Polymer Bulletin 60, 847–853 (2008)
DOI 10.1007/s00289-008-0920-z

Polymer Bulletin

Shearing Effects on the Conducting Polymer Blends

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Received: 7 September 2007 / Revised version: 10 January 2008 / Accepted: 2 March 2008

Summary

To obtain a highly conductive polyblend based on doped polyaniline, an zinc salt based conductive master batch material (MB-13) made from mixing zinc n-dodecylbenzene sulfonate (Zn $(DBS)_2$) and n-dodecylbenzene sulfonic acid (HDBSA) polyaniline ($PANI(DBSA)_{0.5}$) together was compounded with PP in a melt-mixer varying the processing conditions. The SEM pictures show the morphologies of the polyblends were phase-separated into strips of elongated MB-13 for all samples. The elongation was first enhanced at shear rates ranged from 20 to 60 rpm. A shear rate of 60 rpm at 180°C can elongate the conductive master batch phases (filler) to obtain both the highest aspect ratio and least resistance by keeping the secondary dopants of $Zn(DBS)_2$ stay within MB-13 from losing its conductivity and deformability.

Keywords

Conducting polyblend; Secondary doping effect; Shear rate

Introduction

The blending of neat doped polyaniline with other matrix polymers or nanoclays has been studied for several years [1–8]. However, the conductivity, processability, and other properties of the resultant conducting polyblends were not enhanced due to poorly dispersed nature of polyaniline in the matrix polymers due to its strong positive and negative intra– or inter molecular interaction and concentrated H-bondings.

O. Ikaala etc. [9–10] proposed a simple way to find out a suitable dispersing agent which can be a dopant for preparing a conductive polyaniline by mixing EB with zinc n-dodecylbenzene sulfonate ($Zn(DBS)_2$) prepared from the neutralization of zinc oxide with n-dodecylbenzene sulfonic acid (HDBSA). After mixing (complexation) with $Zn(DBS)_2$, the EB is complexed with long side chains from the organic salts

($Zn(DBS)_2$) and becomes doped in the mean time, causing the polyaniline to be both conductive and dispersible in polymer matrix.

Since there is a high possibility that EB is not entirely doped by HDBSA, we use HDBSA doped polyaniline ($PANI(DBSA)_{0.5}$) to replace EB and further doped with organic zinc salts prepared from HDBSA to become a conductive master batch (MB) to improve the degree of doping for a better conductivity and compatibility between dispersing agent and polyaniline. The MB material is highly conductive since the included polyaniline was doped both with primary (HDBSA) and secondary ($Zn(DBS)_2$) dopants and can be well-dispersed and deformed in a matrix polymer during processing (melt-mixing) for a conducting polyblend. Only few matrix polymers are entirely miscible with the MB material for a molecular level mixing, the best way to increase the conductivity of an immiscible polyblend will be to provide a deformable MB filler which can be deformed into thin films or threads to reach a higher conductivity with the higher aspect ratio even though they are not entirely miscible with matrix polymer at a molecular level. It can be accomplished when a high viscosity difference between MB and matrix polymer is created to induce a strong deformation to straighten the immiscible MB domain during processing at higher temperature and shearing. However, it is possible the organic zinc salts will be spin out the MB if either the temperature or shear rate is too high due to its already liquefied property at the processing temperature (the melting point for $Zn(DBS)_2$ is only 130°C which is much lower than the processing temperatures of the regular matrix polymers).

The following studies concerning about finding out the best processing condition when the MB can be highly deformed without $Zn(DBS)_2$ being spin out to obtain a highly conducting polyblend with the less amount of conductive MB.

Experimental

Synthesis and Sample Preparation

Preparation of DBSA-doped Polyaniline

Similar to regular polymerization method [7, 11, 12], 12 ml aniline, 21g HDBSA (behaving as both dopants and emulsifiers), 160 ml distilled water were mixed and mechanically stirred in a 250 ml four-necked flask in a ice-bath with purging nitrogen gas. The polymerization was initiated with the addition of an ammonium APS aqueous solution (17g APS in 30ml distilled water) drop wise. The obtained polyaniline was then precipitated out in a 750 ml acetone bath, followed by filtration and the filtered cake was washed with excessive acetone to remove the residue HDBSA and dried in vacuum at 40°C for 24 hr. The obtained polyaniline is named as PANI(DBSA)0.5.

Preparation of organic zinc salt ($Zn(DBS)_2$)

HDBSA (n-dodecylbenzene sulfonic acid) was first dissolved in toluene in a three necked separable 1 liter glass reactor and various proportional zinc oxide was put into the solution in purging N_2 and mechanically stirred. The mixtures were maintained in molten state at around 150°C until the white ZnO powders disappeared with the toluene solvent evaporated simultaneously. The $Zn(DBS)_2$ was available with cooling at room temperature.

Preparation of master batch material and conducting polyblend

PANI(DBSA)$_{0.5}$ was mixed with Zn(DBS)$_2$ in a PLASTOGRAPH® mixer (Brabendar) with weight ratio of 1/3 (named as MB-13) at 150°C and shear rates of 140 rpm to become a master batch (MB).

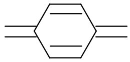
Conducting polyblends were prepared at 180°C with 21.9 wt% of MB-13 and PP mixed in the Brabendar set at various shear rates (rpm).

Characterization

A Milliohm meter (LUTRO MO–2001) was used to measure the volume resistivity (ρ) of the polyblends. A HR–SEM of HITACHI S4200 with an accelerating voltage of 15kV was used to take SEM pictures of the polyblend samples which have been cut into fresh surfaces in liquid N_2 and have been coated with Au followed by drying at 60°C in a vacuum oven for at least 24 hr. About 8 mg of sample was subjected to a MDSC of TA-2920 and heated at 10°C/min from 40 to 150°C, in purging N_2. The conductivity of all samples was measured by a 4-probes milliohm conductivity meter.

Results and discussion

Characterization

The doped quinoid and benzenoid groups show 1561 cm^{-1} and 1467 cm^{-1} in Fig. 1(a), respectively. Additional absorption peak at 1178 cm^{-1} corresponds to H$^+$N  N$^+$H and the most significant peak derives from the affluent –B-NH-B- groups of polyaniline main chains. Also there are characteristic absorption peaks at 1030 and 1005 cm^{-1} which correspond to the stretching of sulfonic groups. These assignments were listed in Table 1. The formation of a zinc n-dodecylbenzene sulfonate can be confirmed from the presence of a weak peak at 1200 cm^{-1} derived from the neutralization of HDBSA with ZnO [10] as seen from Fig. 1(b). Other peaks of Zn(DBS)$_2$ can be assigned to the characteristic peaks of the dodecylbenzene sulfonate ions which can also be found in the FTIR spectrum of PANI(DBSA)$_{0.5}$ since it was doped by HDBSA.

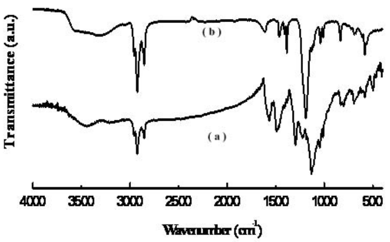


Figure 1: FTIR spectra of (a) PANI(DBSA)$_{0.5}$ and (b) Zn(DBS)$_2$

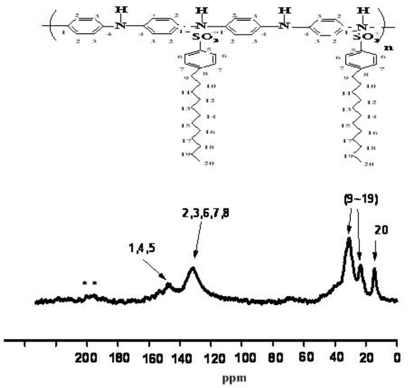
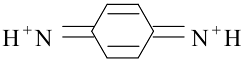


Figure 2: ^{13}C NMR spectra of PANI(DBSA)$_{0.5}$

The solid-state C^{13} NMR spectra were also used to characterize PANI$(DBSA)_{0.5}$. The results are shown in Fig. 2. The resonance peaks of various carbons are illustrated in the attached chemical structures. The absorptions of the aliphatic carbons of DBSA of PANI$(DBSA)_{0.5}$ and can be seen around 20–40 ppm from Fig. 2. The benzene-ring carbons of both aniline and DBSA were approximately at 120–140 ppm.

Table 1: Assignments of FTIR-spectrum of PANI$(DBSA)_{0.5}$

Frequency(cm^{-1})	Assignment
2958	$\nu(-CH_3)$
2924	$\nu(-CH_2-)$
1600	$\nu(-C=C-)$, benzene ring
1561	doped $\nu(-C=N-)$ of quinoid
1467	doped $\nu(-C=C-)$ of benzoid
1307	$\nu(-C-N-)$
1178	
1135	-B-NH-B-
1034	ν_{as} (-S=O) of $-SO_3H$
1006	ν_{sy} (-S=O) of $-SO_3H$
801	ν(C-H) para-substituted aromatic out of plain bending

Conductivity and Morphology from SEM pictures

A master batch (MB-13) prepared from mixing one portion of HDBSA doped polyaniline (PANI$(DBSA)_{0.5}$) and three portions of zinc n-dodecylbenzene sulfonate ($Zn(DBS)_2$) was used to melt-mix with polypropylene (PP) in a Brabendar mixer with recording torque, processing time under the setting temperature and shear rate. With the fusible temperature for PP at 180°C, various shear rates and time were adopted to prepare a conductive PP composite possessing applicable conductivity with the least amount of MB-13 introduced in order to retain the pristine properties (mechanical especially) of PP and reduce the price. It is found no matter what kinds of processing conditions were set (shear rates and processing time), the PP polyblends (composites) always gave similar volume resistivities lower than 10^4 Ωcm with more than 28.6 wt% of MB-13 (40 phr MB-13 and 100 phr PP) present during processing. However, the mechanical property of the matrix PP had found to be destroyed and the composite became an oily, softer material compared with neat PP. When the percentage of MB-13 is below 13.8% (16 phr), the volume resistivities of the polyblends became so high ($> 10^9$ Ωcm) that they are not considered as conducting materials any more. An optional percentage of MB-13 is adopted as 21.9 wt% (28 phr), which includes about 5.5 wt% conducting PANI$(DBSA)_{0.5}$, to take both conductivity and mechanical property into consideration to obtain an are out of the applicable conducting polyblend.

The relative viscosity (RV), defined as the ratio of the torques of MB-13 and PP at 180°C can greatly influence both the degree of deformation and the aspect ratio of the conductive MB-13 in the PP matrix and plays an important role in deciding the final conductivity and mechanical property of a PP based conductive polyblend. Table 2 and SEM pictures (Fig. 3 (d)–(f)) of polyblends prepared with shear rates over 60 rpm show a decreasing and deformed length of MB-13 domains (shorter deformed length is represented by small scaled 10 μm bar) with shear rate which can cause the spinning out of the secondary dopants $Zn(DBS)_2$ as would be found in the following discussion of the thermal property. And the absence of $Zn(DBS)_2$ due to high shearing effect caused no significant deformation of MB-13 during processing. The increasing shear rates and increasing viscosity contrast (decreasing RV) below 80 rpm result in enhanced conductivities and deformations of MB-13 as shown in Table 2 and Fig. 3 (a)–(c), which significantly illustrate the lengths of the deformed MB-13 by SEM pictures.

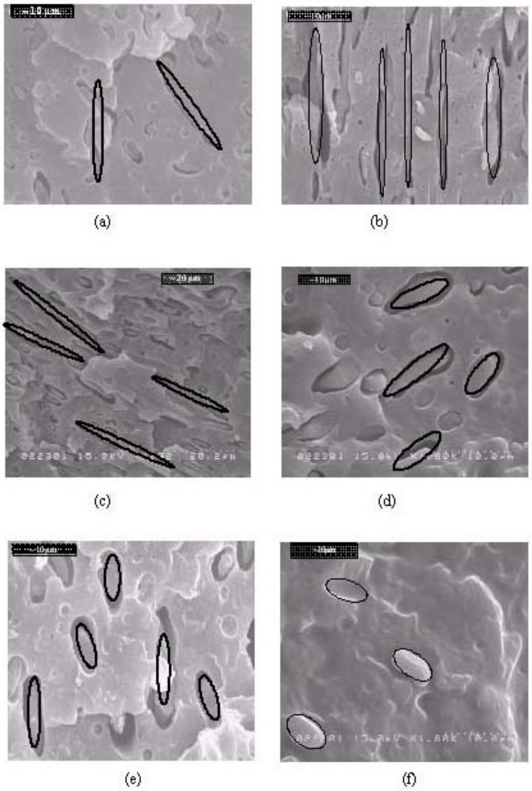


Figure 3: SEM pictures of conducting PP with 21.9 % of MB-13 processed at 180°C, 20 min with (a) 20 rpm (b) 40 rpm (c) 60 rpm (d) 80 rpm (e) 100 rpm (f) 140 rpm

Table 2: Various properties of polyblends processed at 180°C with various shear rates

Shear rate (rpm)	20	40	60	80	100	140
Log ρ (Ωcm)	7.11	5.69	3.67	8.91	11.76	12.2
Maximum deformed L(μm)	16	28	46	12	8	6
τ_{MB-13} (Nm)	7.39	6.36	5.12	3.2	2.55	1.57
τ_{PP} (Nm)	9.47	8.9	8.14	7.45	7.07	5.55
RV = τ_{MB-13}/τ_{PP}	0.78	0.71	0.63	0.43	0.36	0.28

Thermal and Rheological analysis

To make sure the separation of $Zn(DBS)_2$ from MB-13 or not at various shear rates during preparation of conducting polyblends, the DSC thermograms of polyblends with thermal history of 10 min stay at 180°C were compared with that of neat PP with the same thermal history in Fig. 4. Surprisingly, the samples prepared at high shear rates (80–140 rpm) each show an additional exothermic peak around 150°C, which is believed to be the melting point of the separated Zn(DBS)$_2$, except the significant melting point peak of neat PP.

Both volume resistivity and deformed lengths were plotted with shear rates in Fig. 5 to demonstrate that the higher deformation (shear rate 20–60 rpm) obtained lower resistivity and better conductivity, just as expected when the shear rate is below 80 rpm. Therefore, the higher conductivity present at shear rates below 80 rpm might originate from the en-lengthened and deformed (high aspect ratios) MB-13 that still keep the secondary dopant Zn(DBS)$_2$ in it.

According to Fig. 3 (d)–(f) and Table 2, the squeezing effect on MB-13 were due to the high speeding and higher viscosity contrast (represented by torque ratio of MB-13 and PP) at the high shear rates. The loss of lubricant-like Zn(DBS)$_2$ out of MB-13 at high shear rates could harden (viscosity increased) MB-13 and decrease its degree of distortion as seen from Fig. 3(d)–(f). Therefore, the optimum shear rate is 60 rpm around when the conductive fillers MB-13 can be highly extended to demonstrate a lower resistance shown in Table 2 and Fig. 5.

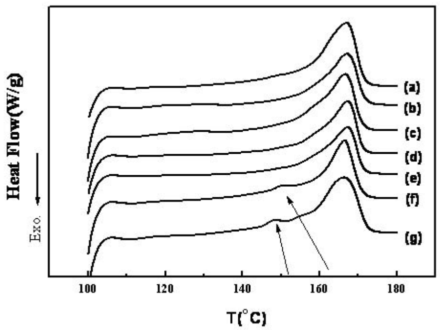


Figure 4: DSC thermograms of Neat PP and its polyblends with thermal history at 180°C, 10 min at various shear rates (rpm) (a) neat PP (b) 20 rpm (c) 40 rpm (d) 60 rpm (e) 80 rpm (f) 100 rpm (g) 140 rpm

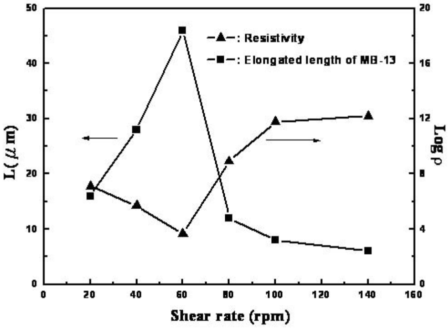


Figure 5: Resistivity (Ωcm) of PP polyblends and deformed length (μm) of 21.9 wt% MB-13 vs. shear rate

Conclusion

The zinc salt based master batch material (MB-13) made from mixing zinc n-dodecylbenzene sulfonate (Zn (DBS)$_2$) together with conductive polyaniline in 1/3 weight ratio was compounded with PP at 180°C at various shear rates for a conducting polyblend in a mixer The Zn (DBS)$_2$ is an effective secondary dopant that can improve the conductivity and processing of the polyaniline . The SEM pictures show the morphologies of the polyblends were phase-separated with strips of elongated MB-13 dispersed in PP matrix due to the relative viscosity difference at various shear rates. The aspect ratios of the MB-13 strips inside PP matrix and conductivity of the polyblends increased regularly with shear rates below 80 rpm without the loss of the zinc salt out of the MB-13 according to the thermal and rheological measurements. Polyblends processed with higher shear rates than 60 rpm can shear the soft zinc salts out of MB-13 and demonstrated slightly elongated MB-13 due to the harder structures caused from losing lubrication and conductivity in the absence of zinc salt. Taylor's equation derived from the balance of the shear and interfacial forces on the deformable fillers can be used to predict the equivalent sizes of them. And the results fitted well with the equation until the shear rate is over 60 rpm when there was a loss of zinc salt from master batch material. Therefore, it is concluded a shear rate of 60 rpm at 180°C can both elongate the conductive master batch phases to obtain a high aspect ratio and keep the lubricating, secondary dopants (Zn $(DBS)_2$) stay inside the conductive fillers, MB-13, from losing the conductivity and deformability.

Acknowledgement. The authors would like to appreciate the financial support from National Science Council in Taiwan, ROC through the grant of NSC 94-2216-E-151-003.

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