

## Effect of the Compatibilizer, on the Engineering Properties of TPV Based on Hypalon<sup>®</sup> and PP Prepared by Dynamic Vulcanization

Asis K. Mandal,<sup>1</sup> Debabrata Chakraborty,<sup>2</sup> Samir K. Siddhanta<sup>3</sup>

<sup>1</sup>Dumkal Institute of Engineering & Technology, Murshidabad 742406, West Bengal, India

<sup>2</sup>Department of Polymer Science and Technology, University of Calcutta, 92 A.P.C. Road, Kolkata 700009, India

<sup>3</sup>Department of Chemistry, The Bhawanipur E.S.College, 5 Lala Lajpat Rai Sarani, Kolkata 700020, India

Correspondence to: S. K. Siddhanta (E-mail: s\_siddhanta@yahoo.com) or D. Chakraborty (E-mail: chakraborty\_deb@yahoo.com)

**ABSTRACT:** Elastomeric Chlorosulfonated polyethylene (Hypalon<sup>®</sup>) and thermoplastic Polypropylene (PP) based thermoplastic vulcanizates (TPVs) were prepared in presence of different doses of compatibilizer, maleic anhydride grafted PP (PP-g-MA) by employing dynamic vulcanization technique. The effect of incorporation in different proportions of compatibilizer on mechanical, spectral, morphological, thermal, and rheological properties of such TPVs was studied and the same were compared to that of virgin PP and amongst themselves. The mechanical analysis of the prepared TPVs exhibited significant improvements in stress at 25% modulus, ultimate tensile strength (UTS), and hardness values. FTIR studies revealed that a chemical interaction had taken place between Hypalon<sup>®</sup> and functionalized compatibilizer during the process of dynamic vulcanization which led to an enhancement of interfacial adhesion between them. The two-phase morphologies were clearly observed by scanning electron microscopic studies. The  $T_g$  values of Hypalon<sup>®</sup> was modified in the TPVs as exhibited by differential scanning calorimetric studies. TGA studies indicated the increase in thermal stability of all TPVs with respect to the elastomeric Hypalon<sup>®</sup>. Rheological properties showed that the compatibilizer reduces the melt viscosity of TPVs and thus facilitates the processibility of such TPVs. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40312.

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### INTRODUCTION

Blending of polymers provides means of fabricating new materials which combines the useful properties of all blend constituents. The elastomeric rubber-thermoplastic blends also affectionately called as thermoplastic elastomers (TPE), technologically became interesting in recent years as they possess the properties of elastomers but are processable as thermoplastics. TPE blends have generally 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 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 matrix. The elastomer particles should be crosslinked to promote elasticity.<sup>1,2</sup>

The best way to prepare TPE blends also termed as thermoplastic vulcanizates (TPVs) comprising vulcanized elastomer particles dispersed in melt processible 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. Crosslinked rubber particles are formed in situ in TPVs during the process of dynamic vulcanization of virgin rubber and are dispersed in thermoplastics which reduce the size of elastomeric phase and thus inhibit reagglomeration of the same during cooling process as well as in subsequent use of TPVs at higher temperatures.<sup>3–6</sup> Phase inversion occurs, the dispersed PP phase being converted to continuous matrix, and the continuous matrix of hypalon is converted into dispersed phase.

Excellent interfacial adhesion to the embedded thermoplastic matrix allows the elastomeric particles to absorb the mechanical energy and transferring it to the thermoplastic and thus it provides high resistance to mechanical stretching and compression. The high level of compatibility between elastomeric and thermoplastic phases governs the interfacial adhesion in these materials. To enhance the adhesion between the two phases and as a result to obtain a stable and reproducible dispersion, compatibilizers have also been applied in situ to the TPVs which lead

**Table I.** Compounding Formulations

Ingredients	Quantity (Parts per hundred parts of CSM, phr)
CSM	100
Mgo	8
NBC	3
DPTT	4

to the desired morphology and properties.<sup>3,7</sup> Therefore, influence of compatibilizers on TPVs has also been investigated by several researchers. A number of investigations have been reported on the preparation of different compatibilized TPVs which include hydrosilylated PP, hydrosilylated PP grafted on styrene-butadiene-rubber, polystyrene modified natural rubber, glycidyl methacrylate-grafted PP and block copolymers, Maleic anhydride grafted styrene-ethylene-butylene-styrene, phenolic modified PP and maleic anhydride grafted PP as compatibilizers.<sup>3,5,7-14</sup>

PP is a crystalline thermoplastic polymer with excellent properties such as electric insulation with extremely low dielectric loss, good solvent resistance and also possesses good processability. Chlorosulfonated polyethylene (CSM) (Hypalon<sup>®</sup>) is an important elastomer, but however, possesses poor mechanical properties as it is a completely amorphous in nature and also suffers from the disadvantages of poor processing. In our earlier investigation,<sup>15</sup> a TPV based on Hypalon<sup>®</sup> as the elastomer and PP as the thermoplastic phase was prepared via dynamic vulcanization process in the absence of any compatibilizer. Owing to the large difference in surface energy and polarity, blending of PP and Hypalon<sup>®</sup> should be phase separated. In this regard, in the present study, an attempt has been made to use maleic anhydride grafted PP (PP-g-MA) as a potential compatibilizer for this TPV system. The objective of our present work is to study the effect of incorporation of compatibilizer (PP-g-MA) on the above-mentioned TPV. The physical, mechanical, spectral, and thermal properties of the compatibilized TPV are discussed herewith in relation to their morphological and rheological properties.

## EXPERIMENTAL

### Materials

Rubber used in this work is Hypalon-40 (CSM) (CI = 35%, S = 1%, manufactured from Dupont Performance Elastomers L.L.C, USA). 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 polypropylene (PP) homopolymer (Repol HO 30SG, having an MFI of 3.0 g/10 min) supplied by M/S Reliance industries Ltd (Mumbai, India). The magnesium oxide (MgO) used as an accelerator activator was manufactured by Konoshima chemical co. Ltd., Osaka, Japan. The dipentamethylenethiuram tetrasulphide (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. The maleic anhydride grafted PP (PP-g-MA) used as

compatibilizer was received from Sigma Aldrich, USA [AC100, MP 156°C, Viscosity 4.0 poise (190°C Brookfield thermoses) (lit), maleic anhydride 8–10%, density 0.934, softening point 157°C (ring & ball)].

### Compounding of Unvulcanized Hypalon<sup>®</sup>

Hypalon<sup>®</sup> 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<sup>®</sup> at an interval of 1 min. The amounts of different ingredients are given in Table I. Finally compounded Hypalon<sup>®</sup> was obtained as a sheet form. The total mixing time required was 8 min.

### Blending

The unvulcanized compounded Hypalon<sup>®</sup> was subsequently blended with PP and compatibilizer (PP-g-MA) in different proportions (as shown in 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.<sup>16</sup> The Hypalon<sup>®</sup>-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, Hypalon<sup>®</sup> and PP were compression-molded in the form of rectangular sheet in a Moore press (temperature: 170°C, Pressure: 35 kg/cm<sup>2</sup>, time: 10 min).

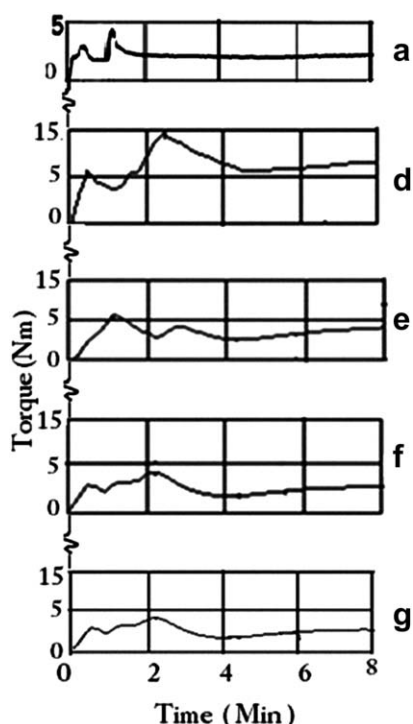
### Characterizations

The torque vs. time curves were recorded in a Brabender mixer with the help of two rotors housed in a case at the speed of 80 rpm. Tensile properties such as stress at 25% modulus, ultimate tensile strength (UTS), 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 were  $\pm 3\%$ . The hardness was determined by means of durometer in shore A Scale following ASTM D-2240-64T.

Fourier transform infrared (FTIR) spectra were obtained using Perkin-Elmer RX-1, FTIR spectrophotometer and employing KBr disc technique. The scanning electron micrographs for

**Table II.** Compositions of Different Thermoplastic Vulcanizates

Sample no.	Composition		
	Hypalon	PP	Compatibilizer (PP-g-MA)
A	100	0	0
B	0	100	0
C	80	20	0
D	80	20	2.5
E	80	20	5.0
F	80	20	7.5
G	80	20	10.0



**Figure 1.** Plot of mixing torque values vs. times of different TPVs based on Hypalon<sup>®</sup>/PP blends containing different amount of compatibilizer: (c) Hypalon<sup>®</sup>/PP TPV without compatibilizer, (d) Hypalon<sup>®</sup> + PP + compatibilizer (2.5), (e) Hypalon<sup>®</sup> + PP + compatibilizer (5.0), (f) Hypalon<sup>®</sup> + PP + compatibilizer (7.5), and (g) Hypalon<sup>®</sup> + PP + compatibilizer (10.0).

gold-coated samples were obtained on a Hitachi (S415A) microscope. For SEM study, the sample was subjected to etching in toluene for one day. PP phase was expected to be removed in this way and finally the test specimen was dried in vacuum at 40°C. DSC measurements were carried out from Shimadzu DSC-50 in an inert atmosphere of nitrogen at a heating rate of 10°C/min. 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 (3° angle), rotational viscometer (Rheotron 2744E from Brabender, Germany) at 200°C.

## RESULTS AND DISCUSSION

### Mixing Torque

Figure 1 gives a comparative idea of the mixing rheology of (80/20) blend of Hypalon<sup>®</sup>/PP and the compatibilized system of the same with different doses of PP-g-MA as compatibilizer. An insight of the torque vs. time curves as obtained from the Brabender mixer machine reveals important features of such TPVs.

The curve C representing the TPV without any compatibilizer is associated with initial rise in torque as soon as the rotors are set in motion. This rise is immediately followed by a small reduction and subsequent sharp rise. Finally, the torque curve falls to a constant value, which does not undergo any change even if the strain is maintained by rotors. The initial rise may

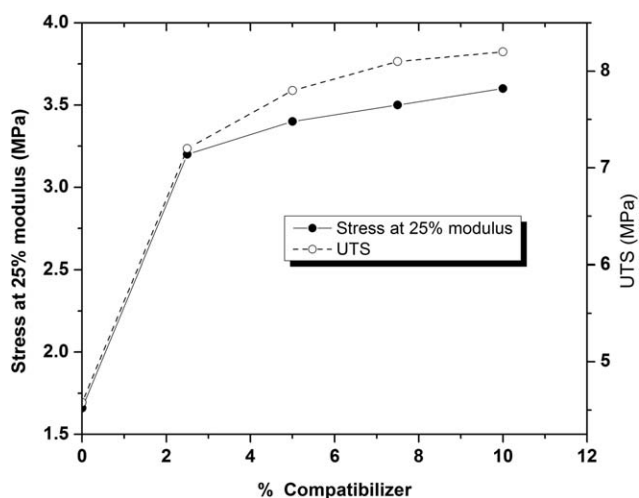
possibly be explained by the resistance offered by highly viscous solid rubber and unmelted PP particles both of which undergo softening with time leading to a reduction in torque. The final rise in torque may be attributed to a number of phenomena occurring almost simultaneously during the period. The compounded rubber vulcanizes, the torque increases but immediately the vulcanized rubber undergoes shearing & tearing and the PP phase being properly melted by this time tends to form the matrix in which shredded rubber particles get distributed during the last phase. The torque thus further falls off and remain static over the period of time of study.

When the TPV formation of this particular composition takes place in presence of compatibilizer the torque undergoes changes which reflect a phase inversions after the second peak is reached (due to vulcanization of Hypalon<sup>®</sup>). The second rise in peak is somewhat delayed possibly because of retardation in curing time due to the presence of acidic compatibilizer. However, the high value of the second peak may be assumed to be due to compatibilized system. The maximum value of torque is, however, achieved at 2.5 parts of compatibilizer incorporation (curve D). On further gradual incorporation of the said compatibilizer in the TPV system (from 5 parts to 10 parts) as shown in curves E, F, and G only leads to deterioration in the peak value (second) of the torque which might indicate incomplete curing and dilution effect.

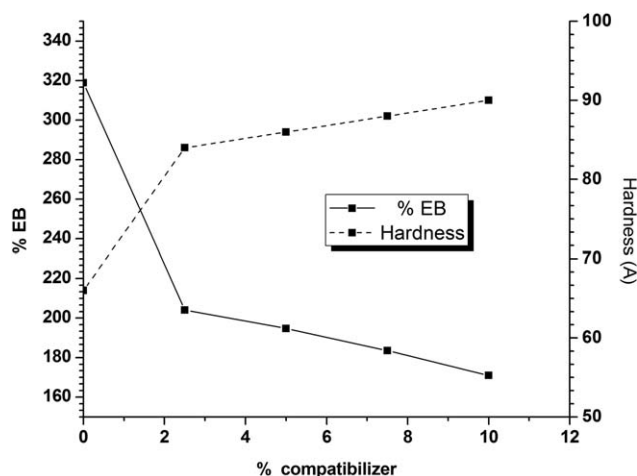
### Mechanical Properties

The mechanical properties of the TPVs of a particular composition (Hypalon<sup>®</sup> 80: PP 20) with variation in content of the compatibilizer (PP-g-MA) have been reported graphically in Figures 2 and 3. The mechanical properties of this uncompatibilized TPV along with other compositions of Hypalon<sup>®</sup> & PP had been reported in detail in our earlier work.<sup>15</sup>

Figure 2 shows the plot of stress at 25% modulus and UTS values of the TPVs as a function of compatibilizer content. Both the parameters undergo a steady increase with the increasing proportions of compatibilizer, (PP-g-MA). The nonpolar PP segments in PP-g-MA moieties are capable of mixing at the

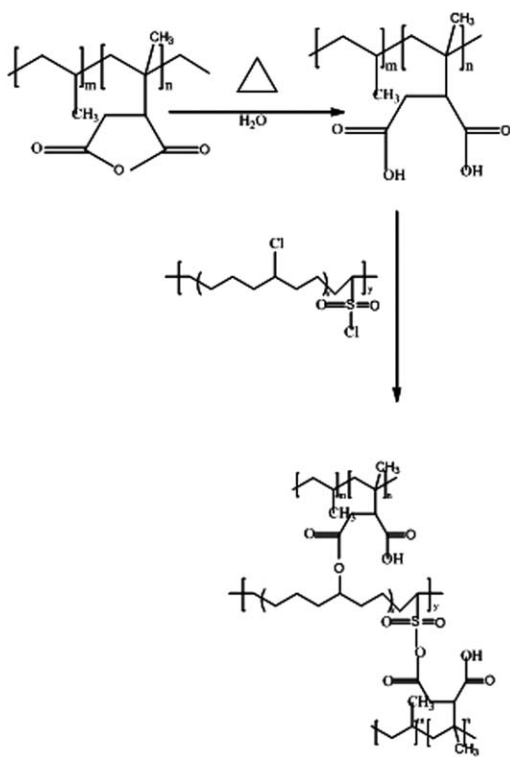


**Figure 2.** Plot of different stress at 25%*M* and ultimate tensile strength (UTS) values of Hypalon<sup>®</sup>/PP TPVs with the % of compatibilizer content.

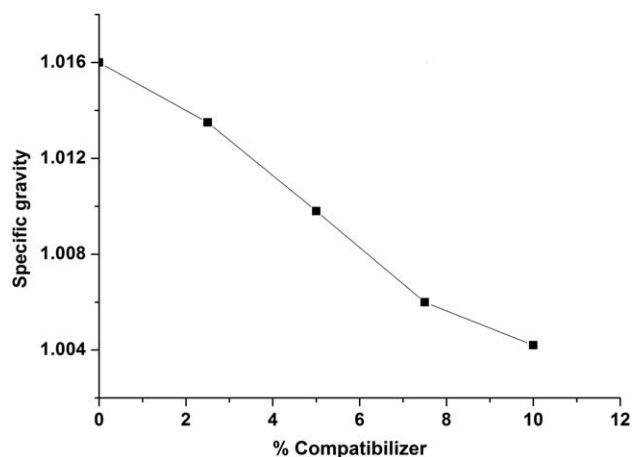


**Figure 3.** Plot of different percent elongation at break and hardness values of Hypalon®/PP TPVs with the % of compatibilizer content.

molecular level with the PP fragments of the TPVs which lead to an increase in the interfacial adhesion with PP. The Hypalon® part, on the other hand, gets compatibilized with the Maleic anhydride part of the compatibilizer through its reactive functional groups,  $\text{SO}_2\text{Cl}$  in particular which undergo chemical interaction as has been shown in Scheme 1. This dual interaction of the compatibilizer enforces a well compatibilized system, which is an essential requirement for the TPV formation. This has been reflected in Figure 2, where both the mechanical parameters exhibit progressive increment with increasing compatibilizer content within the range of study.



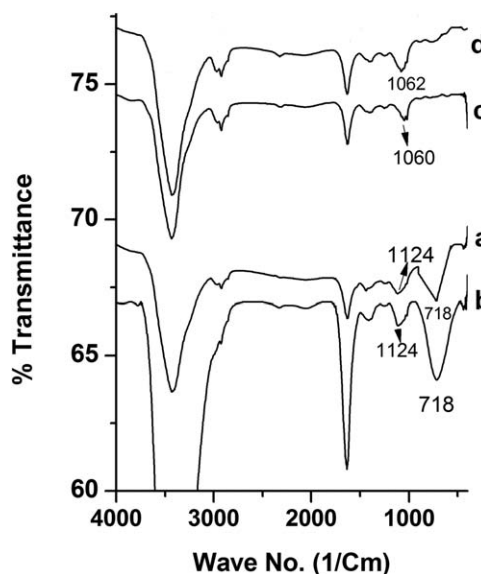
**Scheme 1.** Plausible mechanism for the formation of compatibilized TPV.



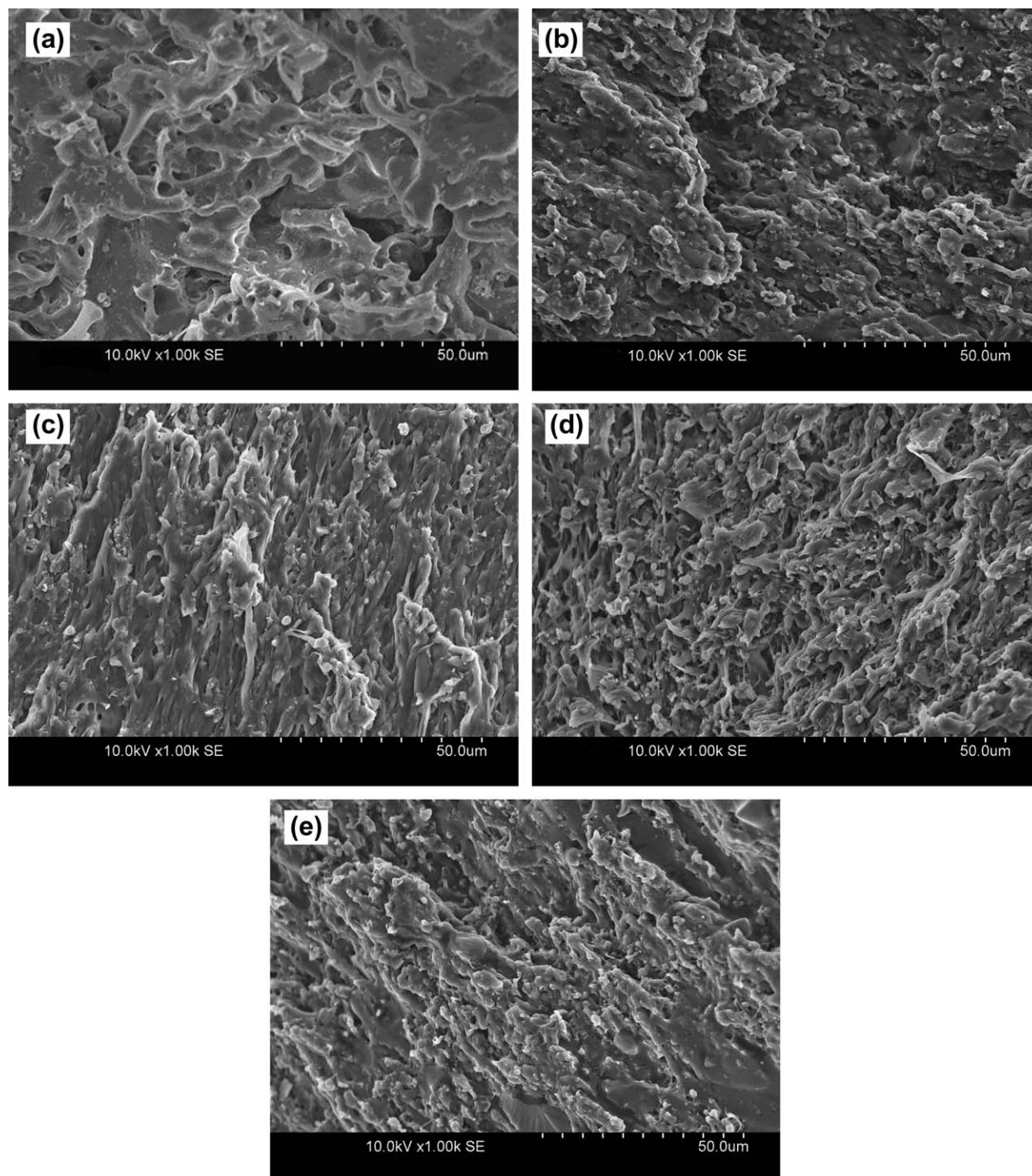
**Figure 4.** Plot of different specific gravity values of Hypalon®/PP TPVs with the % of compatibilizer content.

Figure 3 shows the plots of percent elongation at break (% EB) and hardness values of TPVs with the variation in compatibilizer contents. There is a steady decrease in % EB with the increase in compatibilizer content as expected and thus lead to a stiffer and somewhat brittle matrix. The hardness values of the various TPVs show increasing trend with the increase in proportions of compatibilizer, Figure 3. The compatibilizer by virtue of its well-balanced polar and nonpolar constituents as discussed above is capable of undergoing reaction with the participating polymers as mentioned above and this reaction simulates a chelating type of reaction leading to a reduction in chain mobility and thus increasing the stiffness and hardness as well.

Figure 4 shows the variations of specific gravities of TPVs in relation to the compatibilizer content. This is as per our expectations, as the incorporations of compatibilizer into the comparatively high dense Hypalon® matrix might be expected to lead



**Figure 5.** FTIR spectra of: (a) Hypalon, (b) Hypalon®/PP TPV without compatibilizer, (c) Hypalon®/PP TPV with 2.5 % compatibilizer and (d) Hypalon®/PP TPV with 5.0 % compatibilizer.



**Figure 6.** Scanning electron micrographs of (a) Hypalon<sup>®</sup>/PP TPV without compatibilizer, (b) Hypalon<sup>®</sup> + PP + compatibilizer (2.5), (c) Hypalon<sup>®</sup> + PP + compatibilizer (5.0), (d) Hypalon<sup>®</sup> + PP + compatibilizer (7.5) and (e) Hypalon<sup>®</sup> + PP + compatibilizer (10.0).

to a decrease in density of TPVs. A continuous reduction in specific gravity is observed.

#### FTIR Spectra

FTIR spectra of Hypalon<sup>®</sup> and the different TPVs are shown in Figure 5. Hypalon<sup>®</sup> [Figure 5(a)] shows its characteristic absorption peaks for the presence of C–Cl and SO<sub>2</sub>Cl group at 718 cm<sup>-1</sup> and 1124 cm<sup>-1</sup>, respectively<sup>17</sup> and their appearances

in the noncompatibilized TPV [Figure 5(b)] indicate that they are not involved any type of reaction. The absence of C–Cl bond stretching peak in the spectra of PP-g-MA compatibilized TPVs [Figure 5(c) and (d)] confirms that the Cl atom of C–Cl bond has been replaced by C–O bond due to the chemical interaction of C–Cl of Hypalon<sup>®</sup> with the COOH group of maleic anhydride part of compatibilizer under heating condition. Again the peak at 1124 cm<sup>-1</sup> for SO<sub>2</sub>Cl group of

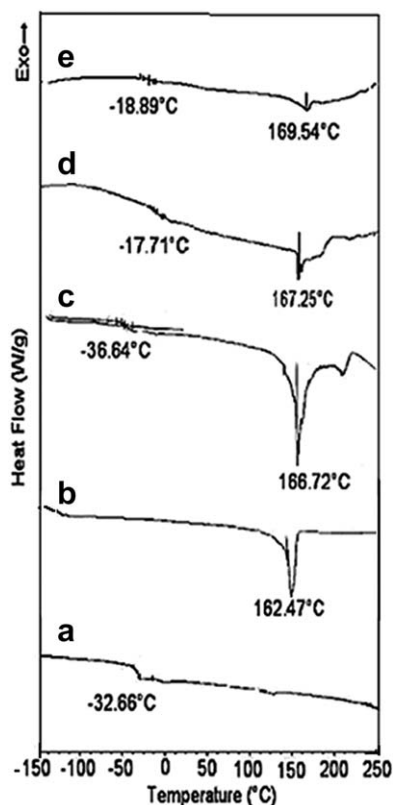
**Table III.** Glass Transition Temperature ( $T_g$ ), Crystallization Melting Temperature ( $T_m$ ), and Enthalpy of Crystallization ( $\Delta H$ ) of Different Thermo-plastic Vulcanizates

Sample	$T_g$ ( $^{\circ}\text{C}$ )	$T_m$ ( $^{\circ}\text{C}$ )	$\Delta H$ (J/g)
A	-32.66	-	-
B	-	162.47	97.54
C	-36.64	166.72	16.28
D	-17.71	167.25	28.91
E	-18.89	169.54	33.62

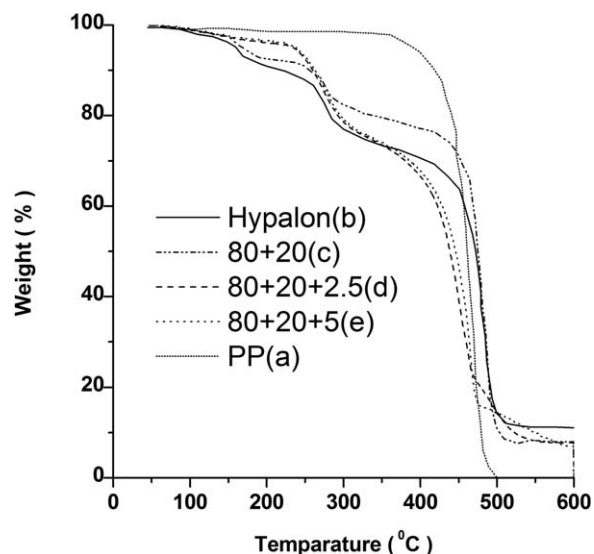
Hypalon<sup>®</sup> has possibly been shifted to lower frequency region ( $1060\text{ cm}^{-1}$ ) which may be owing to the replacement of Cl atom of  $\text{SO}_2\text{Cl}$  group of Hypalon<sup>®</sup> by C-O bond of -COOH part of the compatibilizer. A plausible mechanism for the above mentioned reactions are shown in Scheme 1.

### Morphology

**Scanning Electron Microscopy.** Figure 6 depicts the comparative morphology of the fractured surfaces of the various TPV systems containing varying proportions of compatibilizer (PP-g-MA) and the neat TPV (Hypalon<sup>®</sup>: PP blend) without any compatibilizer as well. It is interesting to note that in absence of compatibilizer (curve a in Figure 6) the fractured surface of TPV is associated with more essentially fibrillar rubbery domains with fewer numbers of spherical micro domains. With



**Figure 7.** DSC plots of (a) Hypalon<sup>®</sup>, (b) PP (c) Hypalon<sup>®</sup>/PP TPV (without compatibilizer), (d) Hypalon<sup>®</sup> + PP + compatibilizer (2.5), (e) Hypalon<sup>®</sup> + PP + compatibilizer (5.0).

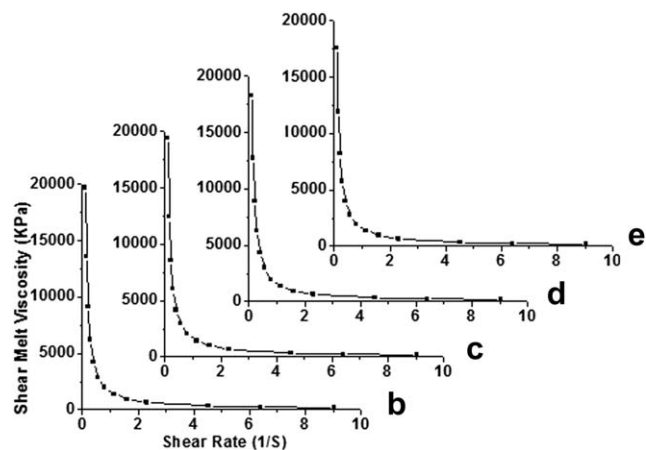


**Figure 8.** TGA of different samples.

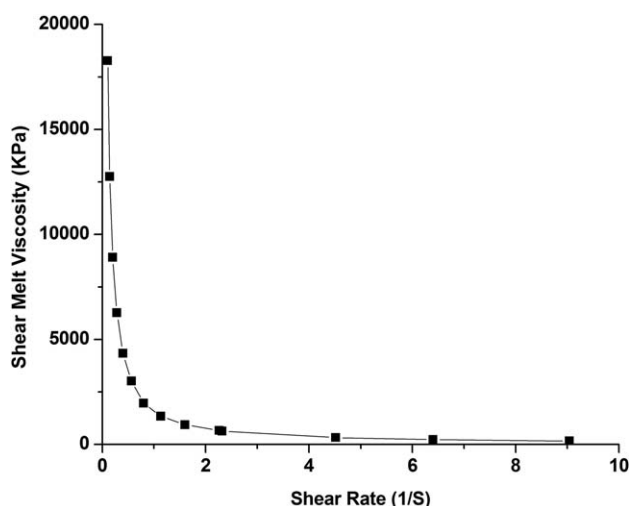
the incorporation of compatibilizer the fibril length or thickness of the dispersed rubbery phase decreases and with increasing proportions of compatibilizer the number of micro domains increases and at a level of 2.5 parts of compatibilizer, a well-balanced distribution of spherical & fibrillar particles is achieved. Beyond 2.5 parts, the fibrillar length again increases and exhibits an agglomerating tendency, a phenomenon which leads to deterioration in properties.

### Thermal Studies

**Differential Scanning Calorimetry.** The glass transition temperature ( $T_g$ ), crystalline melting temperature ( $T_m$ ), and enthalpy of crystallization ( $\Delta H$ ) as obtained from DSC studies on PP, Hypalon<sup>®</sup> and different TPV systems are tabulated in Table III. The typical DSC plots are shown in Figure 7. Both the TPVs (compatibilized and noncompatibilized) show a single  $T_g$  value similar to that of neat Hypalon<sup>®</sup>. The increasing proportion of compatibilizer in the different TPVs is reflected in their corresponding  $T_g$  values also as expected. Addition of



**Figure 9.** Plots of shear melt viscosity vs. shear rate of (b) PP, (c) Hypalon<sup>®</sup>/PP TPV without compatibilizer, (d) Hypalon<sup>®</sup> + PP + compatibilizer (2.5), (e) Hypalon<sup>®</sup> + PP + compatibilizer (5.0).



**Figure 10.** Plots of shear melt viscosity vs. shear rate of Hypalon<sup>®</sup> + PP + compatibilizer (5.0) (same sample as used in Figure 9 further subjected to similar study).

compatibilizer leads to an increase in  $T_g$  values because of the stiffness generated in the polymer chain and that is owing to the formation of new covalent bonding with the compatibilizer as shown in Scheme 1. The increase in chain stiffness is further supported by the fact that the TPV system under consideration has higher melting point with respect to PP which further increases with the increase in compatibilizer content. For each of the systems, the PP phase displays a discrete peak in its crystalline melting temperature. There is a noticeable change in  $T_m$  values in the TPVs compared to PP alone.

**Thermogravimetric Analysis.** The TGA thermograms of PP, Hypalon<sup>®</sup> and of different TPVs are shown in Figure 8. PP alone displays one-step degradation starting at temperature of 370°C and completely degrades at 500°C. Being nonpolar hydrocarbon, it is associated with little moisture, the curve a (PP only) shows no initial moisture loss. However, the pure Hypalon<sup>®</sup> and different TPV systems (both compatibilized and noncompatibilized) considered in the present study, curves b–e, respectively, exhibit stepwise degradation. For most of all, the initial mass loss upto about 155°C is due to absorbed moisture and the second step of degradation occurring between 155°C and 325°C may be due to some unreacted accelerator and antioxidant release for Hypalon<sup>®</sup> and also for TPVs. Again a mass loss ensuing at nearly 325°C and continuing till above 500°C presumably corresponds to large scale thermal degradation, eliminating ethylene, chloroethylene, and sulphochloroethylene from Hypalon<sup>®</sup>.<sup>18</sup> The final stage of degradation observed in the temperature range of 400–500°C is due to the main chain scission and the residue left at 600°C is about 10.5% for Hypalon<sup>®</sup>. The pure Hypalon<sup>®</sup>, though initially less stable than PP, leaves behind appreciable quantity of residue at 500°C, which remains thermally stable even above this temperature. The compatibilized TPVs show higher thermal stability upto 260°C than the noncompatibilized TPV though the latter one is more stable at higher temperature (above 260°C) and all TPVs leave more or less same amount of residue (7.5%) at 600°C.

The weight loss beginning at 260°C temperature from compatibilized TPVs may be due to thermal degradation of compatibilizer (PP-g-MA). Thus, the overall thermal stability of the compatibilized TPVs has remarkably been improved.

### Rheology

The variation of melt viscosity of PP and of different TPVs (with and without compatibilizer) with different shear rate is shown in Figure 9. The melt viscosity in each case at 200°C decreases very sharply initially and gradually the rate falls off with the increase in shear rate. Therefore, these are pseudoplastic (shear-thinning behavior) in nature. Only PP phase is melted during the rheological test and it is observed that the melt viscosities of the TPVs decrease gradually in compatibilized samples within the range of shear rate studied, although towards the higher region of the shear rate under study the melt viscosities of the neat PP and the various TPVs merge together. This decrease in melt viscosity in compatibilized TPVs compared to noncompatibilized one is attributed to the strong interfacial interaction between the polar and nonpolar segments of compatibilizer (PP-g-MA) (in which both exist simultaneously) and the participating components (both PP and Hypalon<sup>®</sup>) which has been confirmed by FTIR study. The flow characteristics being dominated by the elastomeric component, which forms the matrix in the ultimate 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 10), indicating finely dispersed, micron-sized, crosslinked rubber particles, Hypalon<sup>®</sup> uniformly distributed in thermoplastic PP matrix. This result also ensures the formation of TPV.

### CONCLUSION

This study has revealed the effect of incorporation of PP-g-MA as compatibilizer in the TPVs (a fixed amount of 20 parts of PP used). The prepared compatibilized TPVs showed substantial improvement in mechanical properties like ultimate tensile strength, stress at 25% modulus, hardness and also thermal stabilities. FTIR results indicated the existence of chemical interaction between Hypalon<sup>®</sup> and the MA segments of the compatibilizer which led to an enhancement of compatibility between them.

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