

# PVDF based polymer nanocomposite coatings for large area applications

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## ABSTRACT

We demonstrate a technique to blend Polyvinylidene fluoride (PVDF) and ethyl-2-cyanoacrylates (ECA, the main ingredient of 'superglue') in solution to enhance PVDF coating adhesion. ECA monomer was control-polymerized by using a co-solvent before blending. A number of micro- and nano-fillers were dispersed in the polymer solutions to fabricate coatings with strong substrate adhesion and tunable surface hydrophobicity using spray atomization. The influence of filler size, shape and concentration on composite hydrophobicity and microstructure was studied. The wettability of the composites was quantified by measuring static contact angles of water and water/isopropanol mixture droplets. Composite surface wettability ranged from partially hydrophilic to superhydrophobic depending on filler particle size, shape and concentration, while maintaining good substrate adhesion.

**Keywords:** PVDF, PECA, polymer blend, micro/nanofillers, superhydrophobic, alcohol repellent coatings

## 1 INTRODUCTION

PVDF is a biocompatible, piezoelectric, hydrophobic polymer, which possesses outstanding oxidative, thermal and hydrolytic stability, as well as good mechanical and film-forming properties[1-4]. However, PVDF applications are somewhat handicapped by its poor adhesion and inability to disperse functional filler particles. Promising techniques, such as blending with other polymers (e.g. Poly(methyl methacrylate), PMMA), chemical grafting and surface modification have been proposed in the literature to address these issues[5, 6]. Although polymer blending in solution is an easy and cost-effective technique, insolubility of PVDF in many solvents makes it a challenge. Consequently, the search for polymers miscible with PVDF is ongoing. One attractive choice can be the cyanoacrylates (CAs). CAs are biodegradable and used as instant curing adhesives for substrates ranging from metals and plastics, to living tissue. The cyano ( $C\equiv N$ ) group present in CA monomer is electro-active having ferroelectric functionality[7]. As such, the instant polymerization of CAs hinders their use in solution-based

polymer composites. Some inhibitors, such as weak acids, have been suggested to this end[8, 9], but finding alternative ways to control CA polymerization is necessary to facilitate polymer blends and dispersions.

N, N Dimethylformamide (DMF) is a commonly used solvent for PVDF. However, DMF and CA react violently and are nearly impossible to mix. In this work, we have made the solvent blending of PVDF and CA possible by controlled polymerization of one cyanoacrylate monomer in DMF, in the presence of a co-solvent prior to mixing. Furthermore, we add functional micro/nanoparticle fillers to the blend in order to demonstrate the utility of this blend to make functional coatings with controllable wettability and microstructure that are scalable to very large area applications. The wettability of the coatings was tested with the help of static droplet contact angle and droplet sliding angle measurements performed with water and a 90:10 wt. ratio mixture of water and isopropyl alcohol (IPA). It was observed that at sufficiently high content of each type of filler particles, the water contact angle for the coatings approached or exceeded 150 degrees, which is considered a threshold value for a coating to be superhydrophobic. In order to determine the self-cleaning[10] property of these coatings, roll-over angles of liquid droplets on a coated surface were also measured.

## 2 EXPERIMENTAL

In this work we have used ethyl 2-cyanoacrylate (CA) monomer (Sigma-Aldrich, USA) to demonstrate the polymer blending. The following strategy was adopted to control the CA polymerization. In a glass flask equipped with a water-cooling jacket, CA monomer was dissolved in reagent grade acetone (Sigma-Aldrich, USA) to obtain 33 wt. % CA monomer solution. Using a syringe pump, equal weights of reagent grade DMF (Sigma-Aldrich, USA) and acetone were slowly introduced into the CA solution while stirring continuously until the final concentration of CA in the solution reached 8 wt. %. During this process thickening of the mixture was observed. The final mixture was stored overnight at room temperature. DMF acts as a catalyst in rapid anionic polymerization of CA, however, in a co-solvent system, in which the relative amount of DMF in solution is adjusted, the anionic polymerization reaction of CA progresses more slowly. Through such slow polymerization, a poly (ethyl 2-cyanoacrylate) (PECA)

polymer having a high degree of polymerization was obtained, resulting in lower residual strain and elevated flexibility in comparison with polymers obtained by rapid polymerization.

PVDF pellets ( $M_w \sim 530$  kDa) (Sigma-Aldrich, USA) were dissolved in DMF at 60 °C to obtain a 20 wt% solution. The PVDF and PECA solutions so prepared were miscible at any proportion and could be diluted with common solvents, such as acetone and acetates. The blending of the two polymer solutions was performed at room temperature. To prepare the dispersion of micro/nanoparticle fillers into the PVDF/PECA polymer solution, the fillers were added directly and hand shaken without using additional dispersants or surfactants. PVDF to PECA blend weight ratio was kept constant at 60/40 to obtain an optimum level of filler dispersability and adhesion from the polymer blends. The dispersions were coated on Al-foils using a Paasche VL siphon feed airbrush. The dispersions were stable for the time scale of spraying process. Table 1 shows the composition details of the dispersions used to make the coatings. The fillers used include microparticles of polytetrafluoroethylene (PTFE), zinc oxide (ZnO) (Sigma-Aldrich, USA); nanoparticles of ZnO (Alfa-Aesar, USA) and their combinations. The coated foils were heated at 125°C for 45 minutes to cure the coatings and remove solvent residuals. Typically 18 g of dispersion was used to coat a 10"x10" Al-foil.

Ingredient	Concentration (wt. %)
20% PVDF by wt dissolved in DMF	8.33
8% PECA by wt dissolved in DMF/acetone mixture	13.89
Filler particles	2 – 20
Acetone	75.78 – 57.78

Table 1: Composition of particle filled polymer dispersions used to make coatings in this work.

The sessile droplet contact angle was measured by an optical image acquisition system described elsewhere[11]. The contact angles were measured for sessile droplets of water and 90:10 wt. ratio mixture of water + IPA. The droplet roll-over angles were measured by increasingly inclining the coated Al-foil on a tilt stage having angle measure accuracy (graduation) of 1 degree. This technique offers a more severe test of self-cleaning ability as compared to placing the liquid droplets on a pre-inclined surface.[12]

### 3 RESULTS AND DISCUSSION

Three different types of particle fillers were used to demonstrate the versatility of our PVDF/PECA blends in dispersing functional filler particles of different sizes (micro/nano) and surface energy (hydrophilic to

hydrophobic). The fillers were PTFE ( $\sim 1\mu\text{m}$ ), ZnO ( $\sim 5\mu\text{m}$ ) microparticles and ZnO nanoparticles ( $\sim 40\text{-}100$  nm). PTFE particles are hydrophobic, whereas both micro and nano-size ZnO particles should be hydrophilic, as they were not

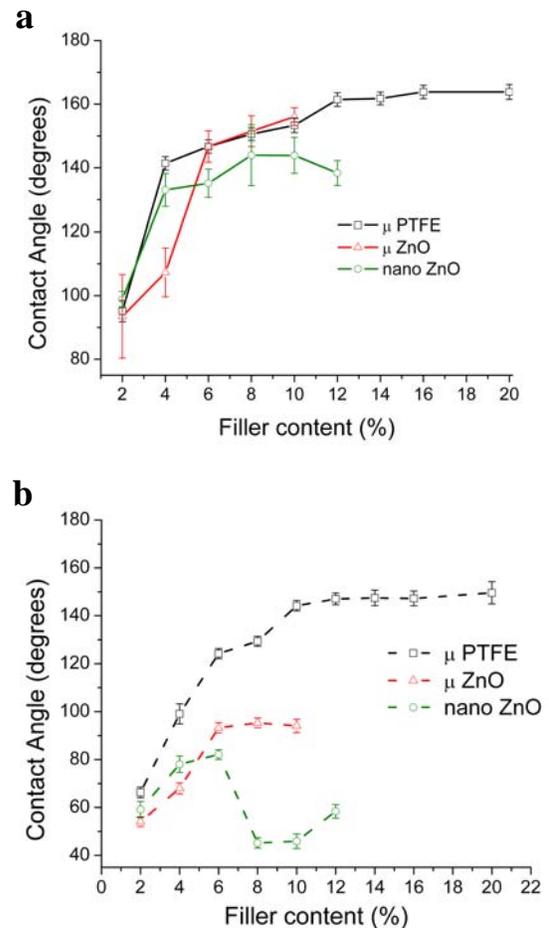


Figure 1: Droplet contact angle change with filler content for coatings containing different fillers tested using two different liquids: a) water, and b) water + IPA mixture functionalized in any way.

The water + IPA (90:10 wt.) mixture has a surface tension of 40.42 mN/m[13] and serves as a measure to determine the alcohol repellency of the present coatings. Alcohol repellency is of great importance for coating medical fabrics. In addition, repellency of such a low surface tension liquid is a more severe test for the surface energy of coatings and, in general, very challenging to achieve for large area coating applications. It should be mentioned here that our coatings consist of biocompatible components, which combined with their alcohol repellency could be especially well suited for medical applications.

In Figs. 1 – 2, we present the change in water (WCA) and (water + IPA) mixture (WICA) droplet contact angles for coatings with content of different fillers. Addition of fillers is expected to influence the wettability of the resulting coatings by two different mechanisms. On one

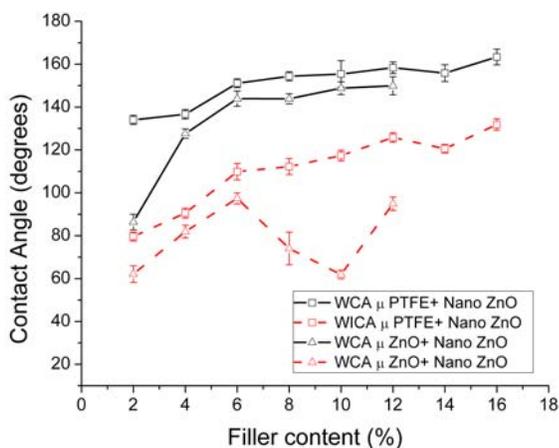


Figure 2: Water (WCA) and water + IPA mixture (WICA) contact angle change with micro + nanofiller content.

hand it should influence the surface roughness, which can change the contact angle of liquid drops on the surface (Wenzel [14] effect), and on the other hand, it can change the surface energy of the coatings depending on whether the particles are hydrophilic or hydrophobic. Further more, addition of micro and nanoparticles simultaneously should help in controlling the microstructure of coatings and potentially obtain a surface morphology with hierarchical micro/nano scale surface roughness. For each type of filler particles used here, we have added particle amounts ranging from the lowest to the maximum possible limit to obtain the entire range of wettability obtainable.

In Fig. 1 we show the change in WCA (Fig. 1a) and WICA (Fig. 1b) with addition microparticles ( $\mu$ ) of PTFE and ZnO and nanoparticles of ZnO individually. Addition of PTFE particles should increase the surface roughness of the coatings and also lower the overall surface energy of the coating, making it difficult to wet. This results in gradual increase in contact angle of both water and water + IPA mixture droplets reaching a maximum of 164 and 150 degrees (see Figs. 1a and b), respectively at

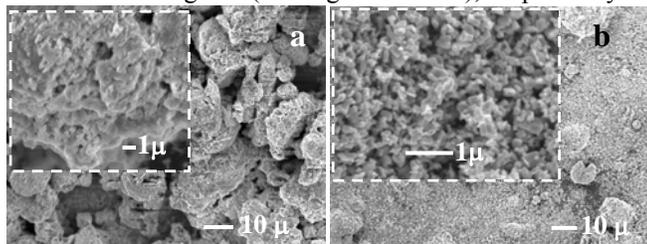


Figure 3: Morphology of our nanocomposite coatings a) 16%  $\mu$  PTFE + Nano ZnO and b) 12%  $\mu$  + Nano ZnO. 20% PTFE content. Addition of hydrophilic ZnO microparticles should increase the surface roughness of the coatings, but increase the surface energy. These two effects are in competition. Therefore, although there is a rise in contact angle for both liquids with addition of  $\mu$  ZnO particles, the rise in contact angle slows down from 6% and higher concentrations (c.f., the corresponding WICA

variation in Fig. 1b). The increase in surface roughness will be less sharp with addition of nanoparticles compared to the same content of microparticles. However, the change in overall surface energy of the coating is expected to be similar to  $\mu$  ZnO particles. This is apparent from the leveling off of WCA in Fig. 1a. The corresponding WICA variation (see Fig 1b) shows initial increase followed by a clear decrease in the contact angle. This indicates that in the beginning the increase in surface effect dominates, but then it gives in to the increase in coating surface energy effect.

The effect of simultaneous addition of both micro and nanoparticles was considered next with the expectation of obtaining hierarchical micro/nanoscale surface roughness morphology, which is essential to obtain superhydrophobic surfaces[15]. The micro and nanoparticles were added in 50:50 wt. ratio with respect to each other. Figure 3 shows the SEM images of two different micro/nanofiller combinations used to make nanocomposite coatings in this work. They both show characteristic hierarchical micro/nanoscale roughness structure. The two insets in Figs. 3 highlight the nanoscale features.

Fig. 2 presents the change in WCA and WICA with addition of  $\mu$  PTFE and ZnO nanoparticles. The overall content of fillers in the dispersions is plotted along the abscissa. Note that for 2% PTFE + Nano ZnO, the WCA is 134 degrees (see Fig 2), whereas the corresponding WCA for 2% only Nano ZnO and  $\mu$  PTFE is 99 and 95 degrees, respectively (see Fig 1a). This indicates the importance of hierarchical surface morphology resulting from addition of both micro and nanoparticles. The

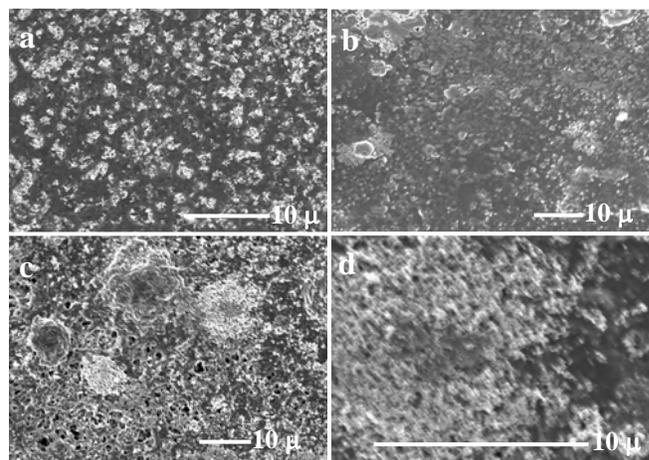


Figure 4: Morphology of coatings with 2% fillers. a) Only Nano ZnO, b) Only  $\mu$  PTFE, c) and d) Nano ZnO +  $\mu$  PTFE morphology of these coatings is illustrated in Fig. 4. At low ZnO content (e.g. 2%), the well-dispersed nanoparticles would get almost entirely buried in the polymer matrix of the coatings and thus the effect of particle functionality (hydrophilicity) is not as clear, and the surface roughness effects dominate. This can help in understanding the slightly higher WCA value for pure ZnO nanoparticles compared to pure PTFE microparticles for 2% particle

content, although the former are hydrophilic. Figure 2 also shows the contact angle variation for coatings with both micro and nanoparticles of ZnO. The contact angle trends appear similar to the case of only ZnO nanoparticle fillers case. However, differences become clear through the sliding angle measurements discussed next.

Table 2 presents the sliding angle measurements for our coatings containing different fillers. W denotes the

Filler content (%)	Sliding Angle (degrees)									
	Filler Type									
	$\mu$ PTFE		$\mu$ ZnO		Nano ZnO		$\mu$ PTFE + Nano ZnO (50:50)		$\mu$ + Nano ZnO (50:50)	
	W	WI	W	WI	W	WI	W	WI	W	WI
2	S	S	S	S	S	S	S	S	S	S
4	35 ± 6	S	S	S	S	S	S	S	S	S
6	9 ± 3	S	17 ± 8	S	S	S	6 ± 1	S	S	S
8	7 ± 2	S	11 ± 2	S	S	S	5 ± 2	S	S	S
10	3 ± 2	69 ± 12	S	S	S	S	11 ± 2	S	63 ± 24	S
12	2 ± 1	21 ± 2			S	S	7 ± 2	S	9 ± 2	S
14	2 ± 1	13 ± 4					8 ± 3	S		
16	2 ± 1	14 ± 3					3 ± 2	S		
20	2 ± 1	10 ± 3								

Table 2: Sliding angle for PVDF based coatings measured with water (W) and water +IPA mixture (WI) droplets.

sliding angle for water droplets and WI that for water + IPA mixture droplets. The errors are calculated by considering both the repeatability of the measurements (2 to 4 for each coating) and the tilt stage accuracy. For  $\mu$  PTFE fillers the sliding angle shows a gradual reduction and reaches minimum values of 2 and 10 degrees, for water and water + IPA respectively. Notice, that water + IPA mixture drops require higher content of PTFE for sliding due to its much lower surface tension. For  $\mu$  ZnO, the water + IPA drops never slide no matter what the particle content. The water droplets do slide for intermediate  $\mu$  ZnO content because the surface roughness effects dominate over surface energy; however, droplets remain stuck (S in Table 2) at 10% particle content where the surface energy effect is stronger. For nano ZnO, droplets remaining stuck on the plate for all different ZnO nanoparticle contents.

In the case of  $\mu$ PTFE + nano ZnO fillers, we see that water + IPA mixture drops (low surface tension) never slide. On the other hand, water droplets slide at 6% or higher particle content. For  $\mu$  + nano ZnO fillers, water drops do slide at high particle contents (10 and 12%), whereas the water + IPA drops never slide.

## 4 CONCLUSION

In conclusion, a simple technique was presented to blend PVDF with cyanoacrylates in solution for the first time. To achieve efficient blending in solution, ethyl-2-cyanoacrylate was control-polymerized using a co-solvent before blending with PVDF. Various composite coatings were produced by spray casting micro and nano-filler dispersed polymer blends. The coating morphology and hydrophobicity was tunable by adjusting filler type, size and concentration in solution, such that coating wettability ranged from partially hydrophilic to superhydrophobic.

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