enhancement and the change of initial conductivity after annealing.

Table 1. The recovery ratio (D_L/P_1) , amplitude of relative change of resistance peak (A_L) , and the hysteretic behavior (A_{Ls}/A_L) during dynamic stretching for samples in Figure 2 and the best ones in reference [2] with CB_1 ; specific focus in this work on the additional italic contribution

0-2%	D _L /P ₁	A_{L}	A_{Ls}/A_{L}
TPU-CB ₂ -10	62%	0.42	35%
OBC-CB ₂ -10	53%	0.03	43%
OBC ₄₀ -CB ₂ /TPU ₆₀ -5-a	48%	0.02	11%
OBC ₃₀ -CB ₂ /TPU ₇₀ -5-a	23%	0.11	26%
OBC ₅₀ -CB ₁ /TPU ₅₀ -10-a	50%	0.26	< 1%
20-40%			
TPU-CB ₂ -10-a	62%	7.3 × 10	2%
OBC-CB ₂ -10	16%ª	6.5×10^{2}	< 1%
OBC ₄₀ -CB ₂ /TPU ₆₀ -7-a	62%	2.3×10^{2}	2%
<i>OBC</i> ₄₀ - <i>CB</i> ₂ / <i>TPU</i> ₆₀ -7-5 <i>POE</i> - <i>g</i> - <i>MA</i>	73%	1.4×10^{2}	< 1%
OBC ₃₀ -CB ₂ /TPU ₇₀ -7-a	70%	7.3×10^{2}	< 1%

4. CONCLUSION

The improvement of the effectiveness and efficiency of immiscible polymer blend and formulation control via straightforward extrusion for piezoresistive sensing is examined by exploiting TPU/OBC/CB system. With appropriate blend mass ratio, CB type and content as well as annealing, the challenging region of both high sensitivity and static strain (GF_{max} > 50 and ϵ_{max} > 100%) as well as reduced dynamic hysteresis can be realized. Alternatively, POE-g-MA can be utilized without annealing.

5. REFERENCES

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