

On the Engineering Properties of TPV derived from Hypalon, PP and a Compatibilizer (PMES-MA) prepared by Dynamic Vulcanization

ASIS K. MANDAL¹, DEBABRATA CHAKRABORTY², MAHUYA DAS³ AND SAMIR K SIDDHANTA⁴

¹JID Engineering & Management College, Baruipur, South 24 Pgs-743610, West Bengal

²Department of Polymer Science & Technology, 92, A.P.C. Road, Kolkata 700009, West Bengal

³Department of Chemistry, JIS College of Engineering, Kalyani, Nadia-741235, West Bengal

⁴Department of Chemistry, The Bhawanipur Education Society College, Kolkata-700020

ABSTRACT

Elastomeric chlorosulfonated polyethylene (Hypalon) and thermoplastic polypropylene (PP) based thermoplastic Vulcanizates (TPVs) were prepared in presence of different doses of partial methyl ester of styrene-maleic anhydride copolymer (PMES-MA) as compatibilizer employing dynamic vulcanization technique. 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 and 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 Tg values of hypalon were 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. Rheological properties showed that the compatibilizer reduces the melt viscosity of TPVs and thus facilitates the processibility of the same.

KEYWORDS: *Hypalon, Polypropylene, Compatibilization, Mechanical properties, Thermal properties.*

INTRODUCTION

Thermoplastic elastomer (TPE) is a distinctive type of polymer-based flexible material which amalgamates the elastic behavior of elastomer with easy processibility of thermoplastics at ambient room temperature. The modern development over TPE is thermoplastic vulcanizates, an elastomer-thermoplastic blends prepared by dynamic vulcanization technique. In the process of dynamic vulcanization, the elastomeric phase is cured in the presence of a suitable crosslinking agent, along with the melt mixing of the thermoplastics phase with its components resulting in dispersed domain of elastomer particles in a thermoplastic matrix. Hence, this process provides more uniform and finer distribution of the crosslinked elastomeric phase distributed in melt processable thermoplastic materials leading to more stable uniform morphology of the system^[1-4].

Excellent interfacial adhesion to the embedded thermoplastic matrix allows the elastomeric particles to absorb the mechanical energy applied and thus it provides high resistance to mechanical stretching and compression. The high level of compatibility between elastomeric and thermoplastic phases governs the actual interfacial adhesion in these materials. To enhance the adhesion between the two phases different compatibilizers have also been applied in situ to TPVs which leads to the desired morphology and properties^[2,5]. Therefore, study of the influence of compatibilizers on TPVs is the key interest by several groups of researchers. A number of investigations have been reported on the preparation of different compatibilized TPVs which includes hydrosilylated polypropylene (pp), hydrosilylated

PP grafted on styrene-butadiene-rubber, glycidyl methacrylate-grafted PP and block copolymers, phenolic modified PP, maleic anhydride grafted EPDM, maleic anhydride grafted PP, triethylene tetramine and polystyrene modified natural rubber as compatibilizers^[2,5,14].

PP is a tough, semi-rigid and crystalline thermoplastic with excellent properties such as electric insulation with extremely low dielectric loss, good chemical resistance and also possesses good processibility and impact resistance. Chlorosulfonated polyethylene (CSM) (hypalon) is a special purpose elastomer having ideal balance of properties such as ozone, oxygen, weather, heat, oil, and chemicals resistance but however, possesses poor mechanical properties as it is a completely amorphous in nature and also suffers from the shortcomings of poor processibility. In our earlier investigation^[15], a Hypalon-PP blend was prepared in the absence of any compatibilizer via dynamic vulcanization technique. Owing to large difference in surface energy and also polarity of the two components, PP-Hypalon blend resulted in materials with inferior mechanical properties. In another study^[16], maleic anhydride grafted PP (PP-g-MA) was used as the compatibilizer for the preparation of TPV from Hypalon and PP. The prepared compatibilized TPVs showed a substantial improvement in mechanical properties like ultimate tensile strength (UTS), stress at 25% modulus, hardness and also thermal stabilities.

The present work is focused on the study of the different properties of PP and Hypalon based TPV system in presence of partial methyl ester of styrene - maleic anhydride copolymer

(PMES-MA) as compatibilizer by the dynamic vulcanization process. The compatibilizer used here is a copolymer of styrene & maleic anhydride in which some fragments of the maleic anhydride has been esterified with methyl alcohol to incorporate some hydrocarbon fraction as methoxyl group and hence to reduce the hydrophilic nature so as to enhance the compatibility of PP and Hypalon. Such TPV was then evaluated with respect to the physical, mechanical, and thermal properties in relation to their morphological and rheological properties.

the present investigation was 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 received from PMP groups of industries, India. PMES-MA, partial methyl ester of styrene-maleic anhydride copolymer (copolymer of styrene and maleic anhydride with a mole ratio of 1:1, SCRIPSET 550, Sp. gr. 1.26) used as compatibilizer was obtained from Synthetic resin by Monsanto, St.Louis, USA.

EXPERIMENTAL

Materials

Elastomer used in this study is Hypalon-40 (CSM) (CI=35%, S=1%, manufactured from Dupont Performance Elastomers L.L.C, USA). Properties of Hypalon-40 are: Mooney viscosity M L (1+4) at 1000°C ≈ 56, Specific gravity 1.18. The thermoplastic used in

Compounding of Unvulcanized Hypalon

Hypalon was masticated initially for 5 minutes in Open two-roll mill (mastication was conducted at ambient temperature, the friction ratio between the two roller being maintained at 1:1.25, the front roll being rotated at 40 rpm under a rotor H.P.7.5, the roller diameter mentioned are diameter. 6 inches & length 12 inches) then MgO, NBC and DPTT were added gradually one after another to the masticated Hypalon at an interval of 1 min. The

TABLE 1: Compounding formulations

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

amounts of different ingredients are given in Table 1.

Blending

The unvulcanized compounded Hypalon was subsequently blended with PP and compatibilizer,

(PMES-MA) in different proportions (as shown in Table 2) at 1700°C for 10 min in a Brabender mixer with the help of two rotors housed in a case at the speed of 80 rpm^[17]. The Hypalon-PP blend was collected as a lump form. The sheet form with required thickness of

TABLE 2: Compositions of thermoplastic Vulcanizates

Sample No.	Hypalon (A) (by weight)	PP (B) (by weight)	PMES-MA compatibilizer (by weight)
S0	80	20	0
S1	80	20	2.5
S2	80	20	5.0
S3	80	20	7.5
S4	80	20	10.0

such blends was prepared from its lump in a two-roll mill.

Processing

Sheets were fabricated in the form of rectangular sheet from all the blends with or without compatibilizer by compression-molding technique at a Moore press applying 170°C temperature and 35 Kg/Cm² pressure for 10 min.

Characterizations

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 characterization. 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 employing KBr disc technique. The

scanning electron micrographs (SEM) for gold-coated samples were obtained on a Hitachi (S415A) microscope. For SEM study, the sample was subjected to etching in toluene for one day to remove PP phase. Finally the test specimen was dried in vacuum at 400°C. Differential Scanning Calorimetry (DSC) measurements were carried out from Shimadzu DSC-50 in an inert atmosphere of nitrogen at a heating rate of 100°C/min. Thermogravimetric analysis (TGA) of different samples was carried out in a Perkin-Elmer Delta series TGA-7 under nitrogen atmosphere at a heating rate of 200°C/min. The melt rheological properties of various blends were evaluated employing a constant shear rate plate and cone (3° angle), rotational viscometer (Rheotron 2744E from Brabender, Germany) at 200°C.

RESULT AND DISCUSSION

Mechanical Properties

The mechanical properties of the prepared TPVs with variation in content of the compatibilizer (PMES-MA) have been reported graphically in Fig.1 and Fig. 2. The mechanical properties of the uncompatibilized TPV along with the other composition of

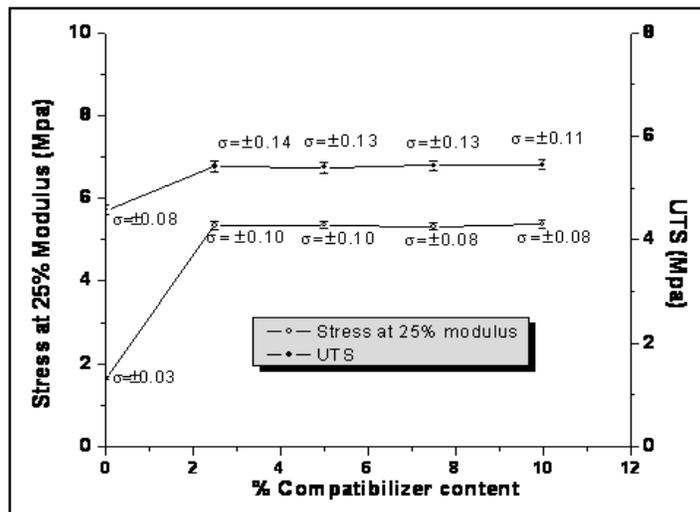


Fig. 1. Comparison of different stress at 25% M and Ultimate Tensile Strength (UTS) values of TPVs with the variation of compatibilizer content.

Hypalon-PP blends have been reported in our earlier study^[15].

The Fig. 1 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 content. The nonpolar PP segments in the compatibilizer moieties are capable of mixing at the molecular level with the nonpolar part 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 parts and also partial methyl ester part of the compatibilizer through its reactive functional groups, SO₂Cl in particular which undergo chemical interaction with the acidic parts of

the compatibilizer. This type of dual interaction of the compatibilizer enforces a well compatibilized system, which is an essential requirement for the TPV formation.

The Fig. 2 depicts the elongation characteristic and surface hardness value of the TPVs with the variation in compatibilizer content. As expectation, the general principle of decreasing in % EB with increasing UTS, we can find here also very sharp decrease in % EB value with the increase in compatibilizer content and this lead to a stiffer and somewhat brittle matrix. The surface hardness value exhibits a sharp increase up to a level of 2.5 phr of compatibilizer incorporation beyond which there is a steady rise in surface hardness with increasing proportion of the compatibilizer. The compatibilizer by virtue of its well-balanced

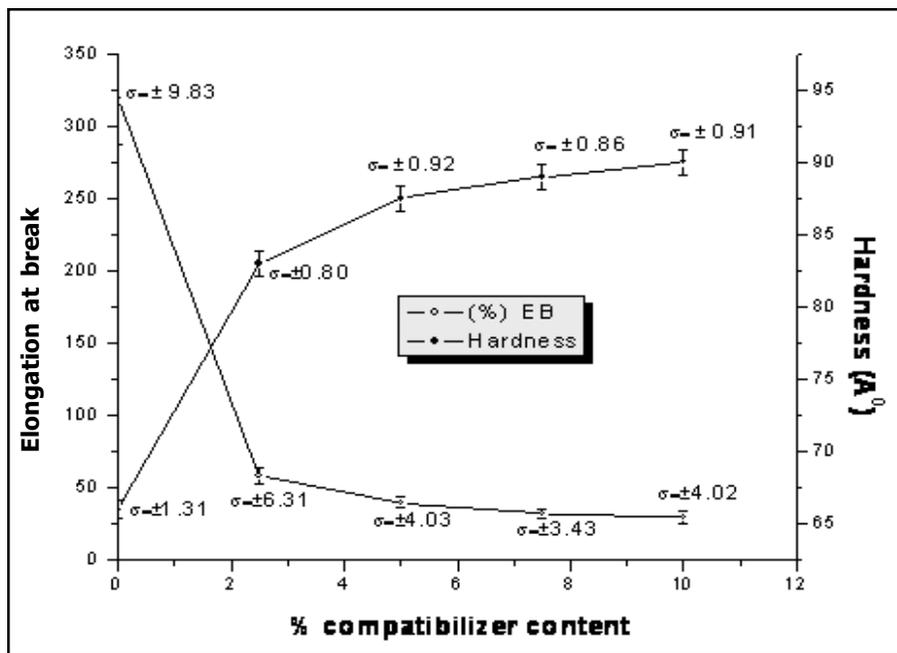


Fig. 2. Comparison of different percent elongation at break and hardness values of Hypalon/PP TPVs with the variation of compatibilizer content.

polar and non polar constituents is capable of undergoing reaction with the participating polymers as mentioned above and this interaction simulates a chelating type of reaction leading to a reduction in chain mobility and thus increasing the stiffness and hardness as well.

Specific Gravity

The Figure 3 shows the variation of Specific gravity (Sp.gr.) of TPVs in relation to the compatibilizer content. As the Sp.gr. of the compatibilizer (1.26) is much higher than those of both the elastomeric and plastomeric components, so the Sp.gr. of the resulting TPVs

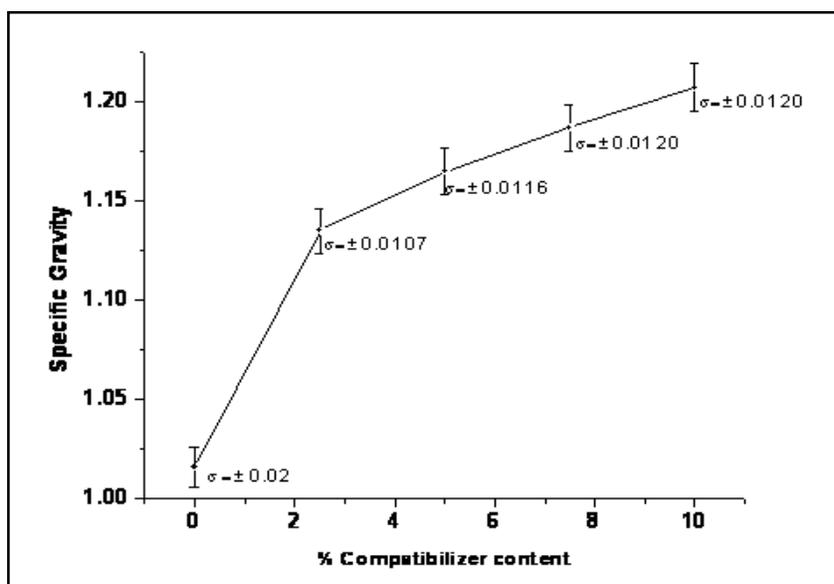


Fig. 3. Comparison of different specific gravity values of Hypalon/PP TPVs with the variation of compatibilizer content.

shows an increasing tendency with the increase in compatibilizer content as expected.

FTIR Spectra

FTIR spectra of PP, hypalon and the different TPVs are shown in Figure 4. Hypalon [Figure 4A] shows all of its characteristic absorption peaks along with the presence of C-Cl and SO₂Cl group at 713 cm⁻¹ and 1105 cm⁻¹ respectively^[18] and their appearances in the uncompatibilized TPV (Figure 4B) indicate that

they are not involved any type of reaction in this case. The absence of C-Cl bond stretching peak in the spectra of the compatibilized TPVs (Figure 4C & 4D) confirms that the Cl atom of C-Cl bond has been replaced by C-O bond owing to the chemical interaction of C-Cl bond of Hypalon with the COOH group of maleic anhydride part of the compatibilizer under heating condition. The peak at 1105 cm⁻¹ for SO₂Cl group of hypalon has also been shifted to lower frequency region (1050 cm⁻¹) may be

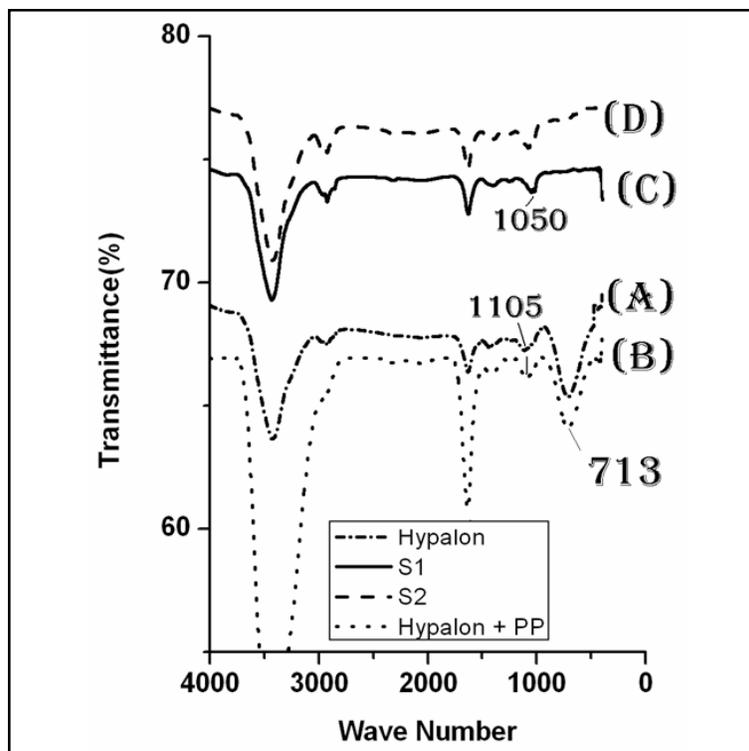


Fig. 4. FTIR spectra of: A) Hypalon, B) Hypalon+PP (without compatibilizer), C) Hypalon+PP (with 2.5% compatibilizer), and D) Hypalon+PP (with 5.0% compatibilizer)

due to the replacement of Cl atom of SO_2Cl group of Hypalon by C-O bond of -COOH part of the compatibilizer.

Morphology: Scanning Electron Microscopy (SEM)

The Figure 5 depicts the comparative morphology of the fractured surfaces of the various TPV systems containing varying proportions of compatibilizer (PMES-MA) and the neat TPV (Hypalon: PP blend) without any compatibilizer as well. Somewhat dispersed fibrillar rubbery phase present in neat TPV (without compatibilizer, A) decreases in compatibilized TPV and with the increasing

proportion 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. This is quite interesting to note here that in spite of the presence of the compatibilizer, the interfaces between the rubbery phase and plastic phase are quite sharp and distinguishable which relate to the facts that these compatibilizer is not capable of reducing the surface energy difference between the components as efficiently as it was observed in our earlier study^[16]. However, because of the spreading of the rubbery phase over a greater area (completely discontinuous) the stress

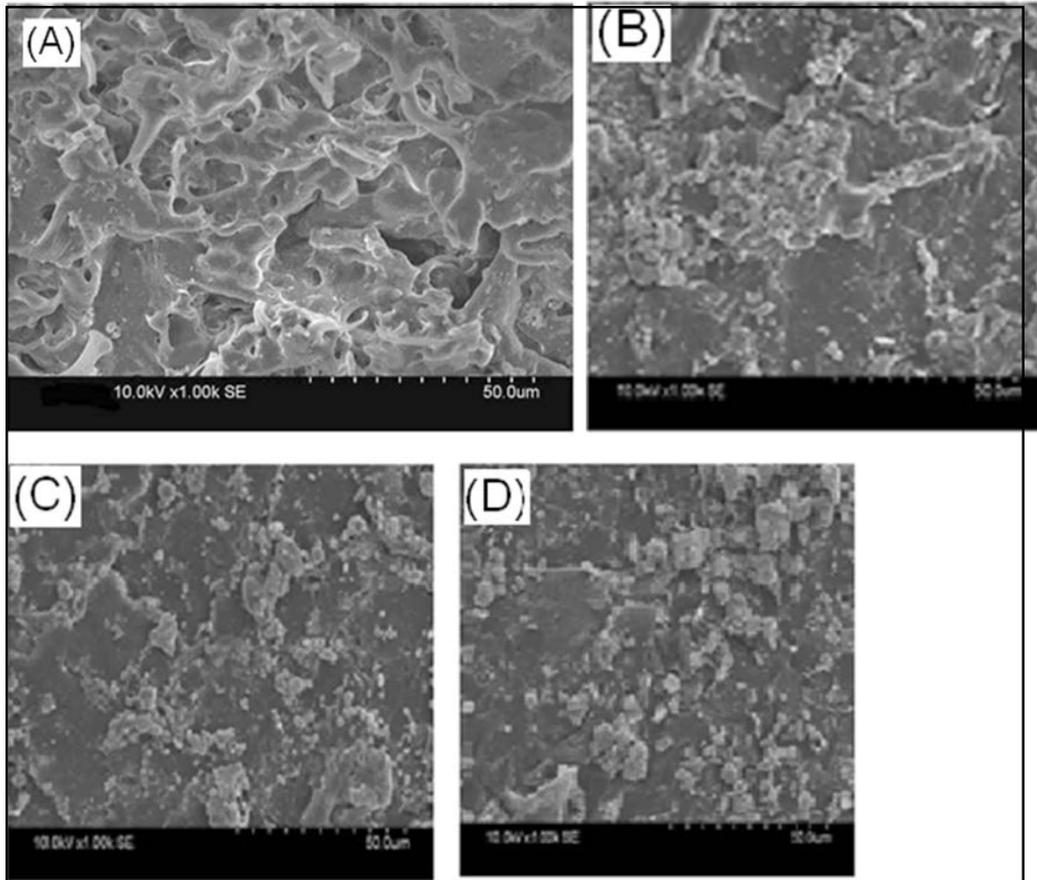


Fig. 5. Comparison of Scanning Electron Micrographs of (A) S0, (B) S1, (C) S2 and (D) S3

reasonably gets an opportunity to spread over relatively large surface area in case of the TPV containing 2.5 phr compatibilizer. Thus marginal improvements are although observed with 2.5 phr of compatibilizer but the effect gradually gets diminished with subsequent increase in compatibilizer content.

Differential Scanning Calorimetry (DSC)

Figure 6 represents the DSC curves of different TPVs having 2.5-5.0 phr of PMES-MA copolymer as compatibilizer. For comparative

studies, the DSC curves of PP, Hypalon and Hypalon/PP::80/20, without compatibilizer are also incorporated in the same Fig. 6. 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 tabulated in Table 3.

From the traces, it appears that the rubbery character of the vulcanized is still maintained but somewhat has been reduced due to

TABLE 3: Glass Transition Temperature (T_g), Crystallization Melting Temperature (T_m), and Enthalpy of Crystallization (ΔH) of Different Thermoplastic Vulcanizates

Sample	Glass Transition Temperature, T_g ($^{\circ}\text{C}$)	Crystalline Melting ($^{\circ}\text{C}$) Temperature, T_m ($^{\circ}\text{C}$)	Enthalpy of Crystallization, ΔH (J/g)
Hypalon	-32.66	-	-
PP	-	162.47	97.54
S0	-36.64	166.7 2	16.28
S1	-13.17	168.6	17.20
S2	-14.36	172.2	22.74

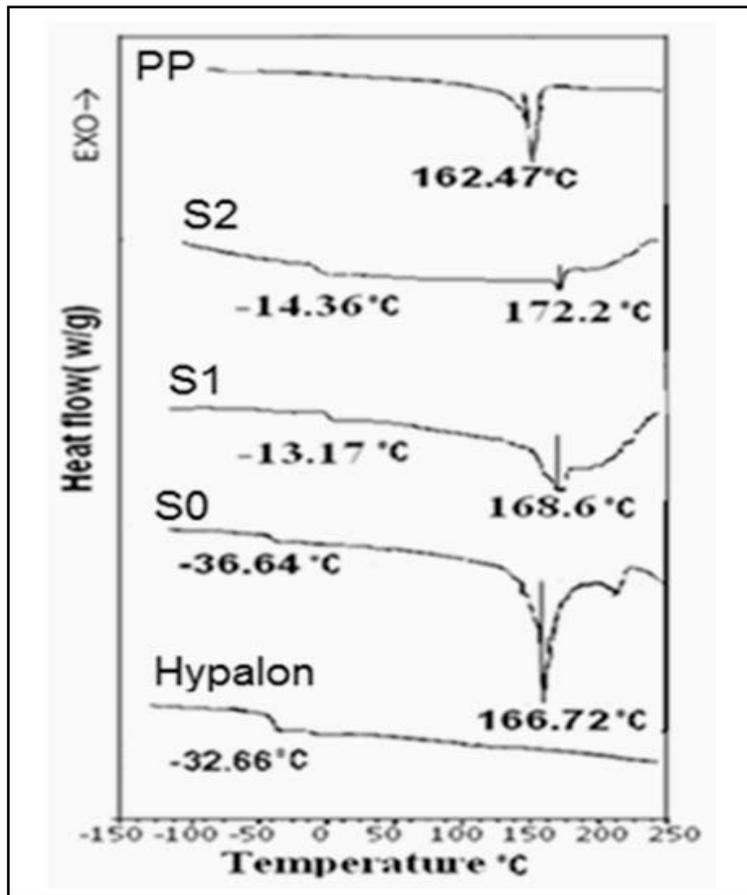


Fig. 6. DSC tracings of Hypalon, PP and different TPV samples.

incorporation of the PMES-MA copolymer as compatibilizer (as reflected by the glass transition temperature, T_g values, which shows an increasing trend with the increase in compatibilizer contents). The presence of benzene ring in the structure of the compatibilizer and also formation of the new covalent bonding with the same interpreting some chain stiffness which is possibly responsible to the reduction in chain mobility of the ultimate vulcanized compared to that of only Hypalon. The increase in chain stiffness is again supported by the fact that the TPV system under consideration has higher crystalline melting point (T_m) with respect to

PP which further increases with the increase in compatibilizer content. The PP phase displays a discrete peak, for each of the system, in its crystalline melting temperature. There is a noticeable change in T_m values in the TPVs compared to PP alone. However this increase in T_g is not so much pronounced in relation to that of the TPV containing the minimum amount of compatibilizer (2.5 phr) used in the present study. Beyond this level of compatibilizer incorporation more and grosser phase separation takes place and thus no marked influence in modifying the T_g is observed.

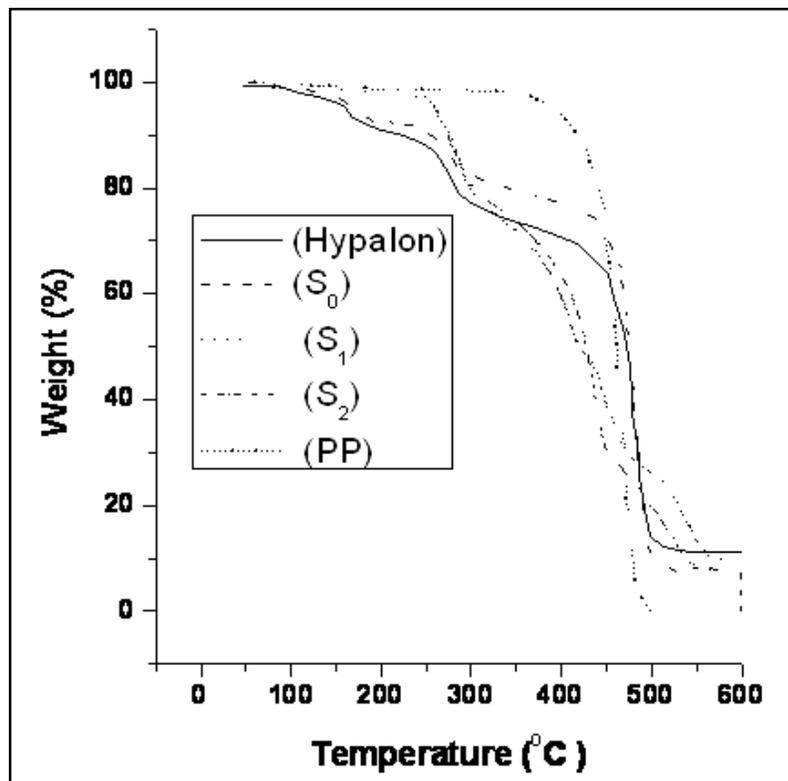


Fig. 7. TGA of different samples

Thermogravimetric Analysis (TGA)

The TGA thermograms of neat PP, neat Hypalon, neat TPV and compatibilized TPV system (2.5 and 5.0 phr compatibilizer) are shown in Fig. 7. PP alone displays one step degradation which starts at 370°C and completely degrades at 500°C. Being nonpolar hydrocarbon, it is associated with little moisture loss. The neat TPV and the two compatibilizer containing systems display multistep degradation [16, 19]. The Hypalon rubber being somewhat polar in nature shows tendency to retain some moisture. This tendency is transformed into the neat TPV and the compatibilized systems. The TPV systems irrespective of the presence or absence of compatibilizer are found to be much more thermally stable (as indicated by the increasing onset temperature of degradation) than the neat hypalon itself. Although the incorporation of

compatibilizer rises the onset temperature of degradation, the subsequent rates of degradation are somewhat faster in these cases in relation to the neat TPV system. The percentage residues left after complete degradation within the range, temperature under study of all the TPVs are higher than the thermoplastic PP but are very closer to that of the neat Hypalon itself.

Rheology

The variation of melt viscosity of neat PP, neat Hypalon and different TPV systems (with and without compatibilizer) with different shear rate has been studied by Rheotron and shown in Fig. 8. An initial sharp reduction in melt viscosity of PP is observed at 200°C and this is followed by a gradual and steady rate of fall with different shear rate [16]. In the TPV systems the thermoplastic PP placed the dominate role

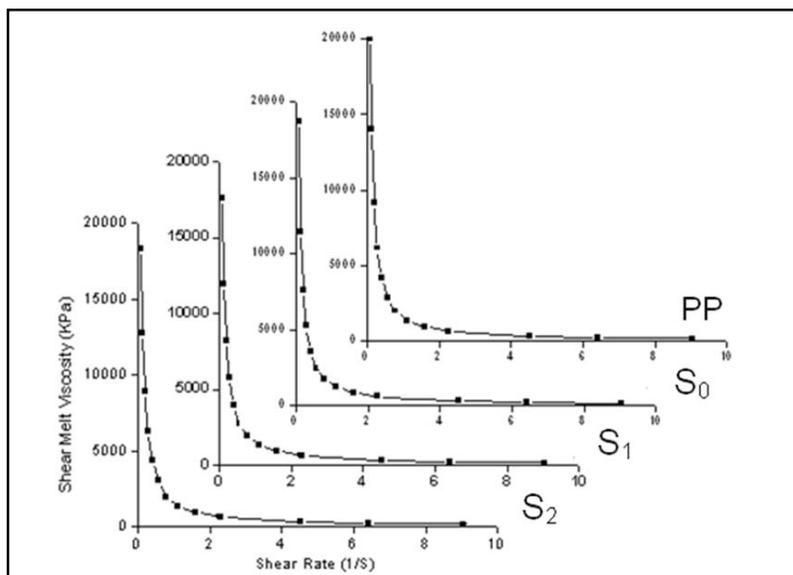


Fig. 8. Comparison of Shear melts viscosity vs. shear rate of PP and different TPV systems

in controlling in melt viscosity since only PP phase is melted during the rheological test although the rubbery Hypalon is the major constituent and dispersed in the form of discrete rubbery domain. This decrease in melt viscosity in compatibilized TPVs compared to uncompatibilized one is attributed to the strong interfacial interaction between the polar and nonpolar segments of compatibilizer (PMES-MA) and the participating components (both PP and Hypalon) which has been confirmed by FTIR study. The presence of compatibilizer marginally effects the flow behavior measured at a temperature considered in the present study.

Recyclability

Different mechanical parameters like stress at 25% modulus and UTS values have been considered for comparison between the different freshly prepared TPV and the reprocessed and remoulded TPV systems and are represented in Fig. 9. All the properties are being observed not to vary too much for the virgin and the reprocessed material. These ensure recyclability of the TPVs without any deterioration in properties.

The TPVs obtained from the rheological studies displayed identical melt viscosity values when

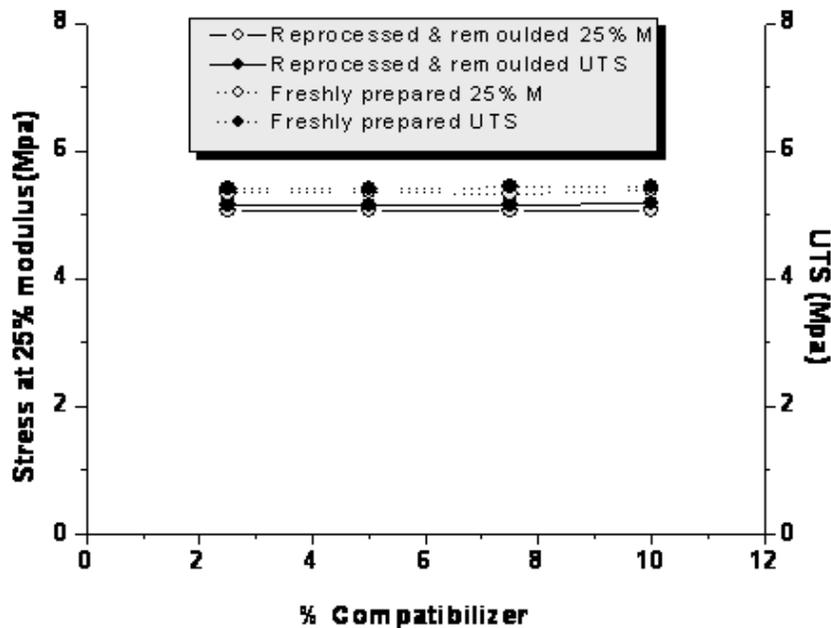


Figure 9. Comparison of different stress at 25% Modulus and UTS values of compatibilized TPV for before and after remolding and reprocessing.

further subjected to the same study in identical conditions (Fig. 10), indicating finely dispersed, micron-sized, crosslinked elastomer particles,

Hypalon uniformly distributed in thermoplastic PP matrix. This result also ensures the formation of TPV.

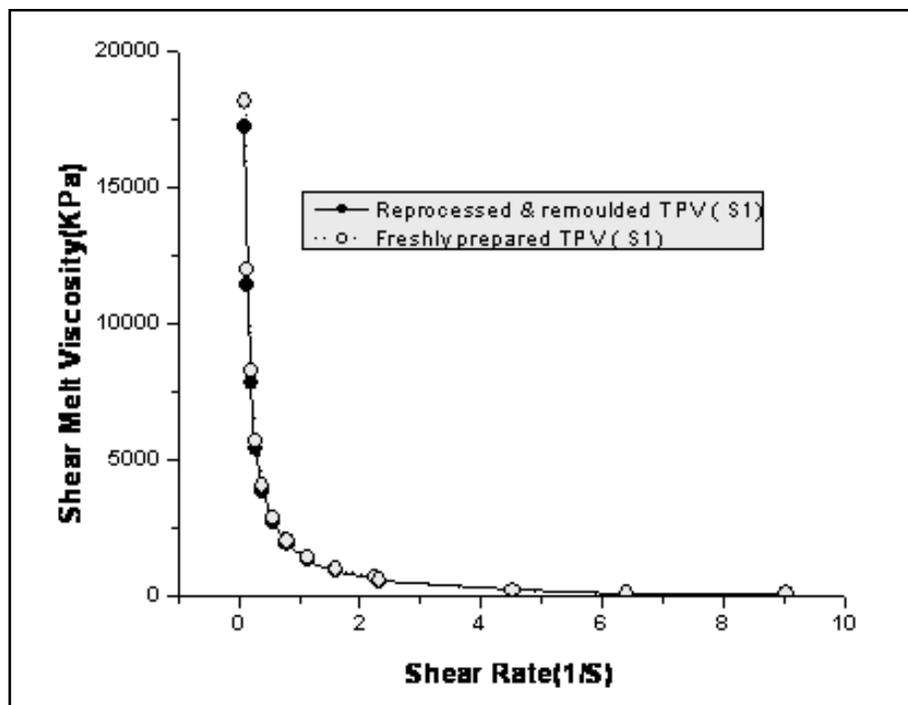


Fig. 10. Comparison of Shear melts viscosity vs. Shear rate of TvE

CONCLUSION

This study has revealed the effect of incorporation of PMES-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 (UTS), stress at 25% modulus, hardness and also thermal stabilities. FTIR results indicate the existence of chemical interaction between hypalon and the MA segments of the compatibilizer which led to an enhancement of compatibility between them. It has been noticed that the compatibilizer PP-g-MA used in our earlier study^[16] and PMES-MA used here both show

more or less identical compatibilizing effect for this Hypalon and PP systems which is reflected in the mechanical properties.

ACKNOWLEDGMENTS

We acknowledge the assistance of Dr. P. K. Maity and Mr. S. Deb Nath from University of Calcutta, Calcutta for carrying out SEM measurements and some mechanical testing.

REFERENCES

1. A. Y. Coran and R. Patel, in "Thermoplastics Elastomers", G. Holden, H. R. Kricheldorf and R. P. Quirk (Eds), Hanser Gardner publications: Cincinnati, 2004, Ch. 5, p.143.

2. S. H. Zhu and C. Tzoganakis, *J. Appl. Polym. Sci.* 118 (2010): 1051.
3. C. Nakason, S. Saiwari, and A. Kaesaman, *Polym. Eng. Sci.* 46 (2006): 594.
4. H. Wu, M. Tian, L. Zhang, H. Tian, Y. Wu, N. Ning and G. H. Hu, *Polymers*, 8 (2016): 127.
5. J. George, N. R. Neelakantan, K. T. Varughese and S. Thomas, *J. Appl. Polym. Sci.* 100 (2006): 2912.
6. D. Feldman, *J. Macromol. Sci. Pure Appl. Chem.* 42 (2005): 587.
7. C. Nakason, P. Wannavilai and A. Kaesaman, *J. Appl. Polym. Sci.* 101 (2006): 3046.
8. P. Phinyocheep, F. H. Axtell and T. Laosee, *J. Appl. Polym. Sci.* 86 (2002): 148.
9. A. S. Hashim and S. K. Ong, *Polym. Int.* 51 (2002): 611.
10. C. Nakason, P. Wannavilai and A. Kaesaman, *J. Appl. Polym. Sci.* 100 (2006): 4729.
11. G. Ranjbar, H. Mirzazadeh, A. A. Katbab and A. N. Hrymak, *J. Appl. Poly. Sci.* 123 (2012): 32.
12. R. N. Uthaman and S. S. M. A. Pandurangan Majeed, *Polym. Eng. Sci.* 47 (2007): 934.
13. B. G. Soares, D. M. Santos and A. S. Sirqueira, *expres. Polym. Let. 2* (2008): 602.
14. B. G. Sores, J. B. freitas, A. A. Silva and A. S. Sirqueira, *Rubber Chem. Tech.* 92 (2019): 546.
15. A. K. Mandal, S. K. Siddhanta and D. Chakraborty, *J. Appl. Polym. Sci.* 127 (2013): 1268.
16. A. K. Mandal, D. Chakraborty and S. K. Siddhanta, *J. Appl. Polym. Sci.* 131 (2014): 40312.
17. Z. Wang, H. Zhao, J. Zhao and X. Wang, *J. Appl. Polym. Sci.* 117 (2010): 2523.
18. B. B. Khatua, C. K. Das, P. K. Patra, M. S. Banerjee and W. M. Millins, *Intern. J. Polym. Mat.* 46 (2000): 347.
19. G. Markovic, M. M. Cincovic, V. Vodnik, B. Radovanovic, J. B. Simendic and O. Veljkovic, *J. Therm. Anal. Calorim.* 97 (2009): 999.

Received: 20-05-2021

Accepted: 25-06-2021