Thermoplastic elastomer vulcanisates (TPVs) are general blends of rubber and thermoplastic\textsuperscript{1–3}. These TPVs present properties that are as good as or maybe better than those of elastomeric block copolymers. TPVs are usually multi-phase polymer systems consisting of hard and soft domains which can either be copolymers or mechanical blends. In these TPVs, the role of rubber is to improve the impact strength and ductility of the plastic\textsuperscript{1,4–5}. The stiffness of the rubber is also increased with the incorporation of plastic into the rubber matrix.

TPVs can be produced by dynamic vulcanisation, which consists of vulcanising rubber during melt mixing with molten plastic. These materials show conventional elastomeric behaviour at low temperatures and the processability of thermoplastics at high temperatures. Since they do not need to be vulcanised during fabrication into end-use parts, they offer a substantial economic advantage. Besides this, these materials can also be readily reground and recycled\textsuperscript{1,6–7}.

Electrically conductive thermoplastic elastomer vulcanisates (TPVs) based on poly(butadiene-co-acrylonitrile) (NBR), polypropylene (PP) and dodecylbenzenesulphonic acid doped polyaniline (PAni.DBSA) were produced by using an internal mixer. A very low electrical percolation threshold (about 1.5 wt %/0.85 volume % of PAni.DBSA) was successfully achieved for TPVs prepared via this technique. All these TPVs showed useful physical properties and also a reasonable good electromagnetic interferences shielding effectiveness (EMI SE). These TPVs could be reprocessed up to four cycles without significant loss of their EMI SE, electrical and physical properties. As a result, this kind of TPV material has a very good potential of industrial application.

**Keywords:** Thermoplastic elastomer; nitrile rubber; polyaniline; electrical conductivity; electromagnetic interference.

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and it provides a high yield\textsuperscript{28}. When PANi base is doped with sulphonic acids, it becomes highly electrically conductive, reaching $\sim 16$ S/cm\textsuperscript{29}. According to Poussin \textit{et al.}\textsuperscript{29} dodecylbenzenesulphonic acid doped PANi [PAni.DBSA] is stable to at least 260$^\circ$C. Hence the PAni.DBSA may be an ideal thermally stable partner for the production of different practical blends.

Reports about the usage of TPVs for the preparation of conductive materials are very limited to the best of our knowledge. De Souza Jr. \textit{et al.}\textsuperscript{2} taught about the preparation of a TPV material which was based on ethylene–vinyl acetate copolymer (EVA) and poly(butadiene-co-acrylonitrile) (NBR), with PAni.DBSA. However, the TPV prepared was only semi-electrically conductive with a volume electrical resistivity $\geq 10^8$ ohm-cm and targeted for the application as pressure sensitive devices.

This work aimed to study the electrically conductive TPVs prepared by mixing of NBR and polypropylene (PP) with different proportions of PAni.DBSA in the presence of maleic anhydride and hydroquinone as compatibilisers. These new class of TPVs were prepared via the thermal-mechanical mixing technique, \textit{i.e.} by using an internal mixing device at controlled mixing conditions. Special interest has been focused on TPV based on NBR and PP due to its excellent resistances in term of chemical, oil and heat ageing. Meanwhile, PAni.DBSA was selected due to its low toxicity, good thermal stability, high electrical conductivities, good compatibility with NBR/PP and well-established synthesis method\textsuperscript{8,10–11,14–16,18}.

In this work, electrical conductivities of these NBR-PP-PAni.DBSA based TPVs were determined. Basic physical properties (tensile strength, elongation at break and hardness) and morphological analysis using field emission scanning electron microscopy (FESEM) were performed in order to study the compatibility level of these three major constituent polymers. The main interest here is to produce a reusable material for the electromagnetic interferences (EMI) shielding application. Therefore, a simple flanged coaxial EMI shielding effectiveness test was performed for all these TPVs. The recyclability of these TPVs in term of their EMI shielding effectiveness, electrical and physical properties was also assessed.

**EXPERIMENTAL**

**Chemicals and Raw Materials**

Aniline monomer (99 wt %, Sigma-Aldrich), ammonium persulphate (APS) (98 wt %, Sigma-Aldrich), 36.5-38 wt % acid hydrochloric (HCl) solution (GPR), ferric chloride solution (FeCl$_3$) (purum, 45% FeCl$_3$ basis, Sigma-Aldrich), 33 wt % ammonia solution (GPR, Sigma-Aldrich) and 70 wt % dodecylbenzene sulphonatic acid (DBSA) solution in 2-propanol (GPR, Sigma-Aldrich) were used. Commercial grade NBR [Krynac\textsuperscript{®} 3345F, manufactured by Bayer Germany, ML 1+4 at 100$^\circ$C = 45 ± 5] was chosen. Commercial grade PP (MFI = 3.5 g/10 min at 230$^\circ$C) was supplied by Plastrade Enterprise Sdn Bhd Maleic anhydride modified polypropylene (PP-g-MA) (MFI = 51.9 g/10 min at 230$^\circ$C) sample was also supplied by Plastrade Enterprise Sdn Bhd The maleic anhydride content of PP-g-MA was 2.4 mmol%. Other chemicals employed as vulcanisation components, \textit{i.e.} reactive phenolic resin (SP-1045), stannous chloride (SnCl$_2$) and triethylene-tetramine (TETA) were of the laboratory reagent grade and purchased from the local industries. Hydroquinone (benzene 1, 4-diyl) was used as received (ReagentPlus\textsuperscript{®}, $\geq 99$ wt %, Sigma-Aldrich).
**Synthesis of PAni.DBSA**

Conductive emeraldine salt PAni.HCl was synthesised by the oxidative chemical polymerisation technique based on an oxidant (APS)/monomer (aniline) initial mole ratio of 1.0. Fifty millilitre of aniline and 125.2 g of APS were dissolved in 375 mL and 276 mL of 2 M HCl respectively, which had been pre-cooled to 1ºC. The aniline solution was placed in an ice bath with an overhead stirrer. After the addition of FeCl$_3$ solution (about 1 mL) as a catalyst, the APS solution was added gradually over a period of 20 min, with constant stirring to ensure thorough mixing. The temperature of the polymerisation mixture was maintained to be ≤2ºC while the pH was adjusted to be ≤1.0 by the addition of concentrated HCl. The mixture was left for 6 h to complete the polymerisation, and the precipitate was allowed to settle before decanting and final washing with distilled water until the filtrate was colourless. PAni emeraldine base (EB) was prepared by deprotonating the wet PAni. HCl in 33% aqueous ammonia solution (about 5000 mL) with 24 h stirring, followed by washing and re-protonation in 1M aqueous DBSA at a molar ratio EB:DBSA of 1.0:2.0. Filtration was performed with a sintered-glass funnel of grade 3 porosity (16-40 microns). All products were washed with large quantities of distilled water until the filtrates were colourless and no odour of ammonia could be detected. Final drying of the powdered filter cake was done in a vacuum oven at 50ºC for 24 hours. This batch of synthesised PAni.DBSA was estimated to have a 50% protonation level on the basis of the S:N atomic ratio.

**Preparation of TPV Blend**

The 50.0:50.0 wt % of NBR-PP TPVs were prepared by using the Haake Rheomix 600 Internal Mixer. A fill factor of 0.80 was used for all mixings. The starting temperature for each mixing was 130ºC, rotor speed was 100 rpm and the total duration was 8 minutes. A mixture of phenolic resin and SnCl$_2$ in a proportion of 10.0:0.5 pphr was used as the vulcanisation system. For the purpose of compatibilising the NBR and PP, the amounts of added PP-g-MA and TETA were 5.0 and 0.2 pphr respectively. Stages of the mixing of this NBR-PP based TPV are summarised in Table 1.

The TPV-PAni.DBSA mixtures were also prepared by using the same internal mixer with the same mixing conditions. The proportions of added PAni.DBSA were 1.0, 2.5, 5.0, 7.5, 10.0, 20.0, 30.0, 40.0 and 50.0 total wt % respectively. The hydroquinone of 1.0 total wt % was also added to each TPV-PAni.DBSA blend as the compatibiliser. The total mixing duration of each TPV-PAni. DBSA blend was

<table>
<thead>
<tr>
<th>Stage of mixing</th>
<th>Timing</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Addition of PP and PP-g-MA</td>
<td>0$^{th}$ minute</td>
</tr>
<tr>
<td>2. Addition of TETA</td>
<td>1$^{st}$ minute</td>
</tr>
<tr>
<td>3. Addition of NBR</td>
<td>3$^{rd}$ minute</td>
</tr>
<tr>
<td>4. Addition of phenolic resin and SnCl$_2$</td>
<td>4$^{th}$ minute</td>
</tr>
<tr>
<td>5. Dumping</td>
<td>8$^{th}$ minute</td>
</tr>
<tr>
<td></td>
<td>(Total time = 8 mins)</td>
</tr>
</tbody>
</table>
4.0 minutes. The resulted TPV-PAni.DBSA blends were injection moulded (Toshiba 1580EPN-2A) under pressure of 0.96 KPa at 170°C.

**Measurement of Basic Physical Properties**

Appropriate amounts of each NBR-PP-PAni.DBSA TPV were injection moulded into samples with dimensions 130.0 mm × 100.0 mm × 2.0 mm thickness, respectively. Test pieces for the basic tensile properties, i.e. tensile strength and elongation percentage at break (BS ISO 3730) were cut out from these moulded sheets. Test pieces in disc shape (with thickness 6.3 mm and diameter 13.0 mm) that were needed for hardness measurement (BS 903-A2631) were prepared via injection moulding. Test pieces were also prepared from the NBR-PP TPV (without addition of PAni. DBSA) for the control purpose.

**Determination of Electrical Conductivities**

The DC electrical conductivities for each NBR-PP TPV (without and with PAni.DBSA loadings) were calculated from electrical resistances measured by guarded 2-probe technique. The equipment employed was a Keithley 6517A Electrometer (with built-in voltage source up to 1kV). A pressed pellet of pure PAni.DBSA (diameter 13.0 mm, thickness 1.5 mm) was placed in a holder with two spring-loaded metallic contacts in order to measure its electrical resistance. Test pieces of NBR-PP and NBR-PP-PAni.DBSA TPV were again cut respectively from the moulded sheets as used for the basic tensile properties measurement. Each of these test pieces was in the dimension of 25.0 mm × 25.0 mm × 2.0 mm thickness.

Electrical conductivities were calculated from the mean resistance values (based on a set of five samples) obtained by the 2-probe method using Equation 1:

\[
\sigma = \left( \frac{I}{R} \right) \left( \frac{L}{A} \right)
\]

where \(\sigma\) is the electrical conductivity, \(R\) is the mean value of apparent resistance (voltage/current) for the moulded sample, \(L\) is the measured electrode spacing distance and \(A\) is the cross-sectional area of moulded sample between the current-carrying electrodes.

**Morphological Study (FESEM)**

Morphological behaviour of all NBR-PP-PAni.DBSA TPVs were studied respectively by using a FESEM (JOEL JSM-6701F) at 10 keV with magnification 500 times. The micrographs were taken from the cryo-fractured surface that was treated with osmium tetroxide (OsO₄) in order to selectively stain the NBR phase.

**Determination of Electromagnetic Interferences Shielding Effectiveness [EMI SE]**

Electromagnetic interference (EMI) can become a problem when emitted electromagnetic fields interfere with the operation of other electronic equipment. Electromagnetic fields are radiated from sources such as television, cellular telephone, radio communication, computer, radar, and other devices32. EMI could also take place due to distant sources such as radio transmitters, antennas, and lightning, which make incident electromagnetic fields similar to plane waves33.

The EMI SE of all NBR-PP and NBR-PP-PAni.DBSA TPV samples was determined by using a Field Fox 10GHz RF Vector Network Analyser. The purpose of any EMI SE test is to determine the insertion loss
(IL) due to introducing a material between the source and signal analyser. The EMI SE is determined by measuring the electric field strength levels with both reference \((E_R)\) and load \((E_L)\) samples:

\[
SE = 20 \log_{10} \left( \frac{E_R}{E_L} \right) = (dB_R) - (dB_L) \quad \ldots 2
\]

\(dB_R\) and \(dB_L\) are the transmission readings from the attenuators for reference sample and load sample respectively. Figure 1 shows the setup for the EMI SE testing system and meanwhile, Figure 2 shows the dimensions of the EMI SE test samples.

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**Study of Reprocessability of NBR-PP-PAni. DBSA TPV**

Reprocessability in terms of basic tensile properties, electrical conductivities and EMI shielding effectiveness of all NBR-PP-PAni. DBSA TPV samples was studied. Each NBR-PP-PAni. DBSA TPV sample was stripped and reground by using a granulator (Plascare PH-500SS). Granulates of these recycled samples were remoulded by using the same injection moulding machine with the same conditions as for the virgin samples. All these processes were repeated up to four times for each sample.
RESULTS AND DISCUSSION

Basic Physical Properties

Results of the degree value of hardness [IRHD] measurement are summarised in Figure 3. The IRHD of NBR-PP-PAni.DBSA TPV increased with increasing proportion of added PAni.DBSA. This was due to the glassy nature of PAni.DBSA and the increased stiffness of blend as the content of conductive polymer increased. The higher the IRHD value, the stiffer the produced TPV material. De Souza Jr. et al.\(^2\) reported that the hardness values of EVA-NBR-PAni.DBSA blends decreased with the loading of PAni.DBSA. This was due to the incompatibility between PAni.DBSA with EVA and hence, majority of the PAni.DBSA was preferably contained in the EVA phase, causing the plasticisation of EVA. The rather low overall hardness of this TPV system would suggest that the NBR is only lightly crosslinked, but this would still be sufficient to preclude PAni.DBSA entering the NBR through this kind of thermal mechanical mixing. It is also highly unlikely that PAni.DBSA is miscible with NBR. On the other hand, the PAni.DBSA could blend well particularly with the PP phase during mixing due to their high compatibility level.

Results of the tensile strength and elongation percentage at break (EB %) are shown in Figures 4 and 5 respectively. All these tensile properties enhanced with the content of PAni.DBSA up to 30.0 wt %. The increase in tensile strength is to be expected in a TPV system when there is an increase in the thermoplastic content through addition of further thermoplastic polymer, with the addition of PAni.DBSA. These tensile properties were decreased for blends with \( \geq 40.0 \) wt % of PAni.DBSA content, due to the more intense level of rupture of the thermoplastic component; which in this TPV system is the composite of PP-PAni.DBSA with the PP as a continuous phase and the PAni.DBSA as a disperse phase (Figure 7).
Figure 3. Hardness (IRHD, Error ± 1°) of the NBR-PP-PAni.DBSA TPV prepared using internal mixer.

Figure 4. Tensile strength (Error ± 0.5 MPa) of the NBR-PP-PAni.DBSA TPV prepared using internal mixer.
Electrical Conductivities

The calculated mean electrical conductivity values for NBR-PP TPV (without and with PAni.DBSA loadings) are shown in Figure 6. The raw NBR-PP TPV (without addition of PAni.DBSA) is an electrical insulator, with conductivity in the region of $10^{-12}$ S/cm. The in-house synthesised PAni.DBSA showed a very good electrical conductivity of $5.6 \pm 0.5$ S/cm.

The electrical conductivities of all blends generally increased with the loading of PAni.DBSA$^8$-19. NBR-PP-PAni.DBSA TPVs prepared with added compatibiliser showed very high electrical conductivities, up to about 1.4 S/cm. It is also suggested that the more compatible constituent polymers favour the formation of higher level of microscopic conductive pathways (Figure 7)$^8$-19.

The conductivity percolation threshold for NBR-PP-PAni.DBSA TPVs was estimated by fitting the data from Figure 6 to a simple percolation model as defined by Equation 3$^{34}$.

$$\sigma_f = C(f - f_p)^t$$

where $c$ is a constant, $t$ is the critical exponent, $f$ is the volume fraction of the conductive medium and $f_p$ is the volume fraction at the percolation threshold. All the weight fractions referred to above were converted into volume fractions for this analysis. By fitting the data to a plot of log electrical conductivity ($\sigma$) versus log ($f - f_p$), it was possible to estimate the values of $t$ and correlation coefficient ($R$) for each set of data. The estimated electrical conductivity percolation threshold for the NBR-PP-PAni.DBSA TPVs is about 1.5 wt %/0.85 volume % of PAni.DBSA (with $t = 3.8$ and $R = 0.99$). A very low electrical conductivity percolation threshold can evidently be achieved for this kind of TPV system; which attributed to the high compatibility level between two particular constituent polymers, i.e. PP and PAni. DBSA. It is strongly believed that a very high concentration of PAni.DBSA was sufficiently dispersed within the continuous PP phase in this TPV system. These results are much better than those regular blends of NBR and PAni. DBSA which show percolation thresholds at around 5.0-6.0 wt % of PAni.DBSA$^8,10$-11,15-19.

Morphological Study

All NBR-PP-PAni.DBSA TPV samples were studied by using FESEM, but only examples of micrograph with 1.0, 10.0 and 30.0 wt % PAni.DBSA loadings are shown in Figure 7. The lighter coloured regions corresponded to the NBR phases which were selectively stained by OsO$_4$. Meanwhile, the darker regions corresponded to the continuous PP phases. Those dispersed PAni.DBSA particles were seen in fine and elongated forms as observed in previous works$^{16-17}$. In Figures 7b and 7c (above the electrical conductivity percolation threshold), the PAni. DBSA particles started to cluster or to form conductive pathways, consistent with the enhanced conductivities of both TPVs.

Electromagnetic Interferences Shielding Effectiveness

Measuring reliable EMI SE data at a broad frequency range for newly developed materials is crucial to determine their properties and potential applications. As a result, the frequency range used for this experiment was 0-10 GHz. EMI SE for all NBR-PP TPVs (without or with addition of PAni.DBSA) was determined in this work and their results are summarised in Table 2.

The EMI SE of a sample has strong dependence on both its thickness and electrical conductivity$^{32}$. However, the thickness of
Figure 5. EB % (Error ± 5 %) of the NBR-PP-PAni.DBSA TPV prepared using internal mixer.

Figure 6. Electrical conductivities for NBR-PP TPV as a function of PAni.DBSA loading (wt %).
all NBR-PP TPV samples tested in this part of work were fixed at 2.0 mm and hence, it was expected those samples with higher electrical conductivities to have a better EMI SE. The raw NBR-PP TPV and NBR-PP TPV with only 1.0 wt % of PAni.DBSA (below percolation threshold) are almost transparent to the electromagnetic interference. The EMI SE of all NBR-PP TPVs was enhanced with the PAni.DBSA loading which was attributed to the increment of electrical conductivities. A reasonable good EMI SE, i.e. 24-32 dB was recorded for NBR-PP TPV with ≥30.0 wt % of PAni.DBSA. These TPVs indicated a performance similar to the aluminium foil, which has EMI SE about 40 dB\(^2\). An example of raw EMI SE results of NBR-PP-PAni. DBSA TPV is presented in Figure 8.

**Reprocessability of NBR-PP-PAni.DBSA TPV**

One of the most interesting aspects related to the use of TPVs is the capability to recycle these materials. TPVs can be reprocessed and...

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**TABLE 2. ELECTROMAGNETIC INTERFERENCES SHIELDING EFFECTIVENESS (EMI SE) FOR NBR-PP-PANI.DBSA TPV**

<table>
<thead>
<tr>
<th>TPV</th>
<th>EMI SE (dB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBR-PP</td>
<td>0</td>
</tr>
<tr>
<td>NBR-PP-PAni.DBSA (*wt % PAni.DBSA)</td>
<td></td>
</tr>
<tr>
<td>*1.0</td>
<td>0</td>
</tr>
<tr>
<td>*2.5</td>
<td>3</td>
</tr>
<tr>
<td>*5.0</td>
<td>8</td>
</tr>
<tr>
<td>*10.0</td>
<td>12</td>
</tr>
<tr>
<td>*20.0</td>
<td>18</td>
</tr>
<tr>
<td>*30.0</td>
<td>24</td>
</tr>
<tr>
<td>*40.0</td>
<td>26</td>
</tr>
<tr>
<td>*50.0</td>
<td>32</td>
</tr>
</tbody>
</table>

---

*Figure 7. Scanning electron micrographs of NBR-PP-PAni.DBSA TPV. (a) TPV with 1.0 wt % PAni.DBSA (b) TPV with 10.0 wt % PAni.DBSA (c) TPV with 30.0 wt % PAni.DBSA.*
moulded many times, without any significant loss of their physical properties. All NBR-PP-PAni.DBSA TPVs were reprocessed and examples of the obtained results for NBR-PP TPVs with 30.0 wt % and 50.0 wt % of PAni.DBSA loading are summarised in Table 3.

All NBR-PP-PAni.DBSA TPVs could be reprocessed without major difficulty. As observed, the reprocessing does not seem to affect the electrical properties and EMI SE of all these TPVs. Their electrical conductivities and EMI SE values remained almost constant throughout the four cycles of reprocessing. It is strongly believed that this phenomenon was attributed to the strong and stable conductivity networks as built up by the elongated PAni. DBSA particles. However, their physical properties were slightly impaired (up to about 10 % at the 4th cycle of reprocessing), regardless of their PAni.DBSA contents, as can be seen from the declines of tensile strength, EB % and hardness with increasing recycling. The thermal degradation of the embedded elastomer phase (i.e. NBR) taking place during the recycling process is thought to be the major factor for such detrimental effect.

CONCLUSION

Electrically conductive (up to 1.4 S/cm) TPVs based on NBR, PP and PAni.DBSA were successfully produced by using an internal mixer. A reasonably high level of compatibility between the NBR, PP and PAni. DBSA was achieved via the introduction of compatibilisers, i.e. maleic anhydride and hydroquinone. The thermal mechanical mixing also keeps the PAni.DBSA particles well dispersed particularly in those continuous PP phases. Subsequently, a very low electrical percolation threshold (about 1.5 wt %/0.85
volume % of PAni.DBSA) was successfully achieved.

This kind of TPV material showed its optimum mechanical properties at about 30.0 wt % of PAni.DBSA loading and their flexibility can be easily adjusted via the regulation of PAni.DBSA content. A reasonable good EMI SE, i.e. 24-32 dB was also recorded for NBR-PP TPVs with ≥30.0 wt % of PAni.DBSA. For instance, it was also observed that these TPVs could be reprocessed up to four cycles without significant loss of their EMI SE, electrical and mechanical properties. This result is very exciting from a technological point of view, because it allows for reusing of the material several times.

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