

ONE-STEP PROCESS TO MAKE ELECTRICALLY CONDUCTIVE THERMOPLASTIC VULCANIZATES FILLED WITH MWCNTs*

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Abstract Electrically conductive thermoplastic vulcanizates (TPVs) filled by multi-walled carbon nanotubes (MWCNTs) are prepared by a simple one-step melt mixing process, based on linear low density polyethylene (LLDPE) and ultrafine full-vulcanized rubber particles (UFRP). An ideal morphology with controlled localization of MWCNTs in continuous LLDPE matrix and appropriate size of finely-dispersed UFRP can be achieved at the same time. The controlled localization of MWCNTs in the continuous phase facilitates the formation of conductive pathway, and thus the volume resistivity of the as-prepared LLDPE/UFRP/MWCNTs thermoplastic vulcanizates is significantly decreased. The results show that both the blend ratio of LLDPE/UFRP and the loading of MWCNTs have remarkable effect on the volume resistivity. Significantly, the electrically conductive TPVs exhibit good mechanical properties due to the fine dispersion of UFRP in LLDPE. The added MWCNTs are capable of imparting reinforcement effects to thermoplastic vulcanizates with just a slight loss of stretchability and elasticity.

Keywords: Thermoplastic vulcanizates; Multi-walled carbon nanotubes; Ultrafine full-vulcanized rubber particles; Volume resistivity; Mechanical properties.

INTRODUCTION

Thermoplastic vulcanizates (TPVs) prepared by blending plastics with vulcanized rubbers are known as important commercial materials because they combine the processability of plastics with the elasticity of vulcanized rubbers. Of significance, electrically conductive TPVs filled by conductive fillers have attracted considerable attention and have been frequently applied in medical, automotive, electronic or electrotechnic fields to provide electromagnetic shielding, electrostatic dissipation or antistatic properties^[1–3]. As for the preparation of electrically conductive TPVs, conductive fillers are required to be distributed in the continuous plastic matrix to form conductive pathway due to the two-phase structure of TPVs with rubbers as dispersed phase in the plastic matrix. As is well known, traditional TPVs were made *via* a dynamic vulcanization process during which rubbers were crosslinked *in situ* and mixed with plastics simultaneously^[4–6]. By this methods, it is difficult to prepare electrically conductive TPVs at the same time as the conductive filler will localize in dispersed rubber phase, which limits the formation of conductive pathway^[7, 8]. In order to control the conductive filler to localize in the continuous matrix, traditional electrically conductive TPVs had to be prepared *via* a two-step process, *i.e.*, the preparation of TPVs and then the blending of TPVs and conductive filler^[9, 10].

In our previous paper, a new kind of ultrafine full-vulcanized rubber particles (UFRP) with the average size of 50–200 nm was prepared by the combined technologies of irradiation and spray drying^[11], which provided a

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new strategy to prepare TPVs^[12–14]. In this paper, electrically conductive TPVs made of linear low density polyethylene (LLDPE)/UFRP/MWCNTs were prepared by simple one-step melt mixing with traditional processing machines and conditions. Since UFRP was fully-vulcanized, a two-phase structure with UFRP dispersed in the LLDPE matrix could be obtained. Additionally, MWCNTs could be excluded by cross-linked UFRP and limited to localize mainly in the continuous matrix which facilitated MWCNTs to form conductive pathway with low MWCNTs content. The effects of LLDPE/UFRP blend ratio and the loading of MWCNTs on the electrical properties as well as mechanical properties of LLDPE/UFRP/MWCNTs thermoplastic vulcanizates were systematically investigated in this article.

EXPERIMENTAL

Materials

LLDPE (DGM 1820) was supplied by Tianjin Petroleum & Chemical Co., China, with a MFI of 2 g/10 min (230°C, 2.16 kg); UFRP (NarpowTM VP-101) with average size of 100 nm was offered by Beijing Research Institute of Chemical Industry, SINOPEC, China; MWCNTs (FloTube 9000, purity > 95 wt%) were supplied by Beijing CNano Technology Limited, China, with the average diameter of 11 nm and the average length of 10 μm .

Sample Preparation

LLDPE/UFRP and LLDPE/UFRP/MWCNTs thermoplastic vulcanizates were fabricated by the conventional melt blending method in an internal mixer (Brabender PLE 651). All the components were added simultaneously into Brabender and then melt-blended at 200°C and 60 r/min for 8 min. The blend ratio of LLDPE/UFRP varied from 70/30 to 30/70. The resultant blends were melt-compressed at 170°C under 8 MPa for 5 min and then cold-compressed under 5 MPa for 10 min at 20°C to form sheets of suitable thickness. Samples for testing were cut from the compressed sheets according to the standards mentioned in the following part.

Testing and Characterization

Volume resistivity

Volume resistivity was measured by using a PC68 Digital Teraohmmeter (Shanghai Precision & Scientific Instrument Co., Ltd). The principle of the test was based on the formula: $\rho = R_v \pi d^2 / 4L$, where L was the thickness of the sample, d was the diameter, and R_v was the measured volume resistance. The voltage applied to the samples was 100 V. Data were collected by averaging over four measurements.

Morphology observation

The morphology of LLDPE/UFRP/MWCNTs thermoplastic vulcanizates was observed by using a transmission electron microscope (TEM, Philips TECNAI 20). Ultrathin sections, about 50–80 nm thick and stained by osmium tetroxide (OsO_4), were used for TEM observation.

Mechanical properties

Tensile tests were carried out on a tensile testing machine (SHIMADZU AG-1, Japan) according to ASTM D412-06a. The adopted speed of the cross head was 500 mm/min. Shore D hardness was determined according to ASTM D2240-05. Compression set was measured at room temperature for 22 h according to ASTM D395-03.

RESULTS AND DISCUSSION

Morphology Observation

TEM images of LLDPE/UFRP/MWCNTs thermoplastic vulcanizates with different LLDPE/UFRP blend ratios are shown in Fig. 1. Two phases are clearly distinguished, the continuous phase being the LLDPE matrix whereas the dispersed phase being stained UFRP. It is evident that UFRP were always finely dispersed in the continuous LLDPE matrix with average size of 1–2 μm even when the LLDPE/UFRP blend ratio varied in a

wide range between 70/30 to 30/70. At high magnification in Fig. 1(f), it is clearly observed that MWCNTs were dispersed in LLDPE matrix as pointed by the black arrows and excluded by the adjacent UFRP particles. This phenomenon was understandable because MWCNTs could not migrate into the cross-linked UFRP and thus mainly localized in the low viscous LLDPE matrix during the melt mixing process. As a result, with increasing UFRP content more MWCNTs were distributed in LLDPE phases and thus had a high possibility to connect with each other to form conductive pathway.

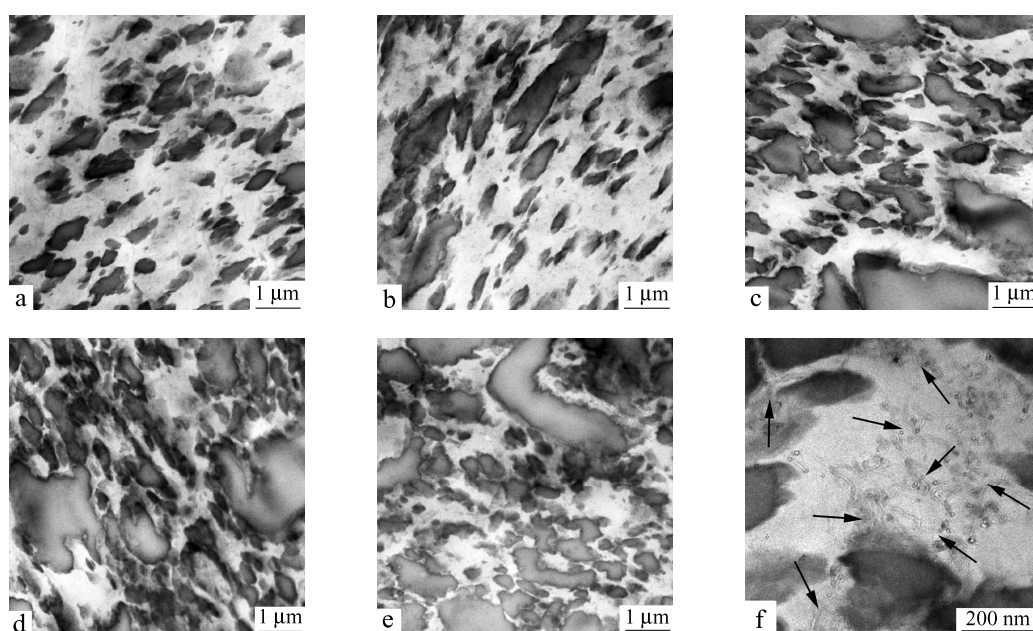


Fig. 1 TEM micrographs of LLDPE/UFRP/MWCNTs thermoplastic vulcanizates with different blend ratios (a) 70/30/4, (b) 60/40/4, (c) 50/50/4, (d) 40/60/4, (e) 30/70/4 and (f) magnified micrographs from (d)

TEM observations revealed that an ideal morphology with controlled localization of MWCNTs in matrix and appropriate size of UFRP was achieved by a simple one-step melt mixing process, which was suitable for preparation of electrically conductive TPVs.

Electrical Resistivity

Effect of LLDPE/UFRP blend ratio on the volume resistivity of LLDPE/UFRP/MWCNTs thermoplastic vulcanizates is shown in Fig. 2. By addition of 4 wt% MWCNTs, the volume resistivity showed a decreasing tendency from $10^9 \Omega \text{ cm}$ to $10^5 \Omega \text{ cm}$ with the LLDPE/UFRP blend ratio changing from 70/30 to 30/70. The results revealed that volume resistivity of the blends was strongly related to blend ratio which could be attributed to the selective localization of MWCNTs in LLDPE matrix as confirmed by morphological observation. Due to MWCNTs being excluded by UFRP, the increasing UFRP content leads to increasing MWCNTs concentration in LLDPE matrix, which facilitates the conformation of conductive pathway. As a result, LLDPE/UFRP/MWCNTs thermoplastic vulcanizates with high UFRP contents showed low volume resistivity.

Effect of MWCNTs loading on the volume resistivity of LLDPE/UFRP/MWCNTs thermoplastic vulcanizates is shown in Fig. 3. As expected, the volume resistivity strongly depended on the MWCNTs loading. LLDPE/UFRP/MWCNTs thermoplastic vulcanizates with 60 wt% UFRP and 70 wt% UFRP showed a low percolation threshold at 3 wt% and 2 wt%, respectively. Above the percolation threshold the volume resistivity could be decreased continuously and the value as low as $10^4 \Omega \text{ cm}$ was obtained when the MWCNTs loading was up to 5 wt%.

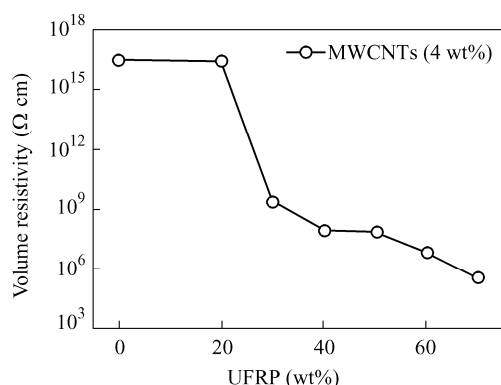


Fig. 2 The volume resistivity of LLDPE/UFRP/MWCNTs thermoplastic vulcanizates as a function of UFRP content

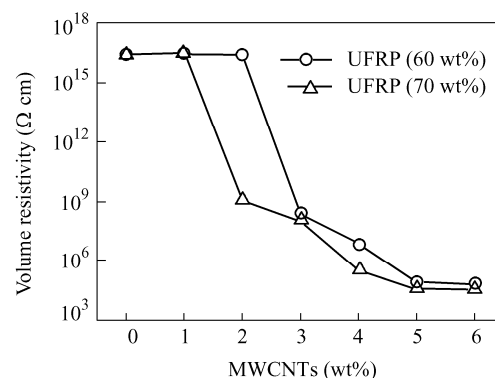


Fig. 3 The volume resistivity of LLDPE/UFRP/MWCNTs thermoplastic vulcanizates as a function of MWCNTs loading

The above results revealed that a series of electrically conductive LLDPE/UFRP/MWCNTs thermoplastic vulcanizates with different volume resistivity could be obtained by controlling the LLDPE/UFRP blend ratio and the MWCNTs loading.

Mechanical Properties

The tensile strength, stress at 100% strain, elongation at break, compression set and shore D hardness of LLDPE/UFRP and LLDPE/UFRP/MWCNTs thermoplastic vulcanizates with different blending ratios are given in Table 1. It is clear that the added MWCNTs showed reinforcement effects for LLDPE/UFRP blends. By addition of 4 wt% MWCNTs, the tensile strength and stress at 100% strain of LLDPE/UFRP/MWCNTs blends were always higher than the values of corresponding LLDPE/UFRP blends. The improvement of the two parameters above could be attributed to the intrinsic high strength of MWCNTs. Similarly, shore D hardness of LLDPE/UFRP/MWCNTs blends was also higher compared to that of LLDPE/UFRP blends. Interestingly, elongation at break just slightly decreased after addition of MWCNTs and the values of all samples were above 300%, indicating the high stretchability of thermoplastic vulcanizates. As for compression set representing the elasticity of TPVs, it turned out that the values increased due to the enhanced hardness of TPVs after incorporation of MWCNTs. However, with LLDPE/UFRP blend ratio increasing from 70/30 to 30/70, compression set changed from 36.2% to 25.6%, which means the recovered deformation was in the range between 63.8% and 74.4%. That is, electrically conductive LLDPE/UFRP/MWCNTs thermoplastic vulcanizates still possessed good elasticity.

Table 1. Mechanical properties of LLDPE/UFRP and LLDPE/UFRP/MWCNT thermoplastic vulcanizates with different contents of UFRP

Blend ratio (LLDPE/UFRP/MWCNTs)	Tensile strength (MPa)	Stress at 100% strain (MPa)	Elongation at break (%)	Compression set (%)	Hardness (Shore D)
70/30	12.8	7.9	576	30.7	44
60/40	10.4	6.9	476	27.7	40
50/50	9.0	5.9	400	24.0	36
40/60	8.8	5.5	336	22.7	32
30/70	8.7	4.7	344	20.2	28
70/30/4	13.0	9.3	492	36.2	45
60/40/4	12.2	8.4	436	34.1	42
50/50/4	11.4	7.6	376	31.4	39
40/60/4	11.1	7.4	324	27.8	35
30/70/4	9.9	6.1	320	25.6	32

Effects of MWCNTs loading on mechanical properties of LLDPE/UFRP/MWCNTs thermoplastic vulcanizates are shown in Table 2. The LLDPE/UFRP blend ratio kept invariable at 40/60. Tensile strength, stress at 100% strain and shore D hardness increased gradually with MWCNTs increasing from 1 wt% to 6 wt% whereas elongation at break showed inverse tendency to the increasing MWCNTs loading. However, elongation at break only decreased to a little extent. Besides, compression set changed slightly with the MWCNTs loading in the same range of 1 wt%–6 wt%, which suggested increasing MWCNTs loading had little influence on the elasticity of the materials.

Table 2. Mechanical properties of LLDPE/UFRP/MWCNTs thermoplastic vulcanizates with different loading of MWCNTs

Blend ratio (LLDPE/UFRP/MWCNTs)	Tensile strength (MPa)	Stress at 100% strain (MPa)	Elongation at break (%)	Compression set (%)	Hardness (Shore D)
40/60	8.8	5.5	336	22.7	32
40/60/1	9.1	5.9	336	24.3	33
40/60/2	9.9	6.3	332	24.1	34
40/60/3	10.2	6.5	330	26.2	34
40/60/4	11.1	7.3	324	27.8	35
40/60/5	11.1	7.4	300	27.6	36
40/60/6	11.4	7.7	288	26.9	36

Therefore, in combination with aforementioned electrical resistivity, it is concluded that increasing MWCNTs loading induced both reinforcement effects and improved conductive properties without significantly affecting the stretchability and elasticity of thermoplastic vulcanizates.

CONCLUSIONS

A series of MWCNTs-filled electrically conductive TPVs based on LLDPE and UFRP have been successfully prepared by simple one-step melt mixing. The improving conductive properties of TPVs was attributed to selective localization of MWCNTs in the LLDPE phase. The combination of electrical and mechanical properties made the as-prepared electrically conductive TPVs suitable for various applications.

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