

Chlorosulfonated Polyethylene–Polypropylene Thermoplastic Vulcanizate: Mechanical, Morphological, Thermal, and Rheological Properties

Asis K. Mandal,¹ Samir K. Siddhanta,² Debabrata Chakraborty³

¹Dumkal Institute of Engineering and Technology, Murshidabad 742406, West Bengal University of Technology, West Bengal, India

²Department of Chemistry, The Bhawanipur E.S.College, Kolkata 700020, India

³Department of Polymer Science and Technology, University of Calcutta, Kolkata 700009, India

Correspondence to: D. Chakraborty (E-mail: chakrabarty_deb@yahoo.com)

ABSTRACT: Different thermoplastic vulcanizate (TPV) blends were prepared from elastomeric chlorosulfonated polyethylene (CSM) and thermoplastic polypropylene (PP) by employing dynamic vulcanization technique. The mechanical properties of such blends were compared in respect of their stress at 25% modulus (25%M), ultimate tensile strength (UTS), percent elongation at break, and hardness to those of pure CSM. The mechanical analysis showed substantial improvement in stress at 25%M, UTS, and hardness values with the incorporation of 15–40 parts of thermoplastic contents (PP) (per hundred parts of blend). The two-phase morphologies were clearly observed by **scanning electron microscopy** studies. The thermal properties were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). DSC studies showed a decreasing trend in glass transition temperature (T_g) and TGA studies indicated the increase in thermal stability of all TPV blends with respect to the elastomeric CSM. Rheological studies showed that there is an increasing trend in shear melt viscosity of TPV blends with the increase in PP amount as the higher content of isotactic PP used in the present case increases the melt viscosity. The TPVs obtained after the rheotron studies displayed identical shear stress/strain pattern when further subjected to the same study. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Thermoplastic elastomer (TPE) blends have become technologically useful in recent years as they have many of the properties of elastomers but are processable as thermoplastics. TPE blends generally have the structure with two distinct phases where one is of low modulus and easily deformable and the other one is rigid which acts as a link between the soft and the flexible regions. When this type of blend is heated above the melt processing temperature of the rigid phase, it will melt and allow the polymer to flow. At a temperature below this, it will behave like an elastomer. The ideal TPE blend comprises finely divided elastomer particles dispersed in a relatively small amount of plastic. The elastomer particles should be crosslinked to promote elasticity.^{1,2}

The best way to prepare TPE blends also termed as thermoplastic vulcanizates (TPVs) comprising vulcanized elastomer particles dispersed in melt processable thermoplastic materials is by

dynamic vulcanization. The TPVs produced in this way are characterized by finely dispersed, micron-sized, crosslinked rubber particles distributed in a thermoplastics matrix. As the rubber particles of such blends are vulcanized, the different properties such as mechanical, permanent set, and elastic recovery, resistance to effect by fluids, etc., are remarkably improved.^{3–5} Considerable efforts have been directed to the area of TPVs based on polypropylene (PP), polyamides (nylon), high-impact polystyrene, etc., as continuous phase and different elastomers such as natural rubber (NR) and also some synthetic rubbers, for example, ethylene-propylene-diene monomer (EPDM), ethylene–octene copolymer, butadiene–acrylonitrile rubber, styrene-butadiene rubber, silicone rubber, etc.^{2,6–12} Different modified forms of NRs such as epoxidized NR and grafted copolymers of NR with poly(methyl methacrylate) have also been used to prepare TPVs.^{13,14} The major research studies in the area of TPVs are concentrated mostly on EPDM.

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Chlorosulfonated polyethylene (CSM) (hypalon) is an important elastomer, which, however, possesses poor mechanical properties as it is completely amorphous in nature and also suffers from the disadvantages of poor processing. PP is relatively more crystalline thermoplastic possessing good processability and also good solvent resistance. In the present study, a TPV based on CSM as the elastomeric component, and PP as thermoplastic continuous phase was prepared in the absence of any compatibilizer via dynamic vulcanization process. The mechanical and thermal properties of the prepared TPVs are discussed here in relation to their morphology and rheology.

MATERIALS

Rubber used in this study is Hypalon-40 (CSM, Cl = 35%, S = 1%, manufactured from Dupont Performance Elastomers L.L.C., New York). The typical properties of Hypalon-40 used are Mooney viscosity M L (1+4) at 100°C 56, Specific gravity 1.18. The thermoplastic used in the present study was PP homopolymer (Repol HO 30SG, having an MFI of 3.0 g/10 min) supplied by M/S Reliance industries (Mumbai, India). The magnesium oxide (MgO) used as an accelerator activator was manufactured by Konoshima Chemical, Osaka, Japan. The dipentamethylenethiuram tetrasulfide (DPTT) used as an accelerator and crosslinker was supplied by Flexsys, Singapore. Ni dibutyl carbamate (NBC) used as an antioxidant was obtained from PMP groups of industries, India.

Compounding of Unvulcanized CSM

CSM was masticated initially for 5 min in two-roll mill. Then MgO, NBC, and DPTT were added gradually one after another to the masticated Hypalon at an interval of 1 min. The amounts of different ingredients are listed in Table I. Finally, compounded CSM was obtained as a sheet form. The total time required was 8 min.

Blending

The unvulcanized compounded CSM was subsequently blended with PP in different proportions (Table II) at 170°C for 10 min in a Brabender mixer with the help of two rotors housed in a case at the speed of 80 rpm.⁸ The CSM/PP blend was collected as a lump form. The sheet form with required thickness of such blends was prepared from its lump in a two-roll mill.

Processing

All blends, CSM, and PP were compression-molded in the form of rectangular sheet in a Moore press (temperature: 170°C, pressure: 35 kg/cm², time: 10 min).

Table I. Compounding Formulations

Ingredients	Quantity (parts per hundred parts of rubber, phr)
CSM	100
MgO	8
PETP	3
DPTT	4

Table II. Compositions of Different TPVs

Sample	Compositions (by weight)	
	Hypalon	PP
A	100	0
B	85	15
C	80	20
D	70	30
E	60	40
F	0	100

Characterizations

Tensile properties such as stress at 25% modulus (25%M), ultimate tensile strength (UTS), and percent elongation at break (%EB) were measured according to ASTM D 418-98A using universal testing machine, Instron, Model 4302. The samples were punched from a compression-molded sheet and inspected for pores and nicks before being subjected to testing. The strain rate was 300 mm/min. All measurements were carried out at room temperature. The data reported were averages of at least six measurements and typical scattering range of the results was $\pm 3\%$. The hardness was determined by means of durometer in shore A Scale following ASTM D-2240-64T.

The scanning electron micrographs for gold-coated samples were obtained on a Hitachi (S415A) microscope. For scanning electron microscopy (SEM) study, the sample was subjected to etching in toluene for 1 day. PP phase was expected to be removed in this way and finally the test specimen was dried in vacuum at 40°C. Differential scanning calorimetry (DSC) measurements were carried out from Shimadzu (DSC-50) in an inert atmosphere of nitrogen at a heating rate of 10°C/min. Thermogravimetric analysis (TGA) of various samples was carried out in a Perkin Elmer Delta series TGA-7 under nitrogen atmosphere at a heating rate of 20°C/min. The melt rheological properties of different blends were evaluated employing a constant shear rate plate and cone (angle, 3°), rotational viscometer (Rheotron 2744E from Brabender, Germany) at 200°C.

RESULTS AND DISCUSSION

Mixing Torque

Figure 1 shows the mixing torque–time curves of the TPVs prepared from various blend ratios of CSM/PP in the process of synthesizing TPVs. It can be seen that the mixing torque rose sharply when the rotors were started because of the resistance exerted on the rotors by the unmelted solid blend. The torque then decreased because PP melted and unvulcanized rubber softened on account of mechanical shearing and heat transfer from the heater. This created the first group of peaks of the mixing torque–time curves. The height of the peak increased with an increase in PP contents in the blends. This is obvious as the increasing proportions as isotactic PP imported more stiffness to the blend. A second peak was observed in the mixing torque–time plot, which is possibly owing to the resistance offered by *in situ* crosslinking CSM. It is interesting to note that the second peak becomes more and more prominent as the elastomeric component in the blend increases, whereas the peak becomes almost indistinguishable with the blends having higher

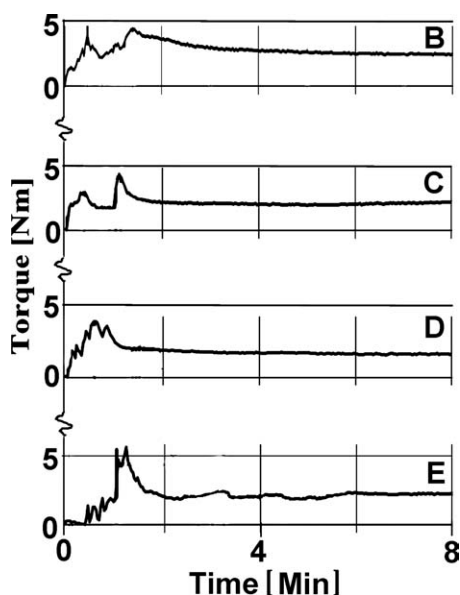


Figure 1. Plot of mixing torque values vs. times of different TPVs based on hypalon/PP blends containing different amounts of PP: (B) 15 parts, (C) 20 parts, (D) 30 parts, and (E) 40 parts.

proportions of PP. Thus, it can be presumed that as the rubber softens and flows afterward, it undergoes vulcanization, which enables the compound to offer more and more resistance, reaching a peak. Subsequently, when the vulcanized elastomer is shredded into microdomains by the shearing action of the rotor, it gets uniformly dispersed into the molten matrix of PP. The torque starts declining reaching equilibrium when the dispersion and distribution throughout the matrix is completed. The torque then maintains a constant value during the subsequent rotation of the rotors so as to ensure thorough and uniform mixing.

However, when the proportion of the elastomeric component decreases, the second peak was not very sharp. It may be assumed that the rate of dynamic vulcanization or the rate of formation of crosslinks in the elastomeric component leading to

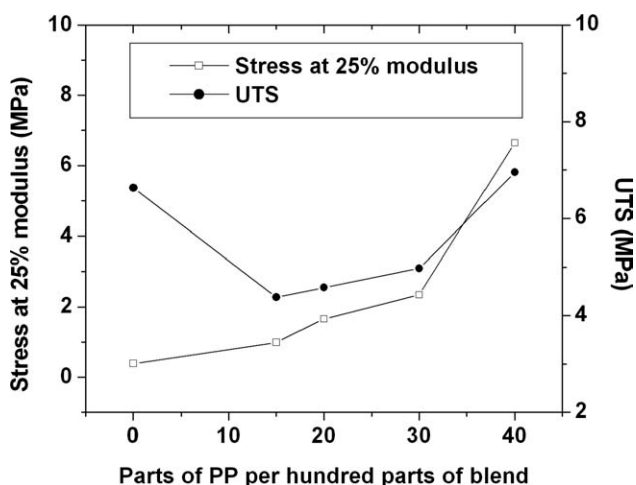


Figure 2. Plot of different stress at 25%M and UTS values of hypalon/PP blends with the variation of PP content.

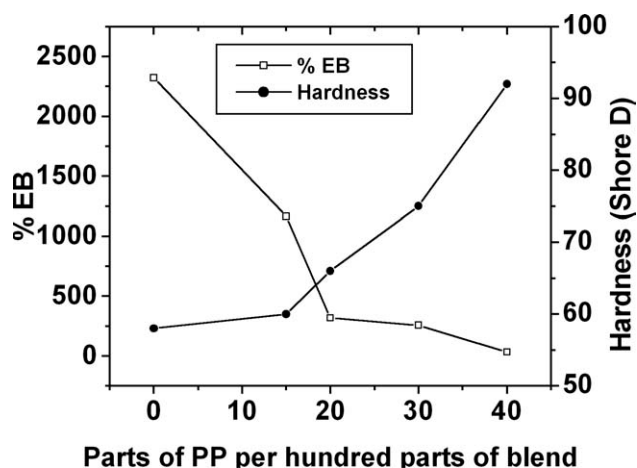


Figure 3. Plot of different %EB and hardness values of hypalon/PP blends with the variation of PP content.

increase in torque might be well balanced by the rate of its disintegration into microdomains. Thus, a dynamic equilibrium is expected to be arrived.

Mechanical Properties

The mechanical properties of the various TPVs as a function of variation in PP content are shown in Figures 2 and 3. Figure 2 shows the plots of different stress at 25%M and UTS values of TPVs with the variations of PP content, which indicates that there is a steady increase in 25%M values as expected with the increase in amount of PP.

Figure 3 shows the plots of %EB and hardness values of TPVs with the variation in PP contents. There is a steady decrease in %EB with the increase in PP content as expected and thus leads to a stiffer and brittle matrix. The hardness values of the various TPVs show increasing trend with the increase in proportions of PP, a phenomenon of normal expectations where moduli increases and %EB decreases.

Figure 4 shows the variations of specific gravities of TPVs in relation to their compositions. This is as per our expectations,

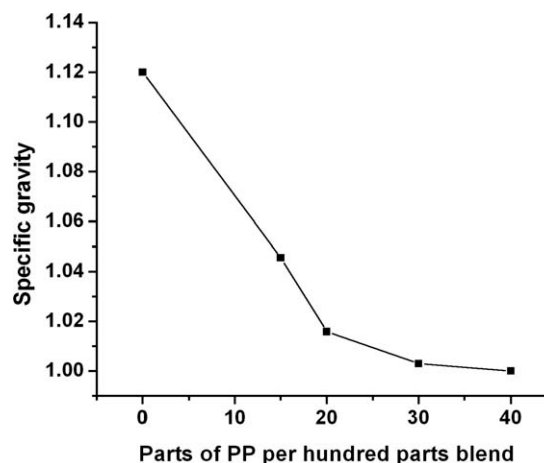


Figure 4. Plot of different specific gravity values of hypalon/PP blends with the variation of PP content.

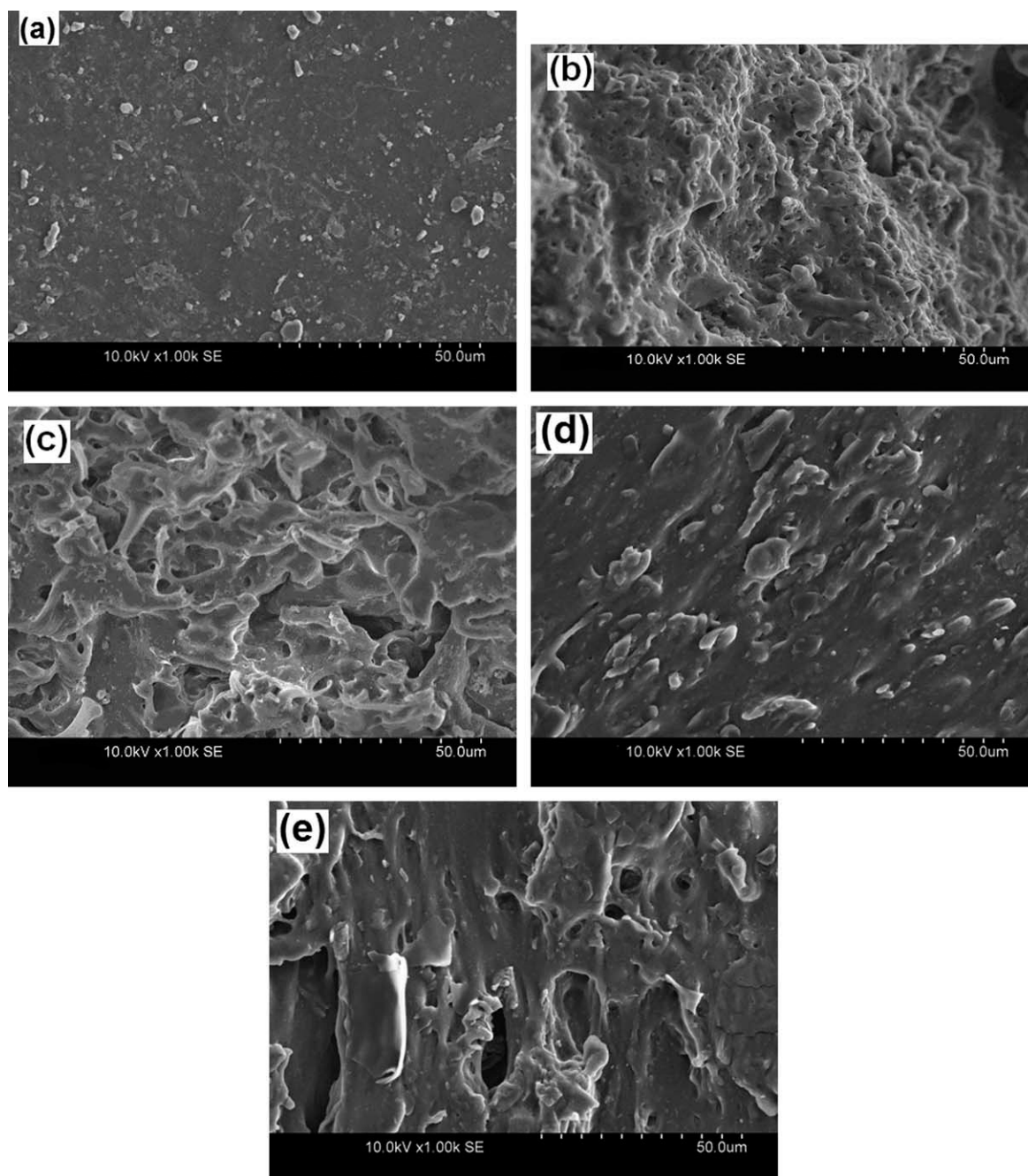


Figure 5. Scanning electron micrographs of (a) hypalon, (b) hypalon/PP blend (15 parts of PP), and (c) hypalon/PP blend (20 parts of PP).

as the incorporations of lighter PP moieties into the comparatively high-dense hypalon matrix might be expected to lead to a decrease in density of TPVs.

Morphology

Scanning Electron Microscopy. The scanning electron micrographs of the tensile fracture surfaces of hypalon and two representative hypalon/PP blends prepared by dynamic vulcanization are shown in Figure 5(a–c), respectively. Figure 5(a) shows a typical amorphous elastomer. Figure 5(b, c), however, exhibits a rough fracture surface, indicating ductile fracture behavior. The

extent of roughness is relatively lower in the pure rubber itself. The nature of the tearing strips on the fracture surfaces indicates thermoplastic behavior with reducing toughness with increasing PP consistent with the observation on elongation [Figure 5(b)]. The nature of the fracture surface is more smooth and continuous in Figure 5(b) than that in Figure 5(c), where the proportion of elastomer is reduced. It can be argued that in a TPV upon elongation the thin thermoplastic layer (which forms the matrix at the equator of the rubber particles) is subjected to plastic yielding and upon relaxation they is drawn back by the elastic rubber domains effectively. This

Table III. T_g , T_m , and ΔH of different TPVs

Sample	T_g (K)	T_m (K)	ΔH (J/g)
A	240.34	-	-
B	237.21	436.93	11.91
C	236.36	439.70	16.28
D	232.58	434.57	36.26
E	237.00	432.73	39.52
F	-	435.47	97.54

phenomenon of yielding and retraction decreases as the percentage of rubbery microdomains in the PP matrix is reduced.^{15,16} TPVs with higher percentage of PP are characterized by plastic yielding more predominantly as has been found in the present case.

Thermal Studies

Differential Scanning Calorimetry. The glass transition temperature (T_g), crystalline melting temperature (T_m), and enthalpy of crystallization (ΔH) as obtained from DSC studies on PP, hypalon, and different TPV systems are listed in Table III. The data were collected from the cooling curves and reheating curves, respectively. The typical DSC plots are compared in Figure 6. The increasing proportion of PP in the various TPV systems is reflected in their corresponding T_g values, as there is a gradual and steady decrease in T_g as PP content increases and

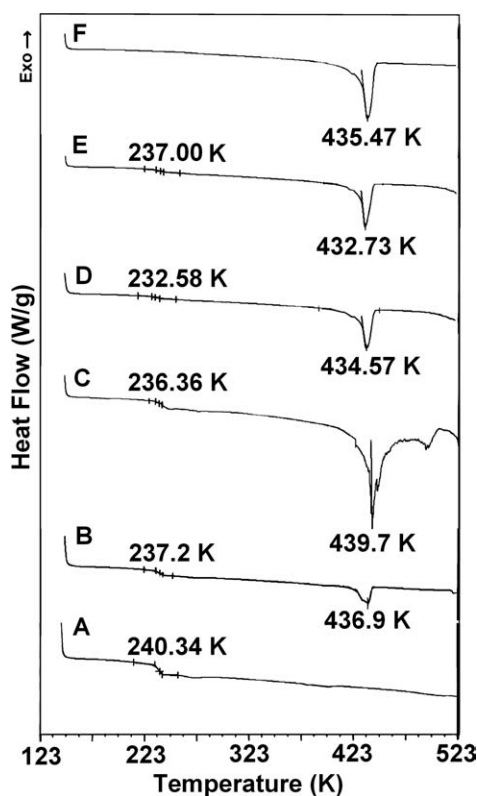


Figure 6. DSC plots of (A) hypalon, (B) hypalon/PP blend (15 parts of PP), (C) hypalon/PP blend (20 parts of PP), (D) hypalon/PP blend (30 parts of PP), (E) hypalon/PP blend (40 parts of PP), and (F) PP.

the value of T_g jumps from 232.58 to 237 K at 40 phr of PP. In the TPVs considered in the present study, the gradual incorporation of increasing proportion of PP appears to have very little influence on the temperature of crystallization. The virgin PP and the various TPVs in which the PP forms the matrix or continuous components to hold the microdomains of hypalon almost possess the identical temperature of crystallization. The T_m of the TPVs in a likewise manner almost remains the same as that for pure PP. Both the crystalline melting temperature and the temperature of crystallization are the thermal characteristics, which are controlled by the matrix only. For each of the blends, the PP phase displays a discrete peak in its crystalline melting temperature.

Thermogravimetric Analysis. The TGA thermograms of PP, CSM, and of different TPVs are shown in Figure 7. Derivative

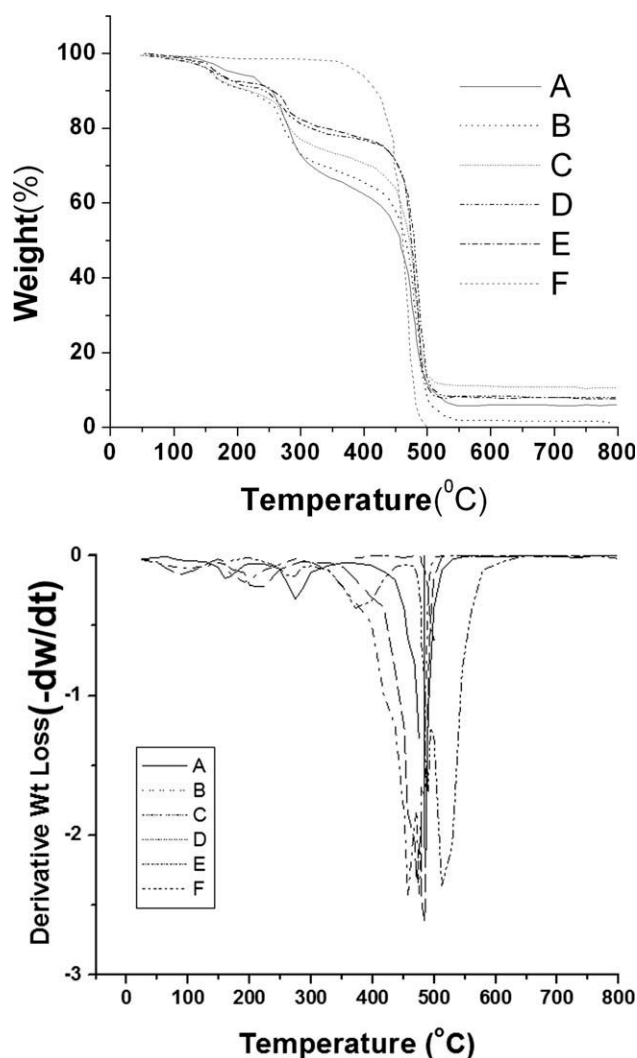


Figure 7. TGA of (A) hypalon, (B) hypalon/PP blend (15 parts of PP), (C) hypalon/PP blend (20 parts of PP), (D) hypalon/PP blend (30 parts of PP), (E) hypalon/PP blend (40 parts of PP), and (F) PP. (a) Derivative weight loss vs. temperature plot of (A) hypalon, (B) hypalon/PP blend (15 parts of PP), (C) hypalon/PP blend (20 parts of PP), (D) hypalon/PP blend (30 parts of PP), (E) hypalon/PP blend (40 parts of PP), and (F) PP.

of weight loss vs. temperature is also plotted in Figure 7(a). This comparative diagram is quite interesting and significant. Pure PP displays one-step degradation. Being nonpolar hydrocarbon, it is associated with little moisture; the curve F (PP only) shows no initial moisture loss. However, the pure rubber and the TPV systems considered in the present study curves A–E, respectively, exhibit stepwise degradation. For all most all, the initial mass loss up to about 210°C is owing to absorbed moisture and may be some unreacted accelerator and antioxidant release for CSM and also for TPVs. Again, a mass loss beginning at nearly 250°C and continuing till above 325°C presumably corresponds to large-scale thermal degradation, eliminating ethylene, chloroethylene, and sulfochloroethylene from CSM.¹⁷ The third stage of degradation observed in the temperature range of 400–450°C is owing to the main chain scission and residue left at 800°C is <10% for CSM. PP forming the matrix in the TPVs is degraded completely at a temperature of about 500°C. The pure CSM though initially less stable than PP leaves behind appreciable quantity of residue at 500°C, which remains thermally stable even above this temperature. The TPVs containing >20 parts of PP (including 20 parts) leave behind more and more residues with respect to either the pure rubber or PP. These TPVs also exhibit lower rate of degradation than the rubber and even with respect to PP, particularly at the higher temperature region under study. Thus, the overall thermal stability of the TPVs containing higher amount (≥ 20 parts) of PP is remarkably improved within the current study.

Rheology

The variation of melt viscosity of PP and of different TPVs with different shear rate is shown in Figure 8. The melt viscosity of PP at 200°C decreases very sharply initially and gradually the rate falls off. Only PP phase is melted during the rheological test and it is observed that the melt viscosity of the TPVs increases with increase in PP content within the range of shear rate studied, although toward the higher region of the shear

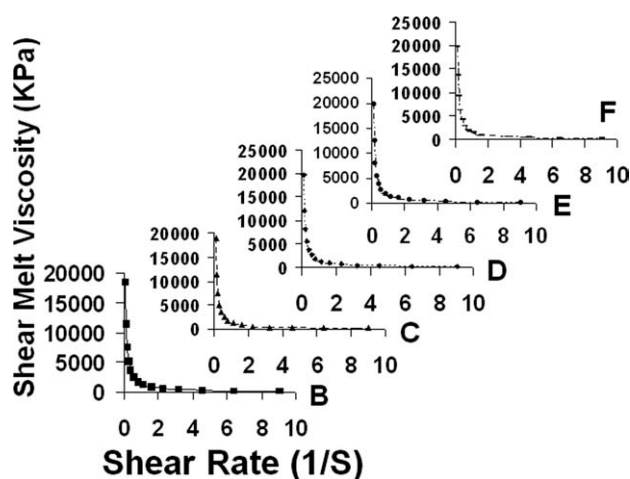


Figure 8. Plots of shear melt viscosity vs. shear rate of (B) hypalon/PP blend (15 parts of PP), (C) hypalon/PP blend (20 parts of PP), (D) hypalon/PP blend (30 parts of PP), (E) hypalon/PP blend (40 parts of PP), and (F) PP.

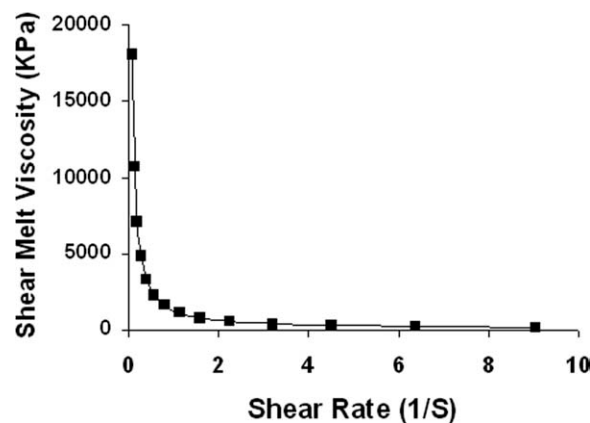


Figure 9. Plots of shear melt viscosity vs. shear rate of hypalon/PP blend (20 parts of PP) (same sample as used in Figure 8 further subjected to similar study).

rate, under study, the melt viscosities of the pure PP and TPVs merge together. The flow characteristics being dominated by the plastomeric component, which forms the matrix in the TPV systems, the flow curves almost resemble each other.

The TPVs obtained from the rheotron studies displayed identical melt viscosity values when further subjected to the same study in identical conditions (Figure 9), indicating finely dispersed, micron-sized, crosslinked rubber particles, hypalon uniformly distributed in thermoplastic PP matrix. This result also ensures the formation of TPV.

CONCLUSION

Different CSM/PP TPVs are prepared by dynamic vulcanization technique. This study has revealed that prepared TPVs show substantial improvement in mechanical properties like stress at 25%M, UTR, and hardness and also thermal stabilities with the incorporation of PP. Mixing torque–time curves and shear melt viscosity analyses are in good agreement with the properties of TPVs.

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