

A Novel Method for Preparing Polyurethane Based Conductive Composites with Low Percolation Threshold

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Abstract: A novel method for preparing conductive carbon black filled polymer composites with low percolation threshold from polyurethane emulsion are reported in this paper. The experimental results indicate that with a rise in carbon black concentration the insulator-conductor transition in the emulsion blended composites occurs at 0.8-1.4vol%. In contrast, the solution blended composites exhibit drastic increase in conductivity at conducting filler fraction as high as 12.3-13.3vol%. It is demonstrated that the composites microstructure rather than chemical structure of the matrix polymer predominantly determines the electrical conduction performance of the composites.

Keywords: Percolation, water-borne polyurethane, conductive polymer composites, carbon black.

As a functional material, polymer composites incorporated with conductive carbon black (CB) have found promising applications in modern industries because of their advantages like light weight, good processability by the techniques common to unfilled polymers, chemical stability, design capability, cost effectiveness, and easy regulation of electrical conductivity within a wide range¹. It is worth noting, however, that the CB concentration needed to achieve sufficient conductivity in these polymer composites used to be quite high. Considering that larger amount of CB leads to processing difficulties and deteriorates mechanical properties², many works have been done to provide polymer composites with electrical conduction ability at reduced CB content. It has been known that conductivity of a polymer exhibits a drastic increase when conductive fillers are added. The mechanism involved can be described on the basis of percolation theory³. The optimal method to lower the percolation threshold lies in the usage of incompatible polymer blends. Tchoudakov and co-workers, for example, employed the blends of polypropylene (PP) and polyamine 6 (PA-6) as the matrix and yielded composites with percolation threshold of 2 ~ 5vol% of CB⁴. Stephen observed electrical percolation at 3.6 ~ 4.2vol% of CB in poly(ethylene-co-vinyl acetate)/high density polyethylene (EVA/HDPE) based composites⁵. In contrast, the typical percolation threshold of single polymer based

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composites has to be as high as 15 ~ 20vol% filler^{6,7}. Recently, Jaime *et al.* prepared conducting composites consisting of CB and poly(vinyl acetate) (PVAc) latex with the aid of plasticizer and emulsifier, and achieved a percolation threshold near 2.5vol% of CB⁸.

The aim of this work is to figure out a way for the preparation of single polymer based conductive composites with reduced percolation threshold. As microstructure and particle size of water-borne polyurethane (WPU) in water can be simply controlled by regulating the ratio of hard segments to soft segments without adding any accessory ingredients such as plasticizer and emulsifier, the authors of the current work select WPU as the matrix polymer in hopes of increasing the contact probability of CB particles and constructing conduction networks of CB throughout the composites at a relatively low filler fraction.

Experimental

To synthesize polyester WPU, a two-step method was applied as follows. Isophorone diisocyanate (IPDI), poly(ethylene adipate) (PEA, molecular weight=2000) and dimethylolpropanic acid (DMPA) were mixed at certain proportion with the addition of small amount of N-methylpyrrolidone. Then the resultant prepolymer was dispersed into distilled water and reacted with the neutralizer triethylamine (TEA) and the chain extender ethylene diamine (EDA), yielding emulsion of the polyurethane with solid content of around 15 wt% and latex particle size of 600 nm.

Polyether WPU emulsion (with latex particle size of 400 nm) was also prepared by the same approach described above except that IPDI and PEA were replaced by toluene diisocyanate (TDI) and poly(ethyl glycol) (PEG, molecular weight=2000), respectively.

For producing conductive composites, commercial CB XC-72 (Cabot Co. Ltd., specific surface area=254 m²/g, diameter=50-70nm), was added to the polyurethane emulsions under high-speed stirring. Then the pasty composites were coated onto an epoxy plate with comb electrodes⁹. Having been dried at ambient temperature and atmosphere, the composites films 40-60 μm thick are ready for electrical measurements.

For purposes of comparing the effects of emulsion blending and solution blending, the dried composite films were thoroughly dissolved in tetrahydrofuran (THF). The solution was then poured onto an epoxy plate again allowing evaporation of the solvent to generate solution blended composite films.

Results and Discussion

Dependence of conductivity of the composite systems on CB loading is illustrated in **Figure 1** and **Figure 2**. Clearly, the ways of composites preparation exert much greater influence on the conduction behavior as compared with the chemical structures of the polyurethane matrix. The insulator-conductor transition in the emulsion blended composites takes place at rather low CB concentration. According to the peak position of the first derivation of conductivity with respect to CB content, it is known that the percolation thresholds are 0.8 ~ 1.4 vol% for the emulsion blended composites and 12.4 ~ 13.3 vol% for the solution blended composites, respectively. The significant difference

Figure 1 Room temperature conductivity (σ) and CB concentration in the emulsion blended composites

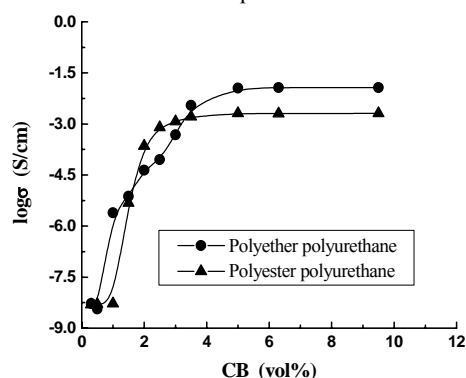
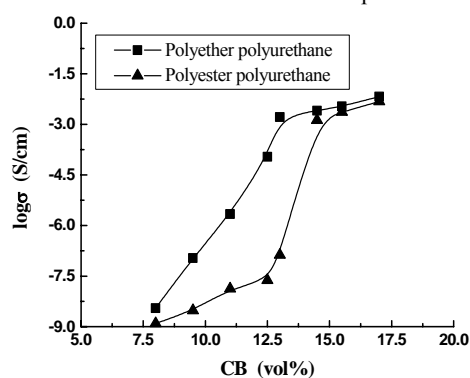


Figure 2 Room temperature conductivity (σ) and CB concentration in the solution blended composites



should be attributed to the microstructural characteristics of the composites. In the case of emulsion blending, the large polymer particles are surrounded by the tiny CB particles. A non-random segregated distribution of the filler particles is thus formed. As the conductive particles in a segregated dispersion are restricted to certain sites promoting formation of reticulated filler structures, the conducting networks can be built up more efficiently¹⁰. With respect to the composites prepared by solution blending, the more homogeneous dispersion nature of the compounding method results in relatively random distribution of the CB particles, so that the contact probability of the well isolated fillers is decreased. The composites have to show conductivity at high CB loadings.

On the assumption that conductive composites are comprised of spherical polymeric particles and conducting filler particles, Malliaris and Turner proposed a model to predict the percolation threshold in terms of the relative size of the components¹¹:

$$V_c = 50P_c[1+(\phi/4)(R_p/R_m)]^{-1} \tag{1}$$

where V_c is the filler volume fraction at the percolation threshold, P_c the first nonzero probability for infinitely long sequence of adjacent occupied lattice sites, ϕ a quantity which depends on the packing mode of the conductive particles, R_p the radius of polymer particles and R_m the radius of the filler particles.

Table 1 lists the comparison of the estimated V_c with the experimental results of the present composites. The following data are used throughout the calculation: $R_m=25\text{nm}$, $P_c=1/3$ and $\phi=1.11$ (supposing a hexagonal arrangement of the particles¹¹). The R_p values of the polyurethane in the emulsion blended composites are obtained from microscopic observation of the latex sizes, while those in the solution blended composites are taken from the nodule dimension of conventional polymers which ranges between 5-20 nm in general. Clearly, the theoretical values of V_c are able to reflect the common differences among the composites, especially when solution blended composites are concerned. It provides supporting evidence for the aforesaid deduction of the dispersion status of CB particles in the composites. On the other hand, the significant deviation of V_c^{calc} from

V_c^{meas} in the case of emulsion blended composites implies that other factors besides geometries of the components should also account for the low percolation thresholds. A further study in this aspect by changing the structures of the matrix polyurethane will be carried out to reveal the mechanism.

Table 1 Comparison between the calculated percolation thresholds (V_c^{calc}) and the measured ones (V_c^{meas}) of CB/polyurethane composites

Composites	Matrix	R_p (nm)	R_p/R_m	V_c^{calc} (vol%)	V_c^{meas} (vol%)
Emulsion blended	Polyether polyurethane	300	12	3.8	0.8
Emulsion blended	Polyester polyurethane	200	8	5.2	1.4
Solution blended	Polyether polyurethane	20	0.8	13.6	12.4
Solution blended	Polyester polyurethane	5	0.2	15.8	13.3

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