Conducting Blends of Poly(*o*-toluidine) and Ethylene–Propylene–Diene Terpolymer

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ABSTRACT: Poly(*o*-toluidine) (POT) is an electroactive polymer with poor mechanical and thermal characteristics. We examined the scope for improving such properties by making blends of POT with ethylene–propylene–diene rubber (EPDM). We prepared POT–EPDM blends containing different weight fractions of POT by intimately mixing known volumes of separate solutions of the two polymers (POT in THF and EPDM in toluene). Films of EPDM and POT–EPDM blends in solution were obtained by spreading, solvent evaporation, and film casting techniques. POT, EPDM, and their blends were characterized in solution by ultraviolet-visible spectroscopy, and the respective dried samples were analyzed by Fourier transform infrared spectroscopy and thermogravimetry. The polymer samples were further analyzed morphologically by scanning electron microscopy, and their tensile strengths were also evaluated. Spectroscopic and thermal studies of the blends indicated some sort of interaction between the two constituent polymers. The direct current electrical conductivity of the blends in increasing order of POT loading (12.5–100%) was in the range 9.9×10^{-5} to 11.6×10^{-2} S cm^{-1}. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 2550–2555, 2003

INTRODUCTION

Electrically conducting polymers have gained significant importance recently.[1–3] Among the inherently conducting polymers (ICPs), polyacetylene (PA), polypyrrole (PPY), polyaniline (PANI), and poly(*o*-toluidine) (POT) have been studied in greater details. Most of them bearing aromatic ring structures are commonly characterized by high stiffness and brittleness and also by high resistance to solubility and fusibility, and hence, they are difficultly processable to finished forms or molded end-use items.

Of the different approaches for making ICPs in processable cohesive form, the *in situ* preparation of specific ICP-based blends and composites has generated greater interest as they exhibit improved optical, electrical, and mechanical properties. Some significant recent reports to this effect relate to making composites[4–6] of conducting polymers with such matrix polymers as poly(vinyl chloride), poly(methyl methacrylate), and polystyrene. POT–polypropylene (PP) composite films with retention of good and uniform mechanical properties of the host polymer PP have also been reported.[7] We reported earlier on the synthesis and characterization of easy processable POT–polyacrylamide composites with the support of polyacrylamide,[8] a water-soluble polymer, during the polymerization of *o*-toluidine by oxidative coupling.

In this article, we report the results of investigations on the thermal, mechanical, and electrical properties of solution blends from ethylene–propylene–diene monomer (EPDM)-based elastomer and the ICP POT with an attempt at assessing their suitability for use as nonbrittle semiconducting coating, molded, and extruded or formed objects.

EXPERIMENTAL

Materials

o-Toluidine (S.D. Fine Chemicals, Mumbai, India) dried over NaOH pellets was purified by double distillation at a reduced pressure before use for polymerization. Ammonium peroxodisulfate [$(NH_4)_2S_2O_8$], tetrahydrofuran (THF), and benzoyl peroxide (Bz_2O_2; all from E. Merck, Mumbai, India), toluene (Process Chemical Industries, Kolkata, India), and EPDM (Nordel 3722, from Du Pont (USA), viscosity = 16–24 Pa S, ethylene content = 69.5%, diene content = 0.95, specific gravity = 0.53) were used without any specific treatment or purification. Reagent grade *N,N*-dimethyl aniline [DMA; $C_6H_5N(CH_3)_2$; S.D. Fine Chemicals), hydrochloric acid (HCl), and ammonium hydroxide (NH_4OH; Biswa Bharati Chemicals, Kolkata, India) were used without further purification.

Preparation of POT

POT was synthesized from its monomer, *o*-toluidine, by an oxidative coupling procedure,[8] with ammonium

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TABLE I
Data Showing Variation in γ and σ with Variation of POT Loading in POT–EPDM Blends

| Sample system | Blend composition | | POT loading per 100 g of EPDM (g) | γ (%) | σ^b (S cm^{-1}) |
	EPDM (g)	POT^a (g)			
A	0.0	2.0	—	12.5	8 $\times 10^{-1}$
B	2.0	2.0	100	4.50	11.6 $\times 10^{-2}$
C	2.0	1.0	50	4.20	5.0 $\times 10^{-3}$
D	2.0	0.8	40	3.75	2.1 $\times 10^{-3}$
E	2.0	0.6	30	3.25	1.8 $\times 10^{-3}$
F	2.0	0.5	25	3.00	1.76$\times 10^{-3}$
G	2.5	0.5	20	2.78	2.60$\times 10^{-4}$
H	3.0	0.5	17	2.60	9.60$\times 10^{-4}$
I	4.0	0.5	13	2.55	9.9 $\times 10^{-5}$

^{a} Dedoped POT was used in blend preparation.
^{b} σ was assessed for doped POT (experiment A) as synthesized and for redoped POT/EPDM blends (film) duly crosslinked.

peroxodisulfate as the oxidant in aqueous $1N$ HCl solution. POT so prepared as a green precipitate in salt (doped) form was converted to its base (dedoped) form by treatment with aqueous $0.1N$ ammonium hydroxide (NH_4OH) solution under vigorous stirring for 5 h to impart ready solubility in THF. The base form of POT, also insoluble in water, was filtered, washed with distilled water, and dried at room temperature under vacuum.

Preparation of POT–EPDM blends

For the preparation of solution blends, dedoped POT was dissolved in THF, and EPDM was taken in toluene to give clear solutions. Appropriate volumes of the two solutions of known concentrations (Table I) were mixed and stirred together for several (4–6) hours to obtain a uniform clear solution of the polymer mixture free from turbidity. Then, a free-radical-generating redox combination of Bz_2O_2 and DMA was added. An overall concentration of 0.5–1% Bz_2O_2 and 0.2–0.5% DMA was maintained in each case to effect the room temperature (30°C) crosslinking of the matrix polymer EPDM during subsequent film casting. Solution-cast, crosslinked films obtained after solvent evaporation were dried under vacuum and subsequently used for characterization [Fourier transform infrared spectroscopy (FTIR), moisture absorption, direct current electrical conductivity (σ), scanning electron microscopy (SEM), tensile strength testing, and thermogravimetric analysis (TGA)]. Trouble-free film casting and film sample release after vacuum drying were possible with greater ease and elegance only after mild/moderate crosslinking was allowed as detailed previously.

Doping POT–EPDM blend films

For redoping, the (dedoped) POT–EPDM blend films so prepared were kept immersed and equilibrated in aqueous $3N$ HCl for 7 days and were finally dried under vacuum at room temperature.

Characterization of POT–EPDM blends

Ultraviolet–visible (UV–vis) spectroscopy

UV–vis absorption spectra of doped POT and dedoped POT, each in THF solution, of EPDM in toluene solution and of selected blends of dedoped POT and EPDM in a 1 : 1 v/v mixture of THF and toluene (with no use of crosslinker in either case here) were recorded with the respective solvents or solvent mixture in the reference cell as required, with a PerkinElmer model 5505 UV–vis spectrophotometer.

FTIR spectra

FTIR spectra of different samples of doped and dedoped POT, EPDM, and isolated, dried, and doped POT–EPDM blends were obtained with a PerkinElmer (1600 series) FTIR spectrophotometer with the KBr disc technique.

Moisture absorption

Moisture absorption (γ; %) of selected polymer samples was calculated with the following procedure. A duly vacuum-dried and weighed (w_1) doped polymer sample was kept over saturated $NaNO_3$ solution (at 65% relative humidity) in a closed chamber for 72 h to attain its equilibrium weight gain, and its final weight (w_2) was noted. The γ value was obtained with the following relationship:

$$\gamma(\%) = \frac{w_2 - w_1}{w_1} \times 100$$

σ

σ of doped POT and of doped POT–EPDM blends with different blend ratios duly dried in a vacuum were measured with the four-probe Van der Pauw technique[9] with the help of a programmable current/voltage generator (Advantest, R 6142, Japan) and a precision digital voltmeter (Solarton, SI 7071, United Kingdom).

SEM

SEM micrographs were obtained with the cast (crosslinked) polymer films coated with gold with a sputter coating technique and with an accelerated voltage of 25 kV on a Hitachi S-415 electron microscope.

Mechanical properties

The mechanical properties (tensile strength) of selected polymer samples were measured in an Instron universal tensile testing machine (model 1.34) according to the ASTM D 41283 test method.

TGA

TGA of different samples of doped POT, EPDM, and solution blends of doped POT and EPDM duly vacuum dried were carried out in a PerkinElmer TGA-7 machine in the temperature range 50–560°C. A test sample with a weight of 6 ± 0.1 mg was used in each case. A heating rate of 20°C/min under flowing nitrogen was maintained for the experiment.

RESULTS AND DISCUSSION

UV–vis spectra

The UV–vis absorption spectra of very dilute solutions of dedoped and HCl-doped POT in THF, EPDM in toluene, and a dedoped POT–EPDM blend (30 : 70 w/w) in THF and toluene (1 : 1 v/v) mixture are shown in Figure 1.

Comparison of spectra (a) and (b) [curve (a) is for dedoped POT, and curve (b) is for doped POT] allows one to appreciate the effect of the doping of POT with HCl in modification of the POT structure. The sharp, narrow, intense absorption peak at 330 nm and a broad moderately intense peak at 600 nm region exhibited by dedoped POT was assigned to excitation of the amine nitrogen of the benzenoid and the imine nitrogen of the quinoid segments of POT, respectively.[8–10,11] Transformation of the blue (dedoped) form of POT to the green (doped) form led to significant broadening of the 330 nm peak with the appearance of a fresh broad band at the region at and above 400 nm indicating a polaron–bipolaron transition, as can be shown in Figure 1; an indication of a notable shifting of the 600-nm peak to a wave-
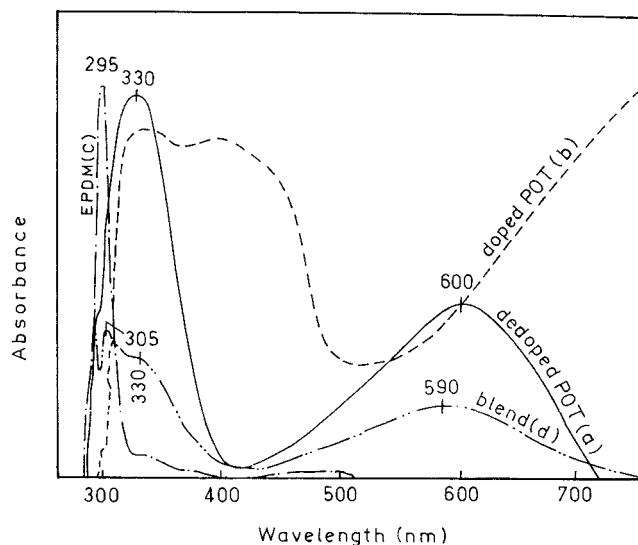

Figure 1 UV–vis absorption spectra of (a) dedoped POT, (b) HCl-doped POT, (c) EPDM, and (d) a (dedoped) POT–EPDM blend (30 : 70 w/w).

length region greater than 750 nm was specifically ascribed to a polaron–bipolaron transition consequent to effective protonation.[8] The sharp narrow absorption peak at 295 nm for EPDM [curve (c)] was due to the presence of the diene, ethylidene norbornene (ENB) in the structure. The spectrum of the blend of dedoped POT and EPDM [curve (d)] in the THF and toluene mixture (1 : 1 v/v) exhibited a broad and relatively weak quinoid band showing a small shift in the peak absorption from 600 to 590 nm; it also showed a hump at nearly 330 nm, indicating the expected absorption features of dedoped POT itself as described previously. The characteristic 295-nm peak of the diene moiety in EPDM was, however, slightly shifted to the 305-nm region in the spectrum for the blend (Fig. 1). A little shift in the absorption peaks as detailed previously was indicative of interactions between the component polymers in the blend.

FTIR spectra

The FTIR spectra of EPDM, dedoped and doped POT, and the POT–EPDM blends (1 : 1 w/w and duly HCl-doped) are presented in Figure 2. For EPDM [curve (a)], the 1630 cm⁻¹ band was due to C=C stretching present in the diene. For dedoped POT [curve (b)], the bands[12] for benzenoid and quinoid moieties appeared at 1596 and 1495 cm⁻¹, respectively.[11] The FTIR spectrum of HCl-doped POT [curve (c)] also exhibited two principal absorption bands at 1556 and 1490 cm⁻¹, which were assigned[8,13] to the ring-stretching modes of the benzenoid and quinoid rings segments, respectively.

The FTIR spectrum of the HCl-doped (POT–EPDM) blend [curve (d)] showed characteristic peaks for both (doped) POT and EPDM with the diene-stretching band
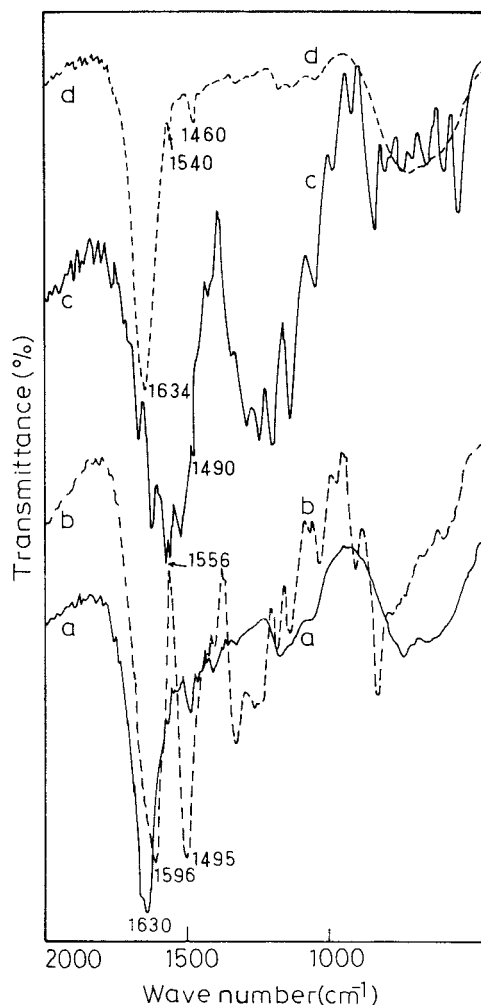
Figure 2 FTIR spectra of (a) EPDM, (b) dedoped POT, (c) HCl-doped POT and (d) an HCl-doped POT–EPDM blend (50 : 50 w/w).

appearing at 1634 cm^{-1}. The benzenoid (1556 cm^{-1}) and quinoid (1490 cm^{-1}) ring-stretching bands for doped POT appeared shifted to slightly lower wave numbers, namely, 1540 and 1460 cm^{-1}, respectively in the spectrum for the corresponding POT–EPDM blend, possibly due to interactions between the two constituent polymers, POT and the diene copolymer EPDM.

Moisture absorption

POT had a moisture absorption value γ (%) that was notably higher than that of EPDM (0.02% Table I). We expected to obtain an almost average value of moisture absorption for the blends. However, for POT–EPDM blends, the observed γ (%) values deviated highly from the weighted average, which can be appreciated from the data in Table I. A higher POT loading in the blend tended to exhibit a somewhat higher γ (%) value, although not in proportion to the enhancement in POT loading, as shown in Table I. For

POT–EPDM blends, the moisture absorption property was largely controlled or dictated by the encompassing matrix phase of EPDM.

D.C. electrical conductivity, σ

The σ values of doped POT (8.1×10^{-1} S cm^{-1}) and of different POT–EPDM blends are shown in Table I; with increasing proportions of POT in the blend, the conductivity of the blend (POT–EPDM) increased from a low value (10^{-15} S cm^{-1} for EPDM) and reached 11.6×10^{-2} S cm^{-1} for the (1.1 w/w) blend, that is, for 100% POT loading of EPDM. Relatively low values of observed σ of the POT–EPDM blends of different POT loading were due to the presence of significant proportions of the insulating matrix polymer EPDM imparting a dilution effect on POT.

Phase morphology and tensile strength

Figure 3 shows scanning electron micrographs highlighting the surface morphology of films of EPDM [Fig. 3(a)] and of EPDM–POT blends [Fig. 3(b,c)]; in each case, the films were obtained by prolonged evaporation of solvent under vacuum. The prominent isotropic phase morphology of EPDM itself [Fig. 3(a)] turned somewhat or notably anisotropic on being lowly (25%) loaded with POT, as shown in Figure 3(b), where the POT phase seemed to have been evenly and intimately distributed and dispersed in a continuous and aligned or oriented matrix phase of EPDM. For higher POT loading (50%), the blend film appeared to gain in brittleness, and the phase morphology turned prominently isotropic again [Fig. 3(c)]. Thus, for low (up to 25%) POT loading, favorable mutual interactions between POT and EPDM chain segments produced appreciable chain alignment and an associated reinforcing effect, inducing notable anisotropy in the phase morphology and, consequently, causing a notable increase in the observed tensile strength (Fig. 4). The reinforcing trend, however, got reversed due mostly to phase segregation for higher POT loading (>30%; Fig. 4).

TGA

Thermograms of EPDM, doped POT, and doped POT–EPDM blends (of different POT loading) are shown in Figure 5. The TGA thermogram [curve (a)] of HCl-doped POT exhibited a two-step weight loss in the range of 50–200°C.[8,12,14] The first step ranging up to 100°C was assignable to the major loss of moisture. In the second step (100–200°C), the elimination of the dopant HCl was expectedly predominant. After that, a slow stage of thermal degradation followed, which became brisk above 400°C. The thermogram of EPDM [curve (b)] showed the beginning of a rapid thermal degradation at 330°C, and the rate of degradation
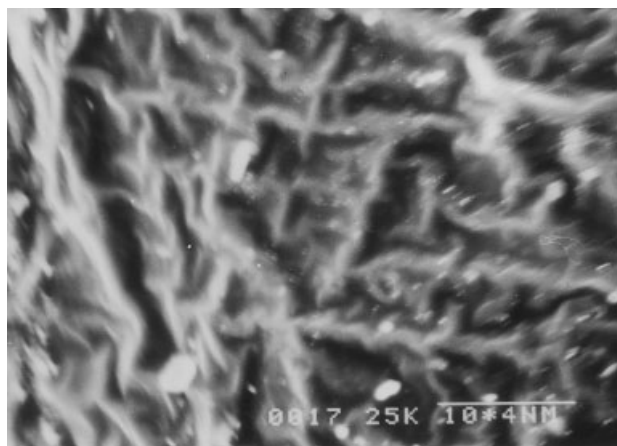
(a)
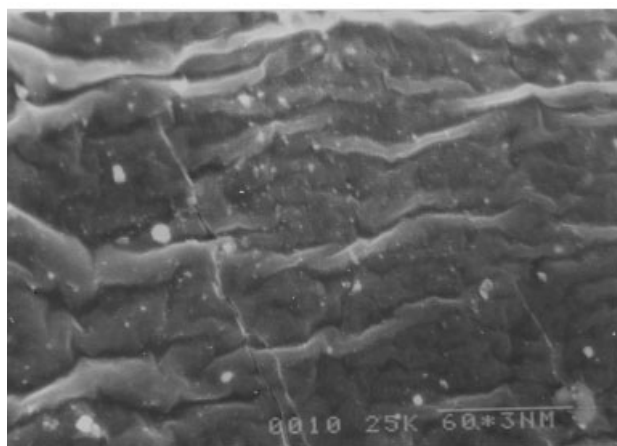
(b)
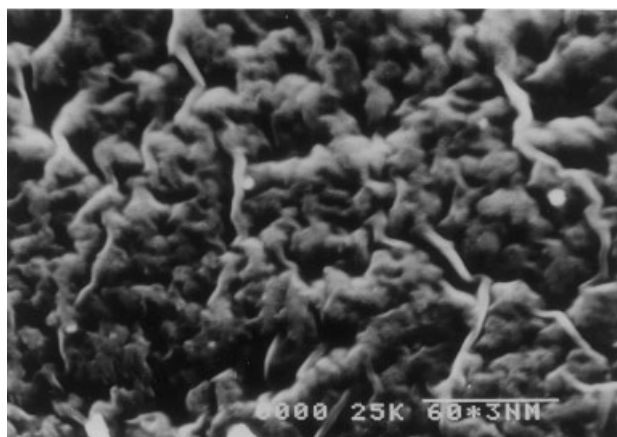
(c)

Figure 3 Scanning electron micrographs of mild or moderately crosslinked EPDM and POT–EPDM blends: (a) EPDM and blends with (b) 25 g of POT per 100 g of EPDM and (c) 50 g of POT per 100 g of EPDM.

apparently peaked at 410°C and went to completion at around 510°C, leaving little residue. The thermograms of doped POT–EPDM blends [curves (c–g)] showed the effect of increasing POT loading in EPDM (Fig. 5
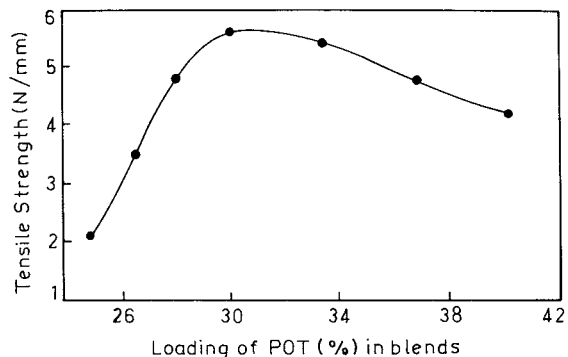

Figure 4 Plot of tensile strength versus POT loading for POT–EPDM blends.

and Table II). The temperature range for moisture release and dopant (HCl) release very much depended on POT loading, a higher POT loading leading to an earlier and more brisk release of moisture and dopant, quite expectedly. The presence of POT apparently made the POT–EPDM blends more resistant to thermal degradation in the subsequent step, showing a prominent synergistic effect, particularly for POT loading up to 50% of EPDM (Table II). The initial moisture and dopant release portion of the thermograms of the doped POT–EPDM blends [curves (c–g)] and also the final portions of the blend thermograms, which showed brisk thermal degradation at high rates, were interestingly found encompassed between the respective portions of the thermograms for POT [curve (a)] and EPDM [curve (b)]. For doped POT, EPDM, and doped POT–EPDM blends of increasing POT loading (25–100%), the temperature corresponding to onset of thermal decomposition (T_{onset}) and that corresponding to thermal degradation at maximum rate (T_{max}) are shown in Table II. When one considers the T_{onset} and T_{max} data, it may be seen that for POT
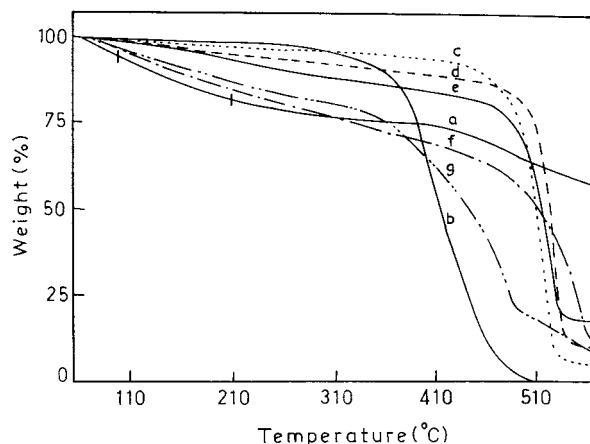

Figure 5 TGA of EPDM, doped POT and redoped POT–EPDM blends: (a) POT, (b) EPDM, and POT–EPDM blends showing POT loading per 100 g of EPDM of (c) 25, (d) 30, (e) 40, (f) 50, and (g) 100 g.

TABLE II
Effect of POT Loading on the Thermal Stability
of Doped POT–EPDM Blends

Polymer sample	T_{onset} (°C)	T_{max} (°C)
I. (a) Doped POT only	370	485
(b) EPDM only	310	410
II. POT–EPDM blends[a] (dedoped POT per 100 g EPDM)		
(c) 25 g	385	500
(d) 30 g	410	520
(e) 40 g	425	522
(f) 50 g	335	535
(g) 100 g	350	480

[a] The isolated blends were HCl-doped (on steeping in $3N$ HCl for 7 days) and then washed and dried in a vacuum at room temperature before TGA.

loading up to 50%, the POT–EPDM blends turned thermally more stable than the isolated component polymers, and for 100% POT loading on EPDM, the blend became nearly comparable with POT in respect to T_{onset} and T_{max} data.

CONCLUSIONS

Spectroscopic (UV–vis and FTIR) analysis of blends of POT and EPDM indicated interactions between the two component polymers, and this was further substantiated by a higher thermal stability with a synergistic effect for the incorporation of a higher dose of POT in EPDM in making the blend. SEM studies further indicated good dispersion of POT in EPDM at low POT (≤25%) loading, showing some reinforcing effect due to an orientational effect, but POT loading (>30%) tended to reverse the trend and for POT loadings of 40% or more, the blends became notably brittle, apparently due to developing trends in phase segregation associated with phase deorientation and phase discontinuities. Semiconducting POT–EPDM blends with σ values in the range 10^{-3} to 10^{-1} S cm^{-1} for 25–100% POT loading showed optimum tensile strength, or mechanical properties, for a POT loading of 30%.

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