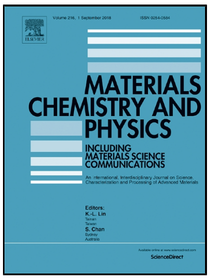

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Thermoplastic Vulcanizates based on poly(vinylidene fluoride)/Epoxidized Natural Rubber blends: Effects of phenolic resin dosage and blend ratio

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Abstract

Epoxidized natural rubber with 50 mol% epoxide groups (ENR50) was used as a blend component in the poly(vinylidene fluoride)/epoxidized natural rubber (PVDF/ENR50) blends. The PVDF/ENR50 blends were dynamically cross-linked with phenolic resin in varying amounts from 0 to 11 phr. It was found that 5 phr phenolic resin was optimal for superior mechanical properties of the PVDF/ENR50 blends. Dynamically cured PVDF/ENR50 blends with various blend ratios were investigated. The tensile strength and tension set decreased whereas elongation at break increased with ENR50 content in the dynamically cured PVDF/ENR50 blend. Furthermore, dynamic mechanical analysis (DMA) revealed a shift in the glass transition temperatures of blend components, and differential scanning calorimetry (DSC) revealed nucleation of PVDF crystallization by the rubber particles in the PVDF/ENR50 TPV, indicating molecular interactions between ENR50 and PVDF phases.

Keywords; Epoxidized natural rubber; Poly(vinylidene fluoride); Thermoplastic vulcanizate; Thermoplastic elastomer; Morphology

1. Introduction

Blending a thermoplastic with an elastomer has been widely investigated to generate novel elastomeric materials that combine properties of thermoplastics and elastomers, so-called "thermoplastic elastomers" (TPEs). These materials advantageously combine the processing characteristics of thermoplastics with the elasticity of rubber. TPEs are widely used materials, with extensive usage in automobiles and in soft-touch applications. The blends can be either simple blends with non-crosslinked rubber phase (Thermoplastic Polyolefin, TPO) or dynamically vulcanized blends with vulcanized rubber phase (Thermoplastic Vulcanizate, TPV) [1, 2]. Simple blends can be prepared by melt mixing without a cross-linker or a vulcanizing agent, whereas thermoplastic vulcanizates (TPVs) are prepared by dynamic vulcanization. In this technique, vulcanizing agents are added in the blend during mixing. The dynamic vulcanization process causes formation of fine cross-linked rubber domains dispersed in the plastic matrix, with stable morphology [2, 3]. The combination of plastic with elastomer in a TPV produces new soft materials with good processability and elasticity. Thus, dynamic vulcanization is common with many blends of elastomers and thermoplastics and helps achieve superior properties.

Thermoplastic elastomers using natural rubber (NR) have been reported, and they tend to exhibit excellent elasticity and mechanical properties. However, NR composed of *cis*-1,4-polyisoprene units has low polarity and is incompatible with polar polymers. Therefore, various types of modified natural rubber, such as epoxidized natural rubber (ENR) and maleated natural rubber (MNR), poly(methyl methacrylate)-grafted natural rubber (NR-*g*-PMMA), are better candidates than NR for blends with polar polymers [4, 5]. Their molecular polarity improves compatibility of phases in the blend. In particular ENR has good compatibility with a number of polymers that also have polar functional groups, such as poly(lactic acid) [6], nylon-12 [7], and polycaprolactone [8].

Poly(vinylidene fluoride) is an engineering plastic with excellent mechanical properties, chemical and weathering resistance, high dielectric permittivity, and unique pyroelectric and piezoelectric properties. Because of its excellent properties, it has been extensively studied in polymer blends and polymer composites [9-11]. There are many recent studies of PVDF blends with various types of rubber. Xu et al. reported on blends of PVDF with acrylonitrile butadiene rubber (NBR) formed via peroxide dynamic vulcanization. They observed 1–3 micron diameter NBR particles in a PVDF/NBR TPV that had high impact strength and large elongation at break. However, NR/PVDF blends are only rarely investigated, probably because the high polarity of PVDF would give poor compatibility and further cause poor mechanical properties [12]. We have previously reported on the morphology and the mechanical properties of ENR/PVDF simple blends. It has been established that ENR with 50 mol% of epoxide groups (ENR50) provides finer co-continuous structure and better mechanical properties than blends with ENR25 [13, 14].

In the present work, PVDF/ENR50 blends were prepared through dynamic vulcanization, using phenolic resin as the curing agent. The aim of this study was to evaluate the effects of vulcanizing agent loading and of blend ratio on the physical and thermal properties of PVDF/ENR blends. The dispersion and size distribution of ENR50 particles in PVDF matrix were characterized by Scanning Electron Microscopy (SEM). Mechanical properties and dynamic mechanical properties, both without cross-linking and for dynamically cured PVDF/ENR50 blends, were also examined and compared. At the same time, the crystallization behavior of PVDF/ENR50 TPV was also studied.

2. Experimental procedure

2.1 Materials

PVDF (KYNAR 740) in pellet form was purchased from Arkema, France. ENR50 (Epoxyprene 50) was purchased from Muang Mai Guthrie, Thailand. Phenolic resin (HRJ-10518) used as the curing agent was manufactured by Schenectady International Inc., New Port, USA. Wingstay L (Eliokem lnc., OH, USA) was used as antioxidant.

2.2 Preparation of PVDF/ENR50 blends

Influence of curing agent content: In this part, dynamically cured PVDF/ENR50 blends with varied HRJ-10518 content (i.e., 0, 3, 4, 5, 7, 9, or 11 phr) were prepared to select the optimal HRJ-10518 content. The blending of PVDF and ENR50 was carried out by melt mixing at 180°C in an internal mixer (HAAKE Rheomix R600). The mixer had capacity of 50 cm^3. PVDF/ENR50 = 40/60 wt%. First, PVDF was added into the mixer and allowed to mix for 3 min prior to adding the ENR50 and antioxidant, and mixing was continued for 5 min. Finally, phenolic resin (HRJ-10518) was added to dynamically vulcanize the PVDF/ENR50 blend with a total mixing time of 13 min. The torque-time relationships of the mixing sequences for PVDF/ENR blend without (TPE) and with the curing agent (TPV) are shown in Fig. 1. The blend was then cooled down to room temperature before testing.

Influence of blend ratio: In this part, PVDF/ENR50 TPVs with various blend ratios (i.e., 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, or 20/80 by weight) were prepared with 5 phr of the curing agent (HRJ-10518). The blending conditions and procedures were as described in the previous paragraph.

After blending, all the PVDF/ENR50 blends were compression molded at 180°C for 10 min to form thin sheets (about 1 mm thick). The samples were allowed to cool down to below 100°C before removal from the mold.

2.3 Mechanical properties

Standard dumbbell-shaped specimens were die-cut from the thin sheets. Tensile properties of the dumbbell test specimens were determined using a universal testing instrument (MTS Q test 25, MTS Systems Corporation, North Carolina, USA). The grip separation speed was set at 500 mm/min. For tension set measurement, the PVDF/ENR50 blends were elongated by 100% and held at room temperature for 10 min, according ASTM D412.

2.4 Morphological assessment

The morphologies of PVDF/ENR50 blends with various curative loadings and blend ratios were examined using a scanning electron microscope (SEM, FEI Quanta 400 instrument, FEI Company). The specimens were fractured in liquid nitrogen prior to microscopy. For a simple blend, the samples without extraction were used to observed morphology of the blend. In order to study the phase structure properly in dynamically cured blends, phase extraction was then performed. That is, the PVDF continuous phase was etched in DMSO at 80°C for 10 min. The etched samples were dried in an oven at 70°C for 48 h. The dried surfaces were sputter-coated with a gold layer, and imaged using SEM. The diameter of rubber particles was analyzed using ImageJ software. The number average diameter (D_n), volume average diameter (D_v,) and polydispersity index (PDI) were calculated according to the following formulas:

$$D_n = \frac{\sum n_i D_i}{\sum n_i} \qquad (1)$$

$$D_v = \frac{\sum n_i D_i^4}{\sum n_i D_i^3} \qquad (2)$$

$$PDI = \frac{D_v}{D_n} \tag{3}$$

2.5 Dynamic mechanical analysis (DMA)

Dynamic mechanical properties were assessed using a Dynamic Mechanical Analyzer (TA Instrument Q800 DMA) in tension mode. Storage modulus and tan δ as functions of temperature were measured at 1 Hz sampling frequency while heating at 2°C/min from -90 to 100°C. Dimensions of the rectangular test strip were 35 mm x 10 mm x 1 mm.

2.6 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) measurements were performed using the DSC 2920 TA instrument. An approximately 10 mg sample was sealed in an aluminum pan and scanned at a heating rate of 10°C/min over the temperature range from -90 to 200°C under helium atmosphere. The data from the second heating run were used for analysis. The percentage crystallinity (X_c) of PVDF or in a blend was estimated from the heat of fusion (ΔH_f) observed in a heating scan, as follows:

$$X_c(\%) = \frac{\Delta H_m (m_c / m_p)}{\Delta H_o} x100 \tag{4}$$

where ΔH_m is the melting enthalpy of a sample, ΔH_0 the theoretical enthalpy for 100 % crystalline PVDF (104.5 J/g) [15], m_c is the weight of the sample and m_p is the weight of PVDF in the blend.

The overall crystallization time (t_c) was calculated as follows:

$$t_c = \frac{(T_c - T_e)}{\beta_0} \tag{5}$$

where β_0 is the cooling rate, T_c is the onset temperature of crystallization and T_e is the final temperature of crystallization [16].

2.7 Swelling test

The PVDF in dynamically cured blends were extracted by DMSO for 72 h at 70°C. After dried at 60°C until constant weight, the samples were accurately weighted (W_1) and then immersed into toluene at room temperature for 72 h. The swollen samples were wiped and weighted (W_2). The swelling ratios (Q) were calculated by using the Eqs. (6) [17]:

$$Q = \frac{W_2 - W_1}{W_1} \quad (6)$$

2.8 FTIR spectra

The FTIR spectra of neat polymer and blends was measured on the smooth film using Thermo Nicolet Avatar 360 FTIR (Thermo Electron Corporation) equipped with a germanium attenuated total reflection (ATR) crystal probe. The resolution of the wavelength is 4 cm^{-1}.

3. Results and discussion

3.1 Effect of phenolic resin content

3.1.1 Morphological properties

Fig. 2 shows the phase morphology, illustrating the effects of phenolic resin content in dynamic vulcanization of the PVDF/ENR50 blend. Without dynamic vulcanization (0 phr of phenolic resin), it is clear that PVDF as the minor phase (40wt%) formed droplets dispersed within the ENR50 matrix (60 wt%), as seen in Fig. 2(a). However, in the case of dynamically cured PVDF/ENR50 blends the morphology was considerably affected by the added phenolic resin (HRJ-10518), as shown in Fig. 2(b-f). The particles in the dynamically cured blends are cross-linked ENR50 phases, because PVDF that is not crosslinked was removed by boiling the TPV in dimethyl sulfoxide (DMSO). The formation of ENR50 particles in PVDF/ENR50 TPV is due to selective cross-linking of ENR50 during the dynamic vulcanization. The phenolic resin (HRJ-10518) in PVDF/ENR50 blend caused the formation of Chroman ring structures by reactions of hydroxyl and methylol groups in the resin with unsaturated bonds in the epoxidized natural rubber (ENR), resulting in the cross-linking of ENR50 chains via chroman structures [18]. The selective cross-linking of rubber phase (ENR50) under intensive mixing and high temperature increased the viscosity of ENR50 phase, which can induce phase inversion. The variation of mixing torque with time further supports the formation of phase inversion. As shown in Fig. 1, the mixing torque obvious rise after addition of phenolic resin, which is related to increment of viscosity in rubber phase due to cross-linking. With continued mixing, it is also worth to notice that the torque reaches a maximum and exhibits plateau after 10 min. At this state, the continuous rubber phase becames elongated further and broken into rubber particles dispersed in the thermoplastic matrix, indicating the occurrence of a phase inversion [19, 20]. In addition, it is well-known that (at the shear rates during mixing) the viscosity of cross-linked elastomer phase is much higher than that of the PVDF phase. The more viscous component tends to form the disperse phase and the less viscous component tends to form the continuous phase [21]. Unlike the blend without dynamic vulcanization, the torque decreases slowly and achieves almost constant until the end of mixing due to the melting of PVDF and homogenization of the blends, as shown in Fig. 1. The rubber particle sizes in PVDF/ENR TPV are shown in Table 1. It can be seen that the particle diameter of TPVs with 3 and 4 phr of phenolic resin was approximately 4 μm to 2 μm, which is larger than in TPVs with higher phenolic resin contents (i.e., 5 to 11 phr). At the comparatively high loadings the curing agent induced high cross-linking density in the rubber, which increased the shear stress. Therefore, the ENR50 with high cross-link density would be expected to break up to comparatively small particles and uniformly distributed in the PVDF matrix [22, 23]. As seen in Table 1, it can be observed that swelling ratio decreased as phenolic resin increased because swelling ratio is inversely proportional to the crosslink density. Thus, this indicates that cross-link density increased with the phenolic resin content, resulting in an extensive break-up of dispersed phases. However, the slightly increased rubber particles size for 9 and 11 phr could be attributed to incomplete phase size reduction during mixing caused by the very high viscosity of ENR50 phase at high phenolic resin content.

3.1.2 Mechanical properties

The effects of phenolic resin loading on the mechanical properties of PVDF/ENR50 blends are shown in Fig. 3. The 40/60wt% PVDF/ENR50 blends with and without dynamic vulcanization showed different deformation behaviors, as seen in Fig. 3(a). That is, the PVDF/ENR50 blend without crosslinking had very high elongation at break exceeding 1000%, while its stress at break was very low. This deformation behavior of the PVDF/ENR50 simple blend is similar to an elastomer without reinforcing filler. The incorporation of phenolic resin improved the tensile stress at a given strain from that without phenolic resin due to the selective cross-linking of ENR50 rubber phase during dynamic vulcanization. The dynamically cured PVDF/ENR50 blends had finely dispersed fully vulcanized ENR50 in a PVDF matrix, as previously described. The fully vulcanized ENR50 particles improved the mechanical properties from those of a thermoplastic-elastomer blend without dynamic vulcanization. This indicates that dynamic vulcanization can improve the mechanical properties of PVDF/ENR50 blends. The mechanical properties (i.e., tensile strength and elongation at break) of PVDF/ENR50 blends are summarized in Fig. 3(b). The PVDF/ENR50 simple blend shows lower tensile strength and higher elongation at break than the dynamically cured 40/60 PVDF/ENR50 blends. The uncross-linked ENR50 phase in the simple blend provides higher extensibility than the crosslinked ENR50 particles in a dynamically cured blend. As shown in Fig. 2(a), ENR50 is the major phase, so this rubber phase without crosslinking gives the blend high elongation and low modulus.

Furthermore, incorporation of phenolic resin into the blends strongly decreased the elongation at break due to the formation of cross-linked ENR50 in PVDF matrix phase during dynamic vulcanization. When the thermoplastic becomes matrix phase, the elongation at break of the blends was reduced because matrix plastic deformation was not prominent. This leads to suddenly decreasing elongation at break. In addition, a sharp increase in tensile strength and elongation at break of PVDF/ENR50 TPV were observed with phenolic resin additions from 3 to 5 phr. This matches the observed rubber particle sizes in TPV. That is, the good mechanical properties with phenolic resin from 3 to 5 phr matches the particle sizes of dispersed ENR50 phase in Table 1. Fig. 3(c) shows the effect of ENR50 particle size on tensile strength of PVDF/ENR50 TPV. Tensile strength decreased rapidly with rubber particle size. It is well-known that the size of cross-linked rubber particles in a TPV plays an important role in its mechanical properties. L'Abee and co-worker stated that the enhancement of tensile strength is achieved via suppression of interlamellar void formation, and improved confinement that prevents the coalescence of voids [24, 25]. Many researchers have reported that decreased size of these rubber particles significantly increases the ultimate tensile strength and elastic recovery of a TPV. It was also reported that the improvement of mechanical properties of TPV is strongly dependent on physical and chemical interactions between the blend components in the TPV [21, 26, 27]. However, above 5 phr of phenolic resin both tensile strength and elongation at break were slightly decreasing. This may be attributed to excessive phenolic resin in the TPV as double bonds in the ENR50 are limited. The unreacted phenolic resin adhered to itself forming micelles in the continuous PVDF phase, and these could act as faults or weak points in the TPV. Hence, poor mechanical properties were observed for TPVs with excessive loading of phenolic resin. This indicates that 5 phr of HRJ-10518 is an appropriate amount for the dynamic vulcanization of a PVDF/ENR50 blend. Additionally, in Fig. 3(d) the PVDF/ENR50 blends with phenolic resin show lower tension set than the case without phenolic resin, and tension set decreased with phenolic resin content. The low tension set indicates improved elastomeric behavior. Possibly the dispersion of crosslinked ENR in PVDF gives the TPV rubber-like properties and minimizes the tension set. Increased network density in the rubbery phase may improve the elastic recovery after tensile deformations [28].

3.1.3 Dynamic mechanical analysis

Fig. 4 shows the temperature dependencies of storage modulus and tan δ for the 40/60 PVDF/ENR50 blend with various amounts of HRJ-10518. Above -10°C, it can be observed that the PVDF/ENR50 blend without crosslinking shows a drastic drop of storage modulus by 4 orders of magnitude, while the dynamically cured PVDF/ENR50 blends show a sharp drop of storage modulus by 3 orders of magnitude. The larger decrease in storage modulus of the PVDF/ENR50 simple blend is due to the low stiffness of ENR50 phase without crosslinking. With added HRJ-10518, the storage modulus in the rubbery region is obviously higher than that of the simple blend. The cross-linked ENR50 domains behave like viscoelastic solids in the blend, significantly increasing the storage modulus [21]. Moreover, storage modulus in the rubbery region slightly increased with phenolic resin content. This is attributed to increased crosslink density in the ENR50 phase. However, a comparatively lower storage modulus was observed for the PVDF/ENR50 TPV with 11 phr curing agent. This matches the loss of tensile modulus in the PVDF/ENR50 TPV with 11 phr of phenolic resin, shown in Fig. 3(a). This loss of storage modulus might be attributed to excess phenolic resin in the TPV, as previously described. Furthermore, it can be clearly seen that the PVDF/ENR50 blends with or without dynamic vulcanization show the maximum peak of tan δ at -10°C, which matches the glass transition temperature of ENR50. The glass transition temperature of these phase separated systems will be discussed in more detail in the next section. The tan δ of dynamically cured PVDF/ENR50 blends is lower than that without phenolic resin, which indicates restricted chain mobility in the dynamically cured PVDF/ENR50 blends [29].

3.2 Effects of blend ratio

3.2.1 Morphological properties

Fig. 5 shows the phase development of dynamically cured PVDF/ENR50 blends with various ENR50 contents. It is clear that spherical cross-linked ENR50 domains were observed in all the dynamically cured blends. Rubber particle size in PVDF/ENR50 TPV depended on the blend ratio. That is, the ENR50 domain size increased with the ENR50 loading. The average sizes of ENR50 particles in PVDF/ENR50 TPV containing 20 and 30 wt% ENR50 were measured to be around 0.7 to 1.0 μm, as shown in Table 2. However, the particle sizes with 50 to 80 wt% ENR50 are in the range from 1.3 to 2.0 μm. This demonstrates that the cross-linked domains became larger with ENR50 content. In the dynamically cured blends with high rubber content, the rubber domains were able to re-agglomerate during blending to coalesce into larger dispersed rubber domains. Moreover, the crosslinking of rubber lead to partial connectivity and co-continuity of the rubber phase in TPVs with high rubber contents. This phenomenon has been reported earlier for blends with high rubber content [30-32].

3.2.2 Mechanical properties

The stress-strain curves of dynamically cured PVDF/ENR50 blends with various blend ratios are shown in Fig. 6(a). It is clearly seen that the blend with highest PVDF content (i.e., PVDF/ENR50 80/20) showed brittle deformation behavior with maximum stress or yield stress at 22 MPa.This reflects the deformation characteristics of the dominant thermoplastic phase in the blend [33]. As ENR50 loading increased, the yield point disappeared and brittleness of the blend was reduced as the deformation of PVDF/ENR50 blend became rubber-like with the final rupture requiring large deformation. Furthermore, the initial slopes of the stress-strain curves (Young's modulus) decreased with ENR50 content as the soft rubber phase lowered the modulus of the blend [34]. The tensile strength and elongation at break for the dynamically cured PVDF/ENR50 blends is summarized in Fig. 6(b). It is clear that the tensile strength decreased whereas elongation at break increased with ENR50 content. It is well-known that rubber phases in a thermoplastic matrix can give rubbery behavior, so the composite becomes a thermoplastic elastomer. The remarkable increase in elongation at break of PVDF/ENR50 TPV with high ENR50 content is mainly attributed to the high molecular chain flexibility of ENR50. This is typical of TPVs with good elastomeric properties. However, it was also found that the elongation at break of PVDF/ENR50 TPV slightly decreased with 80wt% ENR50. This is possibly due to the large particle size of cross-linked ENR50 domains in the PVDF matrix, as seen in Fig. 5(f). Also the continuity of the matrix phase became less robust with high rubber content, causing decreased elongation at break [35]. Fig. 7 shows the effects of ENR50 content on tension set of PVDF/ENR50 TPV. It is clearly seen that tension set decreased with ENR50 content. This indicates reduced permanent deformation and improved elastomeric properties. The cross-linked rubber domains in the TPV contributed to reversibility and small residual strains as the deformation of thermoplastic matrix is partly pulled back by the recovery of rubber domains [22, 35].

3.2.3 Dynamic Mechanical Analysis

Fig. 8 shows temperature dependences of storage modulus and tan δ for the dynamically cured PVDF/ENR50 blends with various blend ratios. The storage modulus was very high (104

MPa) at low temperatures because the polymer was in glassy state. The storage modulus sharply decreases at a certain temperature known as the glass transition temperature (T_g). Above the glass transition temperature is the rubbery region, in which the storage modulus further decreases due to segmental motions of the polymer chains. In this region, the storage modulus of TPV is highly dependent on the ENR50 content. That is, the storage modulus of PVDF/ENR50 TPV decreased with ENR50 content, due to a dilution effect. At low ENR50 contents the modulus is dominated by the PVDF hard phase with high stiffness. As the ENR50 loading increases, the soft phase becomes dominant in the blend that becomes soft elastomeric material [36].

All the blends showed two relaxation peaks (tan δ peaks) in the temperature range from -50 to 0°C, as seen in Fig. 8. The first relaxation peak (-40°C) corresponds to β or α_a-relaxation of the PVDF phase, which is attributed to segmental motions in the amorphous regions [37, 38]. This is the glass transition temperature (T_g) of PVDF. The second relaxation peak appeared at -10°C and corresponds to glass transition of the ENR50 [39]. The dependence of these T_gs of the blend components on ENR50 content is summarized in Fig. 9. It can be observed that the T_g of ENR50 shifted to lower temperatures with the addition of PVDF. In the case of 80/20 PVDF/ENR50 TPV, the T_g of ENR50 phase is 6°C below that of pure ENR50. At the same time, the T_g of PVDF shifted to higher temperatures with increasing ENR50 content. In the case of 50/50 PVDF/ENR50 TPV, T_g of PVDF phase is 9°C higher than that of pure PVDF. TPVs with above 50 wt% ENR50 had only one T_g, that of ENR50, as the T_g of PVDF appeared only as a weak shoulder and could not be determined. Such shifting of T_gs towards each other in polymer blends has been reported previously [40-42]. As shown in Fig. 9, the T_gs of the PVDF and ENR50 shifted towards each other and are close to a single T_g (dashed line). This is due to the restriction of polymer chain mobility imparted by molecular interaction between two phases [5], indicating the partial miscibility of PVDF and ENR50. A schematic illustration of compatibilization between PVDF and ENR50 phases was proposed in Fig. 10. The fluorine atoms can form intermolecular H-bonding with ring opened epoxide groups in ENR50. As shown in Fig. 10(b), it can be observed that the symmetrical stretching vibration of the hydroxyl groups (-OH) shifted from 3347 to 3395 cm^{-1}, suggesting the formation of H-bonding between two phases [43]. These interfacial interactions contribute to phase compatibility and improve mechanical properties of the blends.

3.2.4 DSC measurement

DSC measurements were carried out to study melting and crystallization behaviors of the PVDF/ENR TPVs. Fig. 11 shows the DSC thermograms of PVDF/ENR50 TPVs prepared with different blend ratios. The degree of crystallinity, and crystallization and melting peak temperatures of the blends are summarized in Table 3. The crystallization temperature (T_c) and melting temperature (T_m) of neat PVDF were around 135°C and 168°C, respectively. With increasing ENR50 content, no significant changes in the Tm were observed. However, the Tc of any PVDF/ENR50 TPV was higher than that of neat PVDF. The increased T_c of TPV is attributed to nucleation by the rubber particles in the semi-crystalline polymer matrix phase [44]. According to l'Abee, the nucleating ability originates from amorphous segments of the thermoplastic grafted on rubber particles, which reduces the loss of entropy upon crystallization, and, therefore, gives higher T_c [16]. Thus, the increase in crystallization temperature of PVDF/ENR50 was induced by the partial miscibility of PVDF and ENR50 discussed earlier. This indicates that the molecular interactions of PVDF and ENR50 play a role by trapping PVDF segments on the ENR50 particles and this nucleates the crystallization of PVDF. However, with ENR50 contents 70 and 80 wt% the crystallization temperature (T_c) slightly decreased relative to lower ENR50 contents. This might be attributed to the agglomeration of ENR50 particles, resulting in retardation the growth of PVDF crystals. Moreover, it should be also noted that the crosslinked ENR50 particles decreased the full width at half maximum (FWHM) and the crystallization time (t_c), indicating faster crystallization with the rubber particles as heterogeneous nucleation sites in the TPV [16].

4. Conclusions

The effects of curative content and blend composition on the properties of PVDF/ENR50 blends were investigated. The 40/60 PVDF/ENR50 simple blend shows a dispersed PVDF phase in ENR-50 matrix phase, whereas the dynamically cured 40/60 PVDF/ENR50 blend had dispersed ENR50 in continuous PVDF matrix. The phenolic resin curative reduced ENR50 domain size and altered the phase structure of the blend. Moreover, dynamic crosslinking of the ENR50 phase improved mechanical properties of the PVDF/ENR50 TPV. Tensile strength increased initially with the addition of phenolic resin, reached a maximum at 5 phr and then slightly decreased with further addition of HRJ-10518 curative. The elasticity and rubber-like behavior of dynamically cured PVDF/ENR50 blends strongly depended on their ENR50 content. That is, a high ENR50 loading in the PVDF/ENR50 TPV provided superior elongation at break and elastic recovery, while the tensile strength was reduced. The dynamic mechanical properties revealed two glass transition temperatures for a PVDF/ENR50 blend, which is common for immiscible blends. However, the T_gs of the phases shifted towards each other, indicating partial miscibility in the dynamically cured PVDF/ENR50 blends. Moreover, it appears that the crosslinked ENR50 particles could act as nucleating agents for crystallization of PVDF in the PVDF/ENR50 TPV.

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Table 1. The number-average diameter (D_n), volume-average diameter (D_v), polydispersity index (PDI) and swelling ratio of PVDF/ENR blends with various amounts of the phenolic resin HRJ-10518.

HRJ-10518 content (phr)	D_n (μm)	D_v (μm)	PDI	Swelling ratio
3	4.04	4.40	1.10	7.72 ± 1.00
4	1.80	2.40	1.33	5.44 ± 0.06
5	1.33	1.54	1.16	4.63 ± 0.19
7	1.23	1.45	1.17	4.09 ± 0.06
9	1.71	1.88	1.10	3.94 ± 0.03
11	1.26	1.54	1.22	3.79 ± 0.16

Table 2. The number-average diameter (D_n), volume-average diameter (D_v), and polydispersity index (PDI) of PVDF/ENR blends with various blend proportions.

PVDF/ENR50 TPV (wt%)	D_n (μm)	D_v (μm)	PDI
80/20	0.92	1.14	1.25
70/30	0.77	0.92	1.19
60/40	1.36	1.57	1.13
50/50	1.33	1.54	1.16
40/60	1.47	1.71	1.17
30/70	1.87	2.25	1.20
20/80	2.06	2.58	1.25

Table 3. Thermal properties of PVDF/ENR50 TPVs with various blend proportions.

PVDF/ENR50	**Crystallization peak**	**Melting peak**

TPV (wt%)	T_c (°C)	FWHM* (°C)	t_c (min)	T_m (°C)	ΔH_m	X_c (%)
100/0	135.8	5.8	1.06	168.4	52.55	50.3
80/20	139.1	3.6	0.72	167.8	42.32	50.6
70/30	139.6	4.0	0.62	167.9	37.08	50.7
60/40	137.4	4.3	1.00	167.9	32.11	51.2
50/50	139.0	3.7	0.74	167.6	26.95	52.0
40/60	138.2	3.8	0.86	167.0	21.95	53.5
30/70	137.3	4.6	0.87	166.6	15.49	49.4
20/80	137.6	4.5	0.86	166.4	10.63	50.8

*FWHM: Full Width at Half Maximum of crystallization peak

Figure Captions

Fig. 1. Mixing torque-time relationship of PVDF/ENR50 blends without (TPE) and with dynamic vulcanization (TPV).

Fig. 2. SEM micrographs of 40/60 PVDF/ENR50 blends with select amounts of phenolic resin: (a) 0, (b) 3, (c) 4, (d) 5, (e) 9, and (f) 11 phr. For the blend with 0 phr of phenolic resin, morphology evaluation was investigated without extraction. For a dynamically cured blend, the PVDF continuous phase was etched in DMSO at 80°C for 10 min.

Fig. 3. Mechanical properties of the PVDF/ENR50 blends with various amounts of phenolic resin: (a) stress-strain curves, (b) tensile strength and elongation at break as functions of phenolic resin content, (c) the relation of ENR50 particle size with tensile strength, and (d) tension set as function of phenolic resin content.

Fig. 4. Temperature dependence of storage modulus and tan δ for the 40/60 PVDF/ENR50 blends with various amounts of phenolic resin.

Fig. 5. SEM micrographs of dynamically cured PVDF/ENR50 blends with different blend ratios: (a) 80/20, (b) 70/30, (c) 60/40, (d) 40/50, (e) 30/70, and (f) 20/80.

Fig. 6. Mechanical properties of PVDF/ENR50 TPVs with different blend ratios; (a) stress-strain curves, (b) tensile strength and elongation at break as functions of ENR50 content.

Fig. 7. Tension set of PVDF/ENR50 versus its ENR50 content.

Fig. 8. Temperature dependences of storage modulus and tan δ for the PVDF/ENR50 TPVs with different blend ratios.

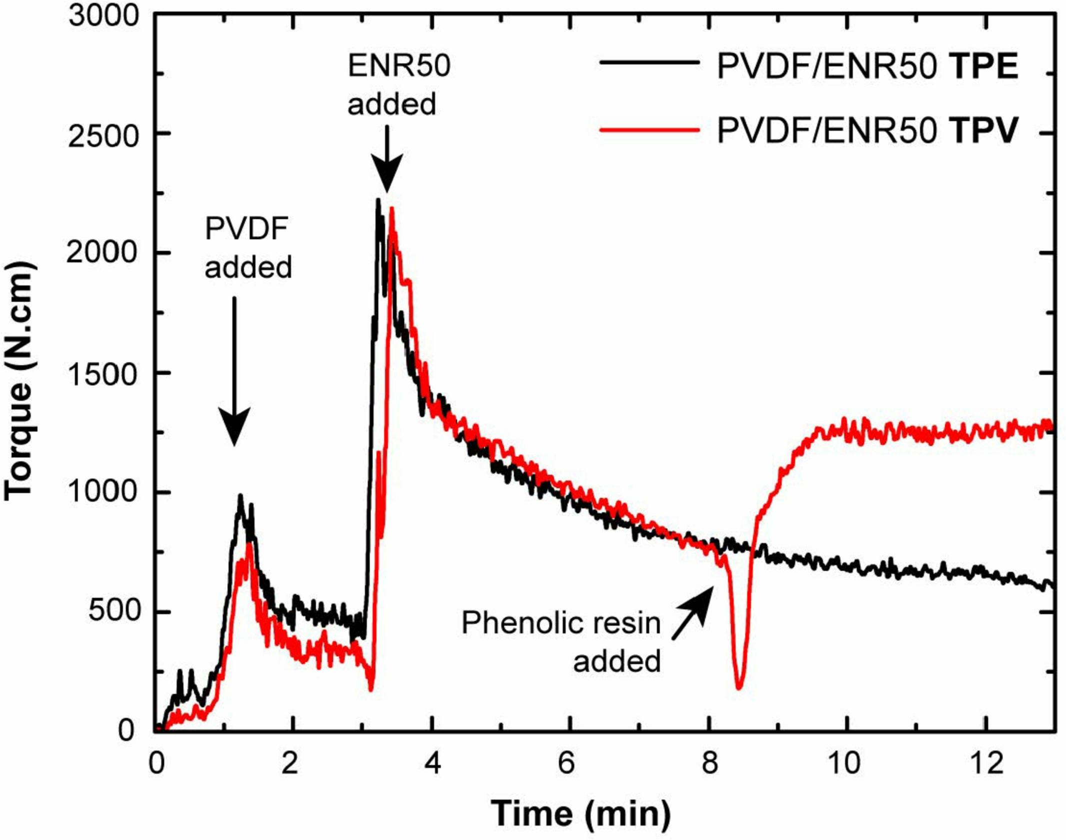
Fig. 9. Glass transition temperatures (T_g) of PVDF and ENR50 phases as functions of ENR50 content in the PVDF/ENR50 TPVs. Dashed line is a single T_g for fully miscible blend.

Fig. 10. Proposed scheme for interfacial interactions in dynamically cured PVDF/ENR50 blend, (b) FTIR spectra of neat PVDF, neat ENR50 and PVDF/ENR50 blend.

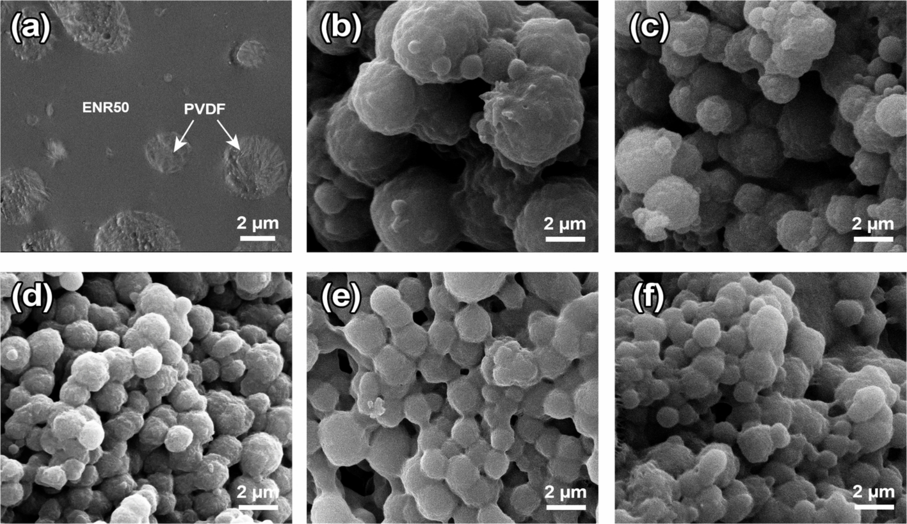
Fig. 11. DSC thermograms; (a) heating, and (b) cooling scans of PVDF/ENR50 TPVs with various blend proportions.

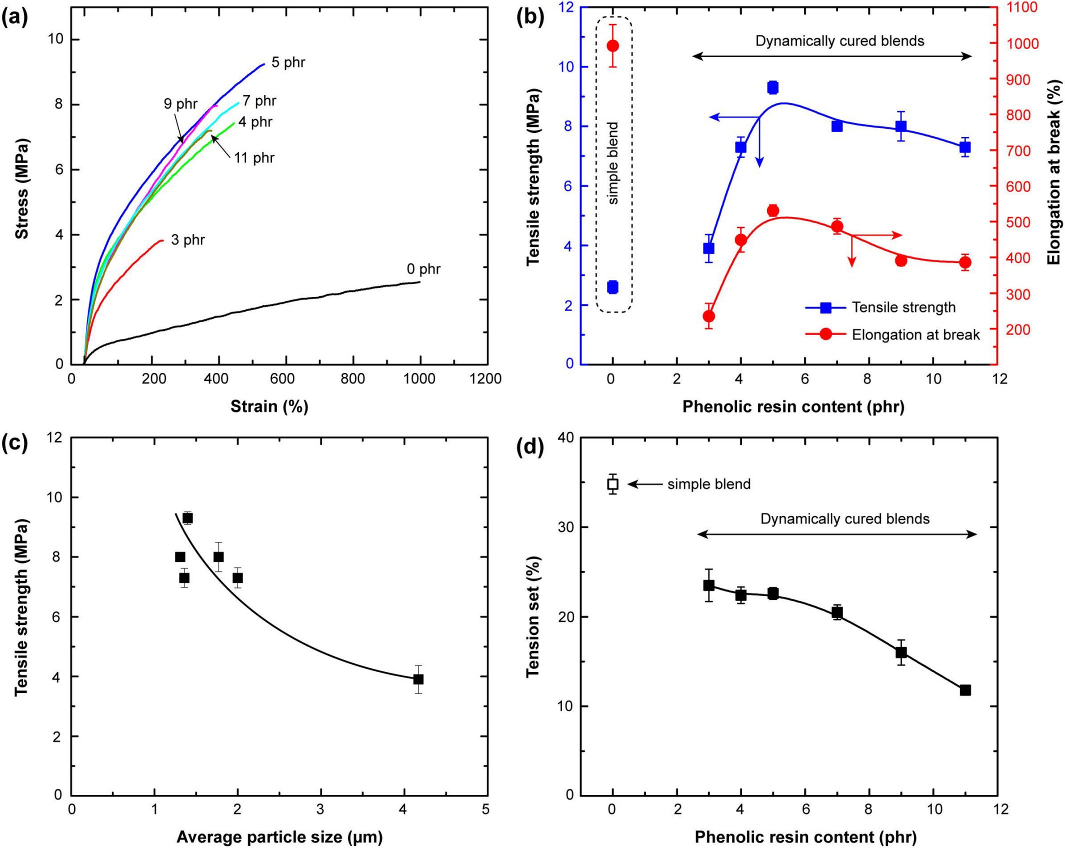
Highlights

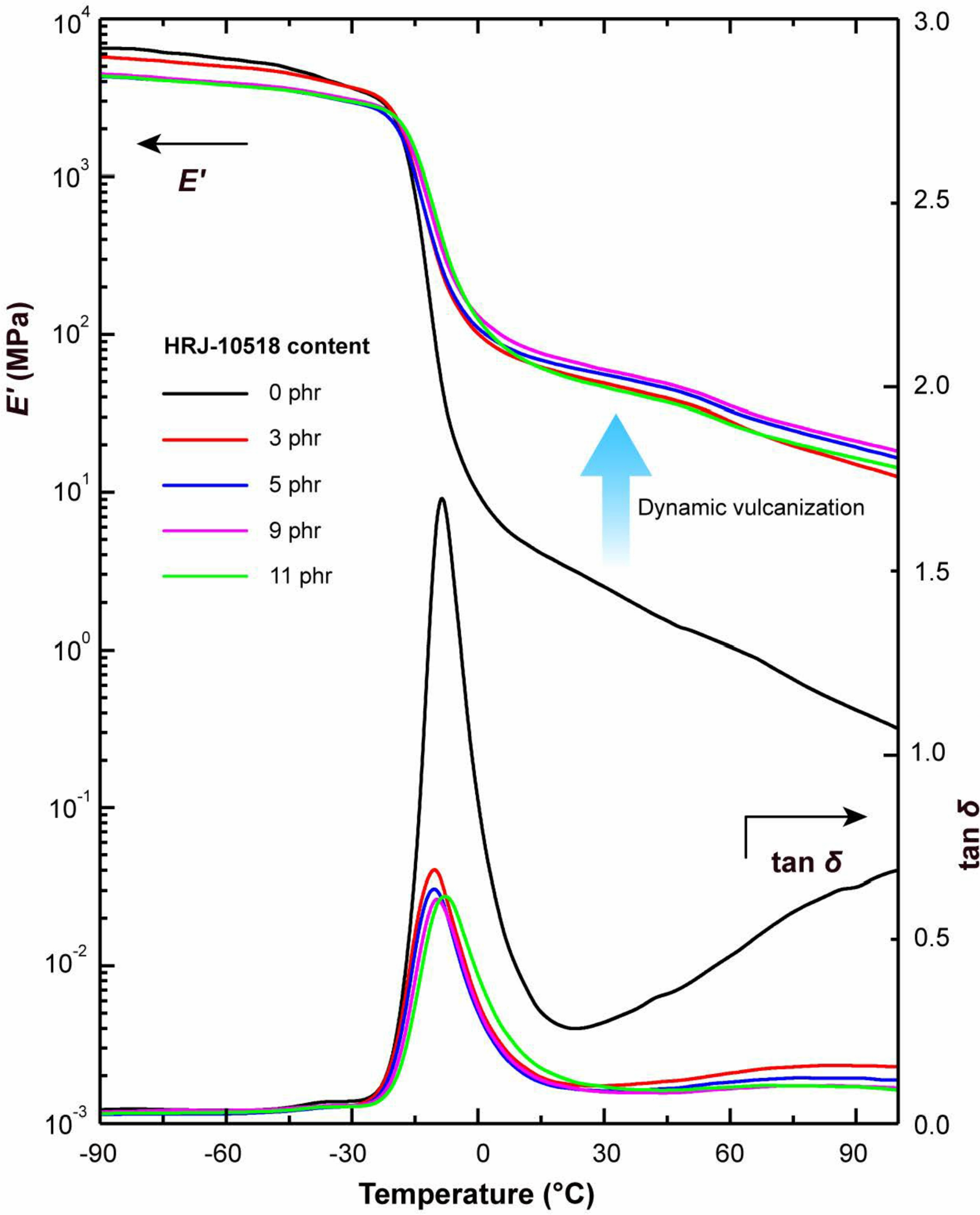
- The effect of phenolic content and blend ratio were investigated.
- The SEM revealed the phase inversion and domain size of rubber phases.
- Improved phase morphology and mechanical properties were archeived by phenolic resin.
- Compatibilization and partial miscibility between PVDF and ENR50 were observed.
- Dynamically cured PVDF/ENR50 blends exhibit excellent mechanical properties and elastic recovery.

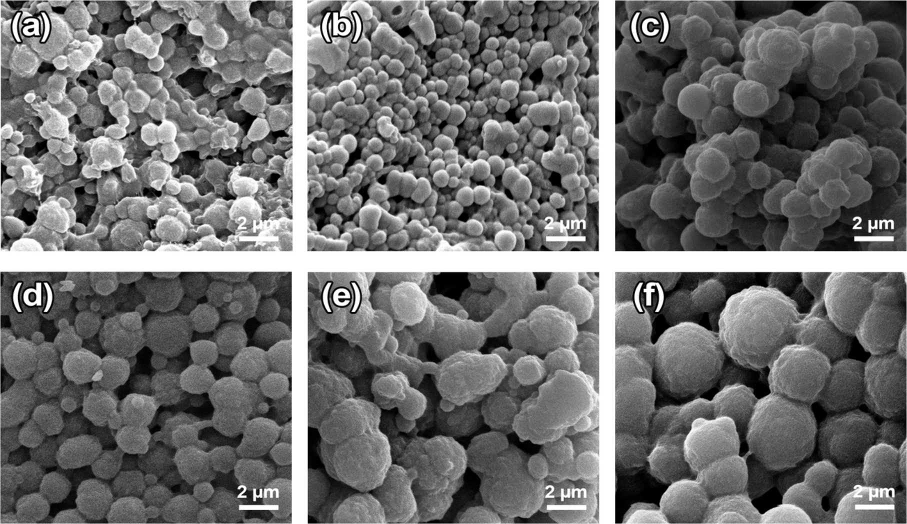


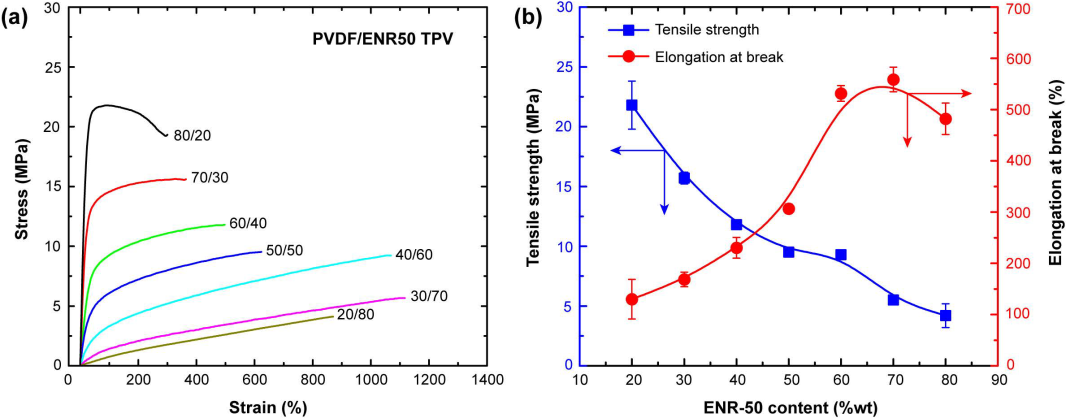
PVDF/ENR50 **TPE**
PVDF/ENR50 **TPV**
PVDF added
ENR50 added
Phenolic resin added
Torque (N.cm)
Time (min)
0
500
1000
1500
2000
2500
3000
0
2
4
6
8
10
12

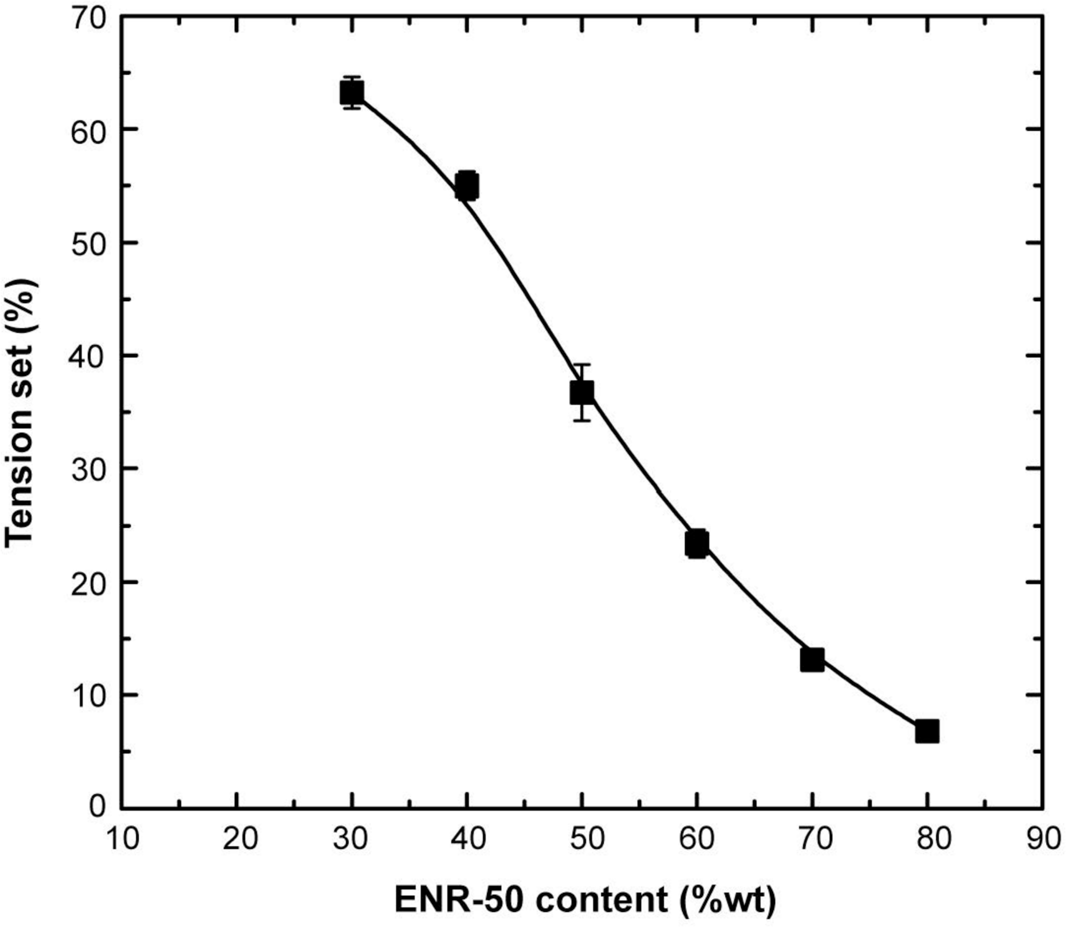

(a)
ENR50
PVDF
2 μm
(b)
2 μm
(c)
2 μm
(d)
2 μm
(e)
2 μm
(f)
2 μm

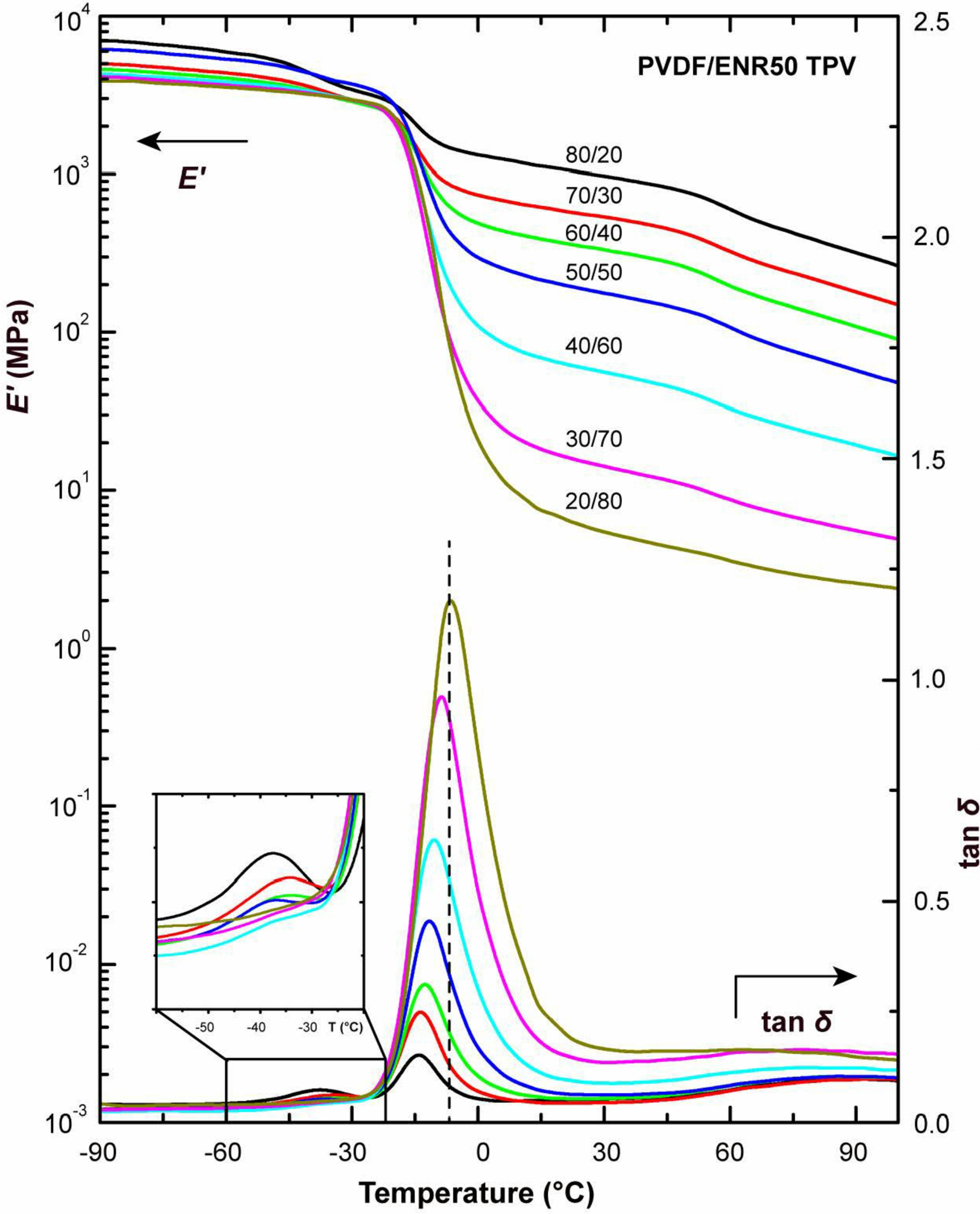

(a)
Stress (MPa)
Strain (%)
5 phr
7 phr
9 phr
4 phr
11 phr
3 phr
0 phr
0
2
4
6
8
10
0
200
400
600
800
1000
1200
(b)
Tensile strength (MPa)
Elongation at break (%)
Phenolic resin content (phr)
simple blend
Dynamically cured blends
Tensile strength
Elongation at break
0
2
4
6
8
10
12
200
300
400
500
600
700
800
900
1000
1100
(c)
Tensile strength (MPa)
Average particle size (μm)
0
1
2
3
4
5
(d)
Tension set (%)
Phenolic resin content (phr)
simple blend
Dynamically cured blends
0
10
20
30
40

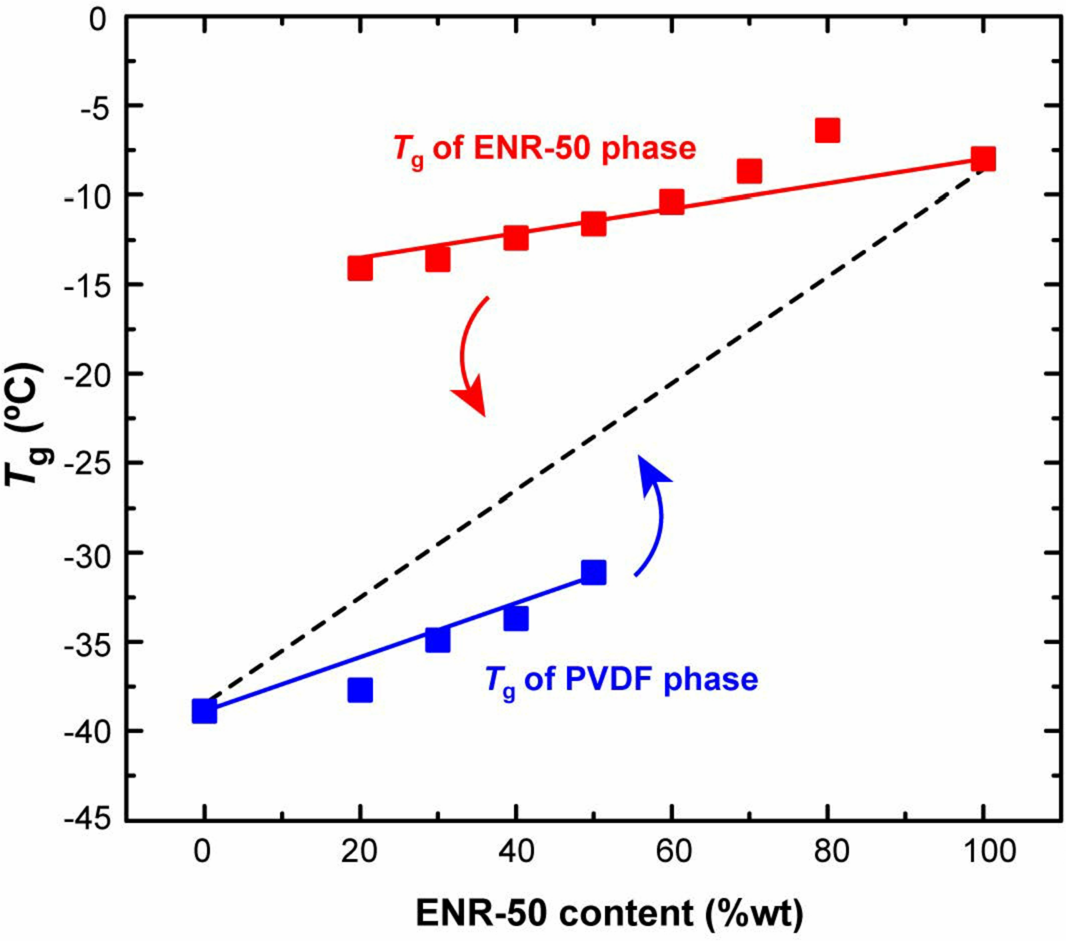

10^4
10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
10^{-3}
E′ (MPa)
E′
HRJ-10518 content
0 phr
3 phr
5 phr
9 phr
11 phr
Dynamic vulcanization
tan δ
3.0
2.5
2.0
1.5
1.0
0.5
0.0
tan δ
-90
-60
-30
0
30
60
90
Temperature (°C)

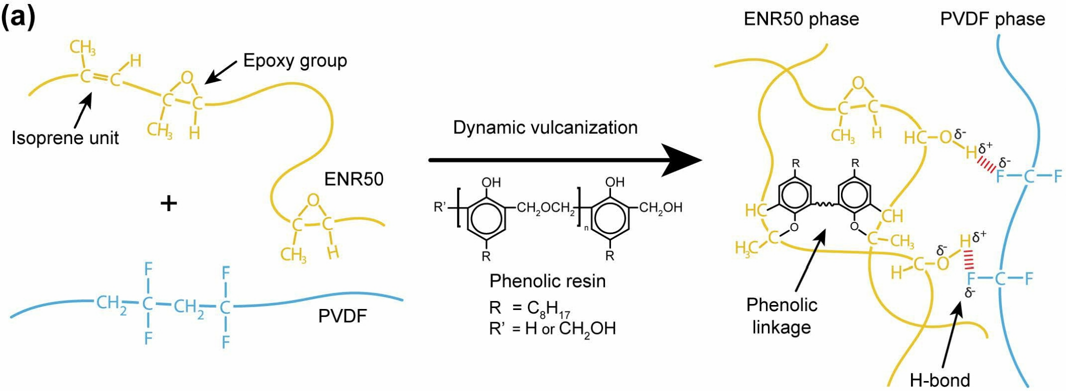

(a)
2 μm
(b)
2 μm
(c)
2 μm
(d)
2 μm
(e)
2 μm
(f)
2 μm

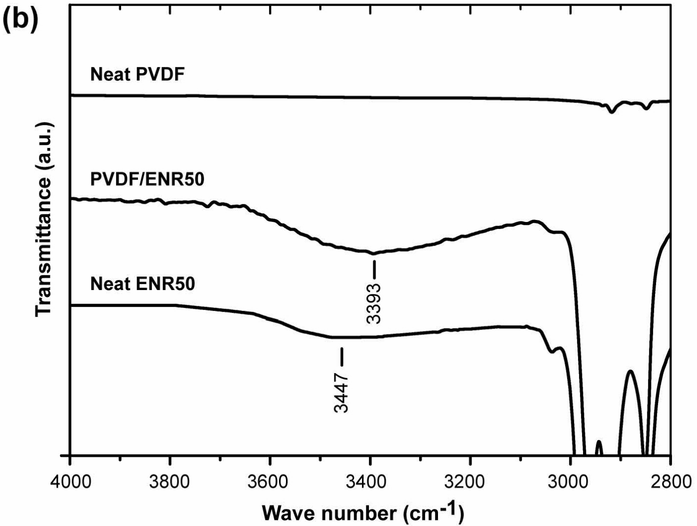

(a)
PVDF/ENR50 TPV
Stress (MPa)
Strain (%)
0
5
10
15
20
25
30
0
200
400
600
800
1000
1200
1400
80/20
70/30
60/40
50/50
40/60
30/70
20/80
(b)
Tensile strength
Elongation at break
Tensile strength (MPa)
Elongation at break (%)
ENR-50 content (%wt)
0
5
10
15
20
25
30
0
100
200
300
400
500
600
700
10
20
30
40
50
60
70
80
90

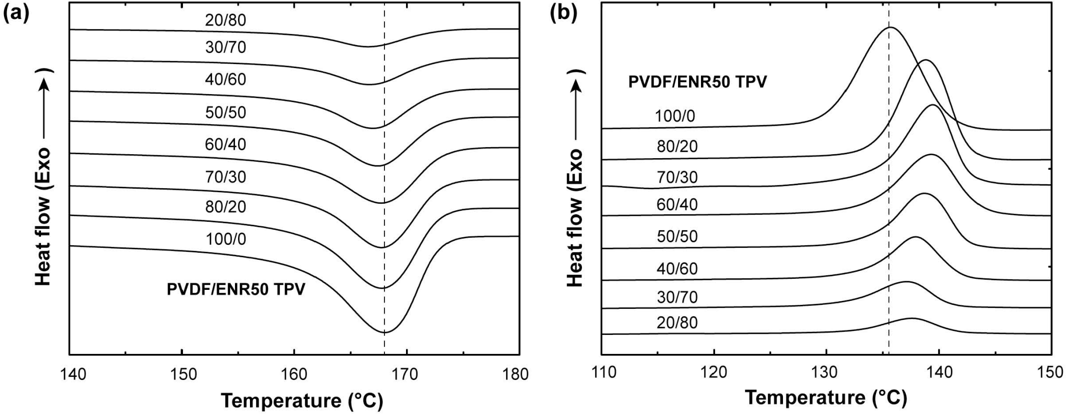

Tension set (%)
0
10
20
30
40
50
60
70
10
20
30
40
50
60
70
80
90
ENR-50 content (%wt)


PVDF/ENR50 TPV
E'
E' (MPa)
tan δ
80/20
70/30
60/40
50/50
40/60
30/70
20/80
10^4
10^3
10^2
10^1
10^0
10^-1
10^-2
10^-3
2.5
2.0
1.5
1.0
0.5
0.0
-90
-60
-30
0
30
60
90
Temperature (°C)
-50
-40
-30
T (°C)


T_g of ENR-50 phase
T_g of PVDF phase
T_g (ºC)
ENR-50 content (%wt)
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
0
20
40
60
80
100


(a)
CH3
H
Epoxy group
O
C
C
C
C
Isoprene unit
CH3
H
ENR50
+
CH2
CH2
F
F
F
F
PVDF
Dynamic vulcanization
OH
OH
R'
CH2OCH2
CH2OH
n
R
R
Phenolic resin
R = C8H17
R' = H or CH2OH
ENR50 phase
PVDF phase
HC
O
δ-
H
δ+
δ-
F
C
F
R
R
HC
CH
H3C
CH3
O
O
δ-
δ+
δ-
Phenolic linkage
H-bond


(b)
Neat PVDF
PVDF/ENR50
Neat ENR50
3393
3447
Transmittance (a.u.)
4000
3800
3600
3400
3200
3000
2800
Wave number (cm-1)


(a)
Heat flow (Exo ⟶)
20/80
30/70
40/60
50/50
60/40
70/30
80/20
100/0
PVDF/ENR50 TPV
140
150
160
170
180
Temperature (°C)
(b)
Heat flow (Exo ⟶)
PVDF/ENR50 TPV
100/0
80/20
70/30
60/40
50/50
40/60
30/70
20/80
110
120
130
140
150
Temperature (°C)