

Conducting Polymer Blends Prepared from Polyaniline with *n*-Dodecylbenzenesulfonic Acid Zinc Salt as the Secondary Dopant

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ABSTRACT: A red-shift of the UV–vis spectra of *n*-dodecylbenzenesulfonic acid doped polyaniline (PANI (DBSA)_{0.5}), resulting from the secondary doping of polyaniline backbones, was found in the presence of *n*-dodecylbenzenesulfonic acid zinc salt (Zn(DBS)₂). It is proved to behave as steric hindrance spacers to induce the extension of the conjugation length through the straightening effect on the polyaniline backbones and the obtained mixtures (PANI(DBSA)_{0.5} plus Zn(DBS)₂) can be used as master batch materials (MB-13) for blending with regular polypropylene polymer (PP). The thermal degradation accompanied with loss of conductivity for MB-13 can be delayed to over 250°C when enough Zn(DBS)₂ was secondarily doped on PANI(DBSA)_{0.5}, which allow the performance of its blending with other nonconducting/regular polymers possible. Below 80 rpm, increasing shear rates would induce higher viscosity difference between the MB-13 and PP

matrix, resulting in elongation of MB-13 in the PP matrix and higher conductivities of the polyblends. The deviation from the Taylor equation, which is used to estimate the degree of elongation for a polyblend, started when shear rate is over 80 rpm. The leakage of Zn(DBS)₂ out of MB-13 can be confirmed by comparing the DSC thermograms and X-ray diffraction patterns with that of neat PP. Gradual deformation for the conductive fillers (MB-13) and a well-defined and expanded layered structure can be found when processing time is below 15 min with 60 rpm shear rate. The layers started to shrink back after 15 min of procession with the loss of the Zn(DBS)₂ from MB-13 in the PP matrix. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3516–3522, 2008

Key words: polyaniline; conducting polymer blend; secondary doping effect

INTRODUCTION

The primary doping on polyaniline by protonic acids can change it from a semiconductor with conductivity less than 10⁻⁷ S/cm to a better conductivity about 10⁻¹ S/cm. This, however, is not well enough compared with the conventional conductors whose conductivity are usually higher than 1 S/cm, for example, conductive carbon black. Besides, the intractable properties of polyaniline remain intact after doping by protonic acids due to the still absence of lubrication that is always needed for a rigid-rod polymer to become soluble or/and fusible during procession. The poor procession properties of them can be solved with the introduction of a protonic acid with long alkyl side chains that provide more spaces between the highly polar main chains and allow the molecules to go on conformational

changes. The problem that was induced when this kind of protonic acids with long alkyl chains is introduced is its nonconductive and bulky size which can effectively dilute and reduce the conductivity. And the presence of the negative ions can bridge amine groups together through either intra- or interchain complexation resulting in the meandering conformations of the backbones, which is unfavorable to convey charges due to the longer touring before they can reach the other end.^{1,2} Therefore, we need other types of dopants that can both dope the polyaniline furthermore and remove the unfavorable factors that induce coiler conformations to obtain a highly conductive and soluble fusible conductive polymer.

The blending of neat doped polyaniline with other matrix polymers or nanoclays has been studied for several years.^{3–9} 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 intermolecular interaction. Therefore, we modify doped

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polyaniline with compatible dispersing agent and prepared the master batch materials from the mixing of organic metallic salt with doped polyaniline to further melt-mix with matrix polymers and to find out the optimum processing conditions for obtaining a conducting polyblend with better conductivity and processability.

Ikaala and coworkers^{10,11} proposed a simple way to find out a suitable dispersing agent which can be a dopant for preparing a conductive polyaniline by mixing EB (emeraldine base form of polyaniline) with $\text{Zn}(\text{DBS})_2$ which is prepared from the neutralization of zinc oxide with *n*-dodecylbenzene sulfonic acid (HDBSA). After the mixing (complexation), the $\text{Zn}(\text{DBS})_2$ with long side chain was attached to EB which render the polyaniline both conductive and dispersible in polymer matrix. To improve the degree of doping for a better conductivity and compatibility between dispersing agent and polyaniline, we use HDBSA-doped polyaniline ($\text{PANI}(\text{DBSA})_{0.5}$) to replace EB and secondarily doped with organic zinc salts based on the HDBSA to become a conductive master batch (MB) which can be blended with conventional polymers instead of poorly fusible/poorly soluble $\text{PANI}(\text{DBSA})_{0.5}$. The MB is highly conductive since it was doped both by primary (HDBSA) and secondary ($\text{Zn}(\text{DBS})_2$) dopants and can be well-dispersed and deformed in a matrix polymer during processing (melt-mixing) in a preparation of a conducting polyblend. Because almost all matrix polymers are not miscible with the MB material in a molecular level, the best way to increase the conductivity of the conductive MB mixed blend will be to deform the MB particles into a thin film or a thin thread with high aspect ratio. Therefore, it will be better to create a high viscosity difference between MB and matrix polymer to induce a strong deformation to straighten the MB domain during processing, which is usually at high temperature and shear rate. However, it is possible the organic $\text{Zn}(\text{DBS})_2$ will be spin out the MB if either the temperature or shear rate is too high due to its already liquidized state at the processing temperature (the melting point for $\text{Zn}(\text{DBS})_2$ is only 130°C which is much lower than the processing temperatures of the conventional matrix polymers).

The following studies aim at finding out the best processing condition when the MB can be highly deformed without being spin out of the polyblend for preparing a conducting polyblend.

EXPERIMENTAL

Synthesis and sample preparation

Preparation of DBSA-doped polyaniline^{12–14}

Similar to regular polymerization method, 12 mL (0.127 mol) aniline (TOKYO KASEI KOGYO CO.), 21 g (0.637 mol) HDBSA (TOKYO KASEI KOGYO CO.),

behaving as both dopants and emulsifiers and 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 drop wise with an ammonium peroxodisulfate (APS: SHOWA CHEMICALS INSTRUMENT CO.) aqueous solution (17 g or 0.075 mol of APS in 30 mL distilled water). To avoid a rise of the reaction temperature during polymerization, the polymerization was initiated by a very slow drops of APS aqueous solution at 0–5°C, that lasted for at least 24 h. The obtained polyaniline was then poured into 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 h. The obtained polyaniline is named as $\text{PANI}(\text{DBSA})_{0.5}$ and the yield was estimated to be around 80%.

Preparation of organic zinc salt ($\text{Zn}(\text{DBS})_2$)

HDBSA was first dissolved in toluene in a three necked separable 1-L glass reactor and various weight ratios of zinc oxides were put into the solution with purging N_2 and mechanically stirred until the temperature was not elevated any more. The mixtures were maintained in molten state at around 150°C by dipping on a silicone oil bath heated on a heating plate with mechanical stirring until the white ZnO powders disappeared with the toluene solvent evaporated simultaneously. The secondary dopant $\text{Zn}(\text{DBS})_2$ was thus obtained by cooling the products which became a hard/rock-like cake at room temperature.

Preparation of master batch material and conducting polyblend

$\text{PANI}(\text{DBSA})_{0.5}$ was mixed with zinc salt (prepared from ZnO and HDBSA with 1/8 weight ratio, 1/2.1M ratio) in a PLASTOGRAPH[®] mixer (Brabender) with weight ratio of 1/3 (molar ratio 1/1), 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 PP and MB-13 mixed in the Brabendar set at various shear rates (rpm) and periods.

Characterization

The samples were first stapled into tablet with defined diameter and the thickness was measured by a micrometer screw gauge. The resistivity (ρ) in Ω cm was calculated from $\rho = RA/t$, where R represent resistance, A surface area, and t thickness. A milliohm meter of LUTRO MO-2001 was used to measure the R value in Ω . A HR-SEM of HITACHI S4200 with accelerating voltage of 15 kV was used to

take pictures on the Au-coated surface of the polyblend samples which have been cut into pieces with fresh (nonoxygen contaminated) surfaces in liquid N_2 and dried at $60^\circ C$ in a vacuum oven for at least 24 h. A RIGAKU D-2000 X-ray generator with Cu $K\alpha$ target ($\lambda = 1.5406E$) was used to obtain X-ray diffraction patterns at $2^\circ/\text{min}$. The scattering angle (2θ) ranged from 2° to 40° . About 8 mg of sample was subjected to a MDSC of TA-2920 and heated at $10^\circ C/\text{min}$ from 40 to $150^\circ C$, in purging N_2 . A Hitachi U-2000 was used to detect the absorbing wavelength ranged from 1100 to 650 nm.

RESULTS AND DISCUSSION

Secondary doping effect and thermal stability

The secondary doping effects of zinc salts were monitored by the red shift of the UV-vis spectra of the protonic acid-doped polyaniline after mixing with $Zn(DBS)_2$ that can complex further with the amine groups of the $PANI(DBSA)_{0.5}$ backbone that are not doped by protonic acid through the complexation with its lone electronic pairs of amine groups to induce the secondary doping and improve the conductivity by increasing the charges density and straightening the conformations to provide a shorter and quicker path for the charges to follow. Therefore, a huge red shift can be found from Figure 1 when the mole of zinc salts is equivalent to that of $PANI(DBSA)_{0.5}$ and the color of the emeraldine salt (ES: doped polyaniline) was changed significantly from dark green to shining green, which is an indication for the improved conductivity. The red-shift of the UV-vis spectra comes from the increase of the conjugation chain length of polyaniline backbones

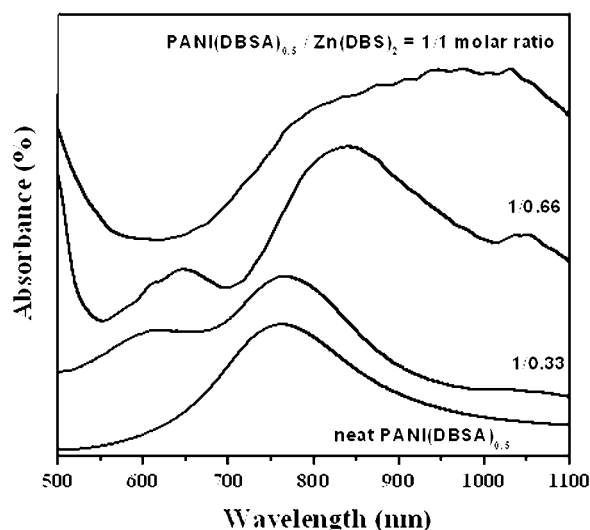
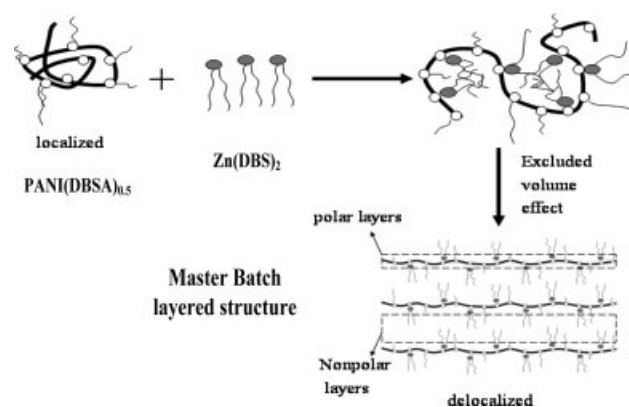


Figure 1 UV-vis spectra of neat $PANI(DBSA)_{0.5}$ and master match materials prepared with different $PANI(DBSA)_{0.5}$ and $Zn(DBS)_2$ molar ratios.



Scheme 1 Formation of layered structure of polyaniline.

resulted from a more straightened conformation with the help of the secondary dopants, $Zn(DBS)_2$, as shown in Scheme 1. The presence of the $Zn(DBS)_2$ can lead to a layer-like structure¹⁵ due to the excluded volume effect of the bulky twin dodecylbenzene sulfonic groups of $Zn(DBS)_2$, which then coordinated with the lone paired electrons of the amino groups of ES. Therefore, these long alkyl groups either from primary dopants (HDBSA) or secondary dopants ($Zn(DBS)_2$) can go on lining up with each other and interdigitating to form a layered structure depicted in Scheme 1 and will also induce a huge diffraction peak at low angle on its X-ray diffraction pattern.

The TGA thermograms illustrated the $Zn(DBS)_2$ can protect $PANI(DBSA)_{0.5}$ from initiating earlier thermal debonding (dedoped) of the primary acid dopants from the backbones of polyaniline, which can also significantly decrease the conductivity. Originally, the $PANI(DBSA)_{0.5}$ can go on degradation at about $180^\circ C$ that is the processing temperature for the preparation of the PP conducting polyblends according to Figure 2. And the thermal deg-

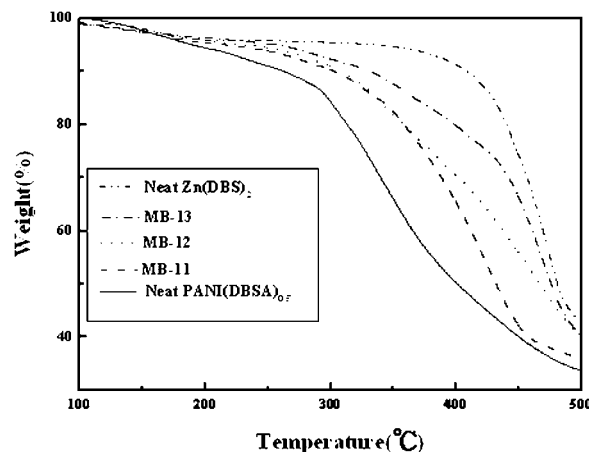


Figure 2 TGA thermograms of neat $PANI(DBSA)_{0.5}$ and master match materials prepared with different $PANI(DBSA)_{0.5}$ and $Zn(DBS)_2$ ratios.

TABLE I
Properties of Conducting Polyblends at Various Shear Rates

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

radation accompanied with loss of conductivity can be delayed to 250°C over if there is enough (equal mole of) zinc salt firmly doped (secondary doping) on PANI(DBSA)_{0.5} as seen from Figure 2. The presence of zinc salts not only improves the conjugation chain length and conductivity but also increases the thermal stability of polyaniline and allows it to be processed at high temperatures with matrix polymers to obtain a conducting polyblend.

MB-13 in a PP-based conducting polyblend

A master batch (MB-13) prepared from mixing one portion of HDBSA-doped polyaniline (PANI (DBSA)_{0.5}) and three portions of Zn(DBS)₂ in weight was used to melt-mix with polypropylene (PP) in a Brabendar mixer with torque, processing time recorded at the setting temperature and shear rate. At the processing (fusible) temperature of 180°C of PP matrix, various shear rates and time were adopted to prepare a conductive PP composite possessing applicable conductivity with the least amount of MB-13 to keep the pristine properties, such as mechanical properties, of PP. 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 10⁴ $\Omega\text{ cm}$ with more than 28.6 wt % of MB-13 (40 phr MB-13 and 100 phr PP) present in processing. However, the mechanical property of the matrix PP had found to be destroyed and the polyblends became oily, softer materials compared with neat PP. Moreover, when the MB-13 is below 13.8% (16 phr), the volume resistivities became so high (>10⁹ $\Omega\text{ cm}$) that is out of the applicable range. Taking both conductivity and mechanical properties into considerations, a percentage of 21.9 wt % (28 phr) MB-13, which includes about 5.5 wt % conductive PANI(DBSA)_{0.5} is optimal to obtain a useful conducting polyblend.

The effects of shear rate on conducting polyblends

The supposed spherical droplet-like MB-13 will be deformed into an elliptic line resulting from the dif-

ferent degree of shear-thinning effects of the deformable fillers (MB-13) and matrix polymers. The optimal shear rate depends on the polyblend's conductivity which is related to both the presence of secondary dopants or not and the degree of elongation (aspect ratio) of the conductive MB-13, prepared from mixing of zinc salts with doped polyaniline, in the PP matrix. The length of the deformed MB-13 inside the polyblends obtained from the SEM pictures depends on the relative viscosity of MB-13 and PP matrix at each temperature and shear rate. The deformation can proceed when there is an imbalance between the interfacial viscous force and interfacial tension, both of which strongly depending on the processing shear rates.

The relative viscosity (η_r), defined as the ratio of the equivalent/plateau torques (obtained from Brabendar) of neat MB-13 and neat PP at 180°C at various shear rates 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, determining the final conductivity and mechanical properties of a PP based conductive polyblend. Table I and Figure 3 demonstrate a decreasing deformed length with losing secondary dopants Zn(DBS)₂ at high shear rates from the DSC thermograms and X-ray diffraction patterns which will be discussed later. The increasing shear rates and increasing viscosity differences (decreasing η_r) below 80 rpm result in enhanced conductivities of the polyblends and deformations of MB-13, as shown in Table I and Figure 3.

Taylor's eq. (1) shows the deformed length of the filler depends on the ratio of the interfacial tension (σ) between filler and matrix and the shearing force of the matrix polymer ($\eta_m G$) during processing plus the effect of the relative viscosity of filler and matrix polymer.¹⁶

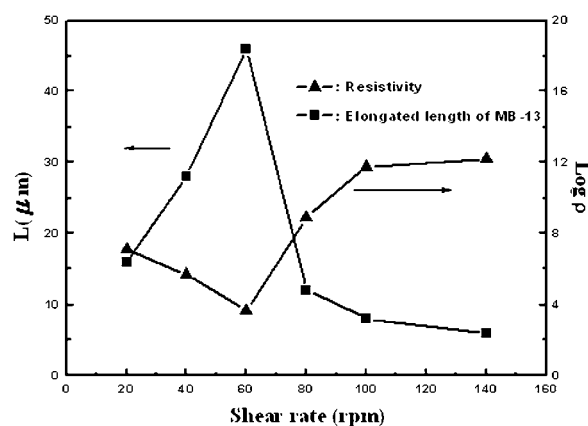


Figure 3 Resistivity ($\Omega\text{ cm}$) of PP polyblends and deformed length (μm) of MB-13 versus shear rate.

$$L = \frac{\sigma}{\eta_m G} f(\eta_r) \quad (1)$$

where L is the deformed particle size, σ is the interfacial tension, η_m is matrix polymer viscosity, G is the shear rate, and $f(\eta_r)$ is the function of viscosity ratio of filler and matrix.

Wu¹⁷ expressed the factor of relative viscosity, $f(\eta_r)$, in power series:

$f(\eta_r) = k(\eta_r)^n$; and $\eta_m G = \tau_{pp}$ in equilibrium, where τ_{pp} is the equilibrium torque of neat PP. Hence,

$$\tau_{pp} L = k\sigma(\eta_r)^n \quad (2)$$

Take logarithm, we have

$$\ln(\tau_{pp} L) = \ln(k\sigma) + n \ln(\eta_r) \quad (3)$$

The equilibrium torques of neat MB-13 and PP processed at 180°C at various shear rates were demonstrated in Table I.

From Table I, we can plot $\ln(\tau_{pp} L)$ versus $\ln \eta_r$ which should be a straight line shown in Figure 4 if there is no leakage of $\text{Zn}(\text{DBSA})_2$ from MB-13. Clearly, the equation was obeyed when $\ln \eta_r$ is between -1.27 and -0.84 with shear rate ranged from 20 to 60 rpm, indicating MB-13 was distorted within PP matrix without losing $\text{Zn}(\text{DBS})_2$. And the negative slope represents the shear-thinning effect found in regular power-law polymer during processing. However, the deviation from the equation started when shear rate (80–140 rpm) is over 80 rpm with the $\text{Zn}(\text{DBS})_2$ starting to be spin out of MB-13 due to the higher shearing rates and higher viscosity difference that can construct a squeezing force for the release of $\text{Zn}(\text{DBS})_2$ from MB-13. The loss of lubricant-like $\text{Zn}(\text{DBS})_2$ out of MB-13 at high shear

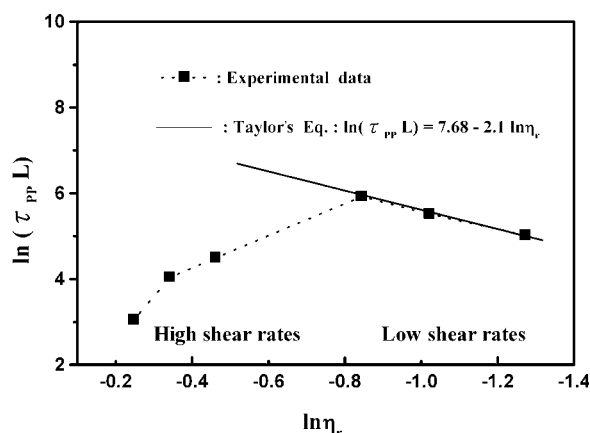


Figure 4 Rheological curve shows the migration of $\text{Zn}(\text{DBS})_2$ from MB-13 by the deviation of experimental data from Taylor's equation at high shear rates.

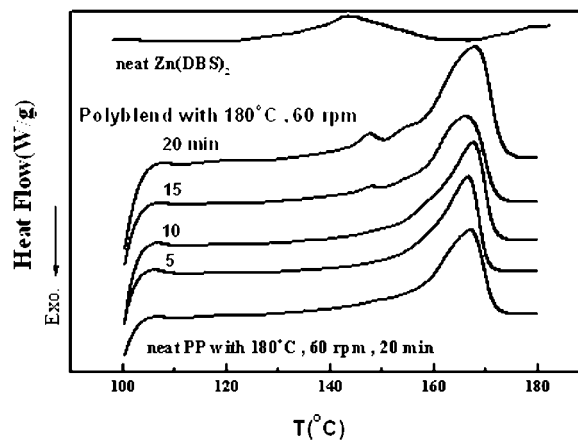


Figure 5 DSC thermograms of neat PP, $\text{Zn}(\text{DBS})_2$ and their polyblends with thermal history at 180°C, 60 rpm at various shear time.

rates could harden (increased viscosity) MB-13 and hindered the deformation. Therefore, the optimal shear rate is found to be at 60 rpm when the conductive fillers MB-13 can be highly extended to obtain a higher conductivity of the polyblend with the high aspect ratio.

The shearing time effect on conducting polyblends

To confirm the leakage of $\text{Zn}(\text{DBS})_2$ from MB-13 during preparation of conducting polyblends, the DSC thermograms of prepared polyblends were compared with that of neat PP and neat $\text{Zn}(\text{DBS})_2$ in Figure 5. The samples prepared at high shearing time (15 and 20 min) show an additional exothermic peak around 150°C, which is close to the melting point of the neat $\text{Zn}(\text{DBS})_2$. And the melting peaks belonging to the PP matrix became less sharpened due to the interference of the separated zinc salts that can be served as an effective plasticizing agent with its twin dodecylbenzene sulfate groups. The loss of $\text{Zn}(\text{DBS})_2$ represented also the disappearance of secondary doping and the decreased conductivity for the conducting polyblends. Therefore, the shearing time at the shear rate of 60 rpm should be kept below 15 min to avoid any leakage of the $\text{Zn}(\text{DBS})_2$, whose presence in MB-13 can soften conductive PANI $(\text{DBSA})_{0.5}$ counterpart and increase the aspect ratio of MB-13 to maintain the high conductivity and processability. Samples with shearing time of 5 and 10 min at 180°C, 60 rpm demonstrated similar DSC thermograms with that of neat PP, indicating the secondary dopants, $\text{Zn}(\text{DBS})_2$, are staying inside the MB-13 and doped firmly with the polyaniline backbones to induce a layered structure that will be shown in X-ray diffraction patterns.

The SEM pictures from Figure 6(a–c) with increasing processing time, revealed the gradual growing

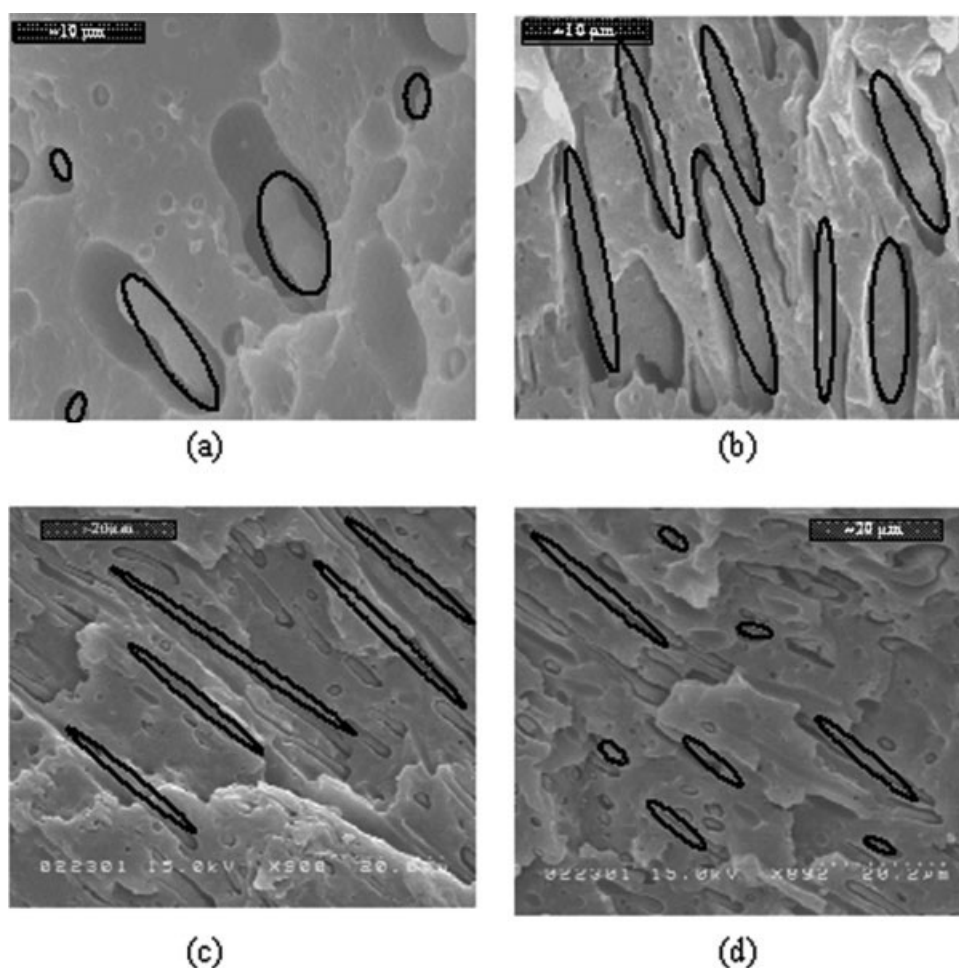


Figure 6 SEM pictures of conducting PP with 21.9% of MB-13 processed at 180°C, 60 rpm with (a) 5 min, (b) 10 min, (c) 15 min, and (d) 20 min.

aspect ratio of the MB-13 that was elongated inside the PP matrix during processing in a Brabender. The length of the filler-like MB-13 reached its maximum when the processing time arrived at 15 min, followed by the retraction (reducing aspect ratio) due to the loss of the lubricating zinc salts which is believed to be squeezed out of MB-13, resulting from the built-up stress from the higher contrast of the viscosities of PP matrix and MB-13 after 15-min procession. In the beginning of shearing, the interfacial tension between MB-13 and PP matrix was not in balance with the shearing force yet, allowing only slight deformation of the fillers. With the gradual shear-thinning effects for both MB-13 and PP matrix, the viscosity difference (represented by torques shown in Table I) enlarged and the fillers were under stronger extending or squeezing force that can induce the spinning off of zinc salt.

The introduction of the zinc salts with twin long alkyl chains into PANI(DBSA)_{0.5} can interfere with the alkyl side chains of it due to the excluded volume effect and pushed the polyaniline backbones

farther away from each other, which allowed the construction of the so-called layered structures after removing the counter ions effect^{1,12-14,18,19} which caused a coiler conformations and less degree of conjugation of the polyaniline backbones as seen in Scheme 1. The *d*-spacings of the layered structures for the samples with various shearing time can be calculated from the X-ray diffraction patterns in Figure 7 which demonstrated significant diffraction peaks of (200) plane (2θ lower than 8°) contributed from the fillers (MB-13). The neat MB-13 owned a not well-defined layered structure with shorter layered distance (*d*-spacing) compared with the polyblends processed with various periods of time, showing a rough diffraction peak at $2\theta = 3.2^\circ$. The shearing forces gradually induced a well-defined layered structure with sharper diffraction peaks which moved to lower angles with processing time, indicating the swelling of the layers with the more extended twin dodecylbenzene side chains of the zinc salts. However, the layers started to shrink and the diffraction peak of the X-ray spectrum shifted

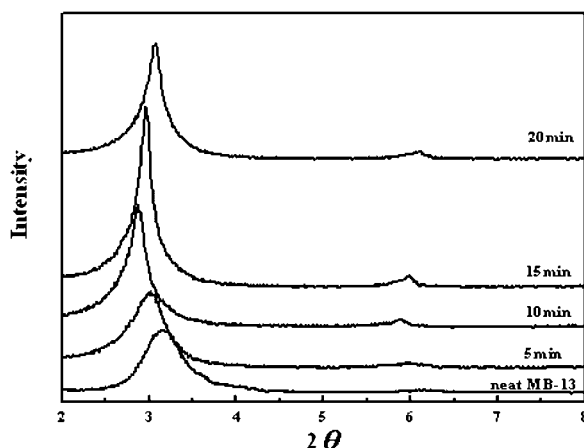


Figure 7 X-ray diffraction patterns at low angles of neat MB-13 and polyblends with 21.9% of MB-13 processed at 180°C, 60 rpm with various shearing time.

backward to the higher angle when some of the zinc salts were spinning off out of the fillers after 15 min procession as seen in Figure 7.

The projected C—C length on the main axis of alkyl group is about 1.27 Å and the estimated *d*-spacing with no interdigitization and fully extended zinc salts of neat MB-13 should be $12 \times 2 \times 1.27 \text{ \AA} = 30.5 \text{ \AA}$. However, the *d*-spacing obtained from its diffraction peak is just 27 Å, which might come from the interdigitized C—C bonds of zinc salts or the tilting of chains.

CONCLUSIONS

The red-shift of the UV-vis spectra of doped polyaniline came from the increase of the conjugation chain length with the help of the Zn (DBS)₂. The thermal degradation accompanied with loss of conductivity can be delayed to 250°C over if there is enough (three times weight) zinc salt doped with PANI(DBSA)_{0.5}. A percentage of 21.9 wt % (28 phr) MB-13 is found to be optimal to obtain a useful conducting polyblend. The increasing shear rates and decreasing viscosity ratio (decreasing η_r) between MB-13, which is more shear-thinning, and PP matrix

below 80 rpm result in enhanced conductivities of the polyblends due to the more deformed MB-13. The deviation from the Taylor equation started when shear rate (80–140 rpm) is over 80 rpm with the Zn(DBS)₂ starting to be spin out of MB-13, which also decreased the conductivity of the polyblends. The leakage of Zn(DBS)₂ from MB-13 during preparation of conducting polyblends can be confirmed by the comparing the DSC thermograms and X-ray diffraction patterns with that of neat PP. The SEM pictures revealed the gradual growing aspect ratio of the MB-13 with processing time until 15 min. The shearing forces induced a well-defined and swollen layered structure with processing time until 15 min. The layers started to shrink and the after 15 min of procession.

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