Impact Modification of SAN by Dynamic Vulcanization with Liquid Isoprene Rubber

Chandresh Mysore Parameshwaraiah* and S. Roopa[#]

*, # Department of Polymer Science and Technology,
Sri Jayachamarajendra College of Engineering,
JSS Science and Technology University, Mysuru 570006, Karnataka, India
scholar.chandreshmysore213@gmail.com, chandreshmp@sjce.ac.in,

Abstract- Poly styrene-co-acrylonitrile (SAN) is a glassy thermo plastic material with industrial importance towards developing polymeric products for structural applications. The drawback of this copolymer is its limited impact strength. This work aims at improving the impact strength of SAN by blending it with liquid isoprene rubber (LIR). Compositions of SAN/LIR viz., 85/15, 80/20, 75/25 and 70/30 were melt mixed and subjected to dynamic vulcanization in a Haake Rheomixer using peroxide as vulcanizing agent. The mechanical properties such as, tensile, flexural and impact strength of all the compositions were measured as per ASTM standards and was compared with neat SAN. The effect of LIR on the thermal properties and phase morphology of the blends were characterized using dynamic mechanical analyzer and scanning electron microscope respectively. Authors observed that, by blending 20% LIR with SAN, there was 6% increase in elongation at break and 45% additional impact modification with a reduction in tensile and flexural moduli. Its microscopic morphology depicted globular and fine dispersion of LIR particles in SAN matrix, which is a well-known phase morphology favoring the toughness. This study offers a novel approach in developing thermoplastic vulcanizates (TPVs) using liquid rubbers in order to toughen the SAN. Which is also an energy efficient process compared to the TPVs developed using solid elastomers.

Keywords- Styrene acrylonitrile (SAN), dynamic vulcanization, liquid isoprene rubber (LIR), impact modification, thermoplastic vulcanizate (TPV), toughening,

I. INTRODUCTION

Commodity thermoplastic materials are versatile polymers. Poly styrene-co-acrylonitrile (SAN) is one such polymer which is a glassy, transparent, thermoplastic material with industrial importance towards developing wide range of polymeric products for structural applications. SAN is available since 1940s, which was developed to overcome the toughness issues of poly styrene (PS). SAN is a random copolymer containing 60-80% of styrene and 20-40% of acrylonitrile. Among the characteristics of SAN, the important features like rigidity and transparency makes it competitive over PS, cellulose acetate (CA), and poly methyl methacrylate (PMMA). Compared to PS, the SAN has good weatherability, stress cracking resistance, surface hardness, chemical and hydrocarbon oil resistance. SAN is cheaper than PMMA and CA; tougher than PMMA and PS; superior in chemical resistance and physical properties compared to PS and CA [1]. As a result of above characteristics, the SAN has been used in production of dials, knobs, and covers for domestic appliances; electrical and car equipment; for picnicware and housewares. However, compared to other engineering thermoplastics, the SAN is slightly brittle with limited impact strength and low fracture energy that limits its dynamic applications. So, to increase the window of its utility, its toughening or impact modification became essential [2-4].

Thus, the toughness enhancement being the driving force behind investigations with SAN, it led to development of a well-known terpolymer in 1950s, that which copolymerized butadiene along with styrene and acrylonitrile, that is, the versatile 'ABS' material [5]. Furthermore, many researchers adapted 'copolymerization' and 'blending of rubbers' with PS and SAN as the ways to- impart high impact strength and reduce the brittle nature of their fracture mechanism; for example, development of the well-known high impact grade of polystyrene (HIPS) and SAN [1]. But, in both of the above-mentioned approaches, there are two major limiting factors that are common. Firstly, the presence of unsaturated rubber content, which is prone to degradation during its processing/ service life. Secondly, the loss of transparency due to change in refractive index which is a resultant of phase separation of rubber. This has led to the investigations that retains transparency (by reducing the particle size of rubber) and reduce the unsaturation (by either reacting the pi bonds present in rubber or using saturated rubbers or other toughening agents like engineering plastics, liquid plasticizers, fibres or fillers) [5-9].

However, among the approaches under toughening of the thermoplastics / thermosets, the use of elastomers as toughening agent in various forms remain to be one of the most widely adapted techniques [10-14]. The elastomers can be blended to the brittle plastics or thermosets by- a) physical blending b) chemical blending (copolymerisation) or c) dynamic vulcanization. Undoubtedly, each of them is found to be beneficial in imparting impact strength but it comes with its own complexity and drawbacks as mentioned ahead.

Ahn et. al. blended 30 parts by weight (pbw) of NBR with SAN and there was an increase in impact strength of SAN. The acrylonitrile content in nitrile rubber contributed to such enhanced performance but with a reduction in tensile and flexural moduli [15]. Hwang et. al. melt blended SAN with ethylene-propylene-diene (EPDM) and chlorinated polyethylene (CPE). The combination of the two rubbers (EDPM and CPE) as impact modifiers produced a synergistic toughening effect but, tensile modulus was reduced [16]. Usually, in the case of physical blends, there is a lack of interfacial adhesion that reduces tensile or flexural strength, and this can be improved by compatibilization.

Liu et. al. grafted methyl methacrylate and acrylo-nitrile onto EPDM and then blended it with SAN to achieve 50 times greater impact strength of SAN matrix [17]. Mai et. al. grafted EPDM with SAN and blended it with neat SAN. The morphological analysis of the blend showed a 'salami' like phase structure with toughening mechanism involving shear yielding of the SAN matrix imparting excellent toughness [18]. There exist many such investigations which enhanced compatibility of blend components and assisted the development of finer dispersion of elastomeric particles in the rigid SAN matrix by incorporating a specially prepared rubbery toughening agent that contributed to greater degrees of impact modification. Examples include; methyl methacrylate grafted butadiene rubber [19], NR-based latex particles coated by PMMA layer [20], acrylonitrile – (ethylene propylene diene) – styrene [21], (ethylene-propylene)-graft-methyl methacrylate and acrylonitrile [22] and (ethene-co-1-butene)-g-methyl methacrylate-acrylonitrile [23]. Such blends of SAN with elastomers showed improved impact strength due to the toughening mechanism that usually involved initiation of craze from the rubber particles, followed by shear deformation. However, in these cases, the phase morphology is prone to change under varying pressure and temperature that the material encounters in different stages of its handling.

This has led to the development of TPVs that offer better processability and impact modification along with the stable phase morphology [24-26]. In the work carried out by Taheri Mouna et. al., EPDM and SAN were reactive blended using peroxides and was studied for its morphology and mechanical properties. There was increased impact strength along with compatibility between the phases [27]. The effect of NBR/SAN ratio and its dynamic vulcanization on mechanical properties and morphology of thermoplastic elastomer (TPE) compositions were studied by Anandhan and others. The blends showed fine dispersion of rubber particles and improvement in mechanical properties [28]. Similarly, the dynamic vulcanization of TPE/nano-composite based on SAN/EVA (ethylene vinyl acetate) and nano-clay was studied by Patel and others, and significant improvement in the mechanical properties was observed [29].

Wang et. al. developed ternary blend of polyamide, SAN and nitrile rubber by dynamic vulcanization using 8 phr of phenol formaldehyde and it resulted in a super tough material having impact strength of 800 J/m due to its optimum micro-structure morphology. Compared to melt blended SAN and elastomers, the toughening mechanism observed in dynamically vulcanized blends is slightly different. It involves energy absorption by the rubber particles followed by debonding at the rubber-glassy matrix interface and finally crazing [30, 31].

Among the efforts to develop high impact grades of SAN using elastomeric moieties, the copolymerization or the compatibilization of blends require an additional step of careful and controlled molecular reactions, which would obviously involve an added time and cost as compared to the simple blending or dynamic vulcanization. And, if a high molecular weight elastomer is involved in the above processes then, it normally increases the blend viscosity and reduces the processability of SAN [15]. In some of the investigations, liquid rubbers have been used as reactive plasticizer with NR [32], and CR-BR (chlorobutadiene – butadiene rubber) compound [33]; The liquid rubbers are even used as impact modifiers with thermosets like unsaturated polyester resin [14],

epoxy resins [34] and also as toughening agents with thermoplastics like nylon [35] and polystyrene [36]. However, utilization of liquid rubber (especially liquid isoprene rubber) to develop TPVs in order to toughen plastics (like SAN) has not been claimed or systematically reported. Hence, the authors in the present investigation have aimed at utilizing liquid isoprene rubber (LIR) for blending with SAN using Haake Rheomixer. Further, the blend is subjected to dynamic vulcanization using di-cumyl peroxide (DCP), which is a well-known free radical source that has been commonly used as an initiator, catalyst or curing agent. When compared with conventional sulphur crosslinking, the peroxides offer advantages of- good heat resistance, no discoloration of base material, transparency, stable C-C crosslinks and thus a good overall ageing resistance along with excellent resistance to compression set at high temperatures [37].

II. Experimental

Materials

Materials used in the present work is listed in Table 1. Among them, SAN is the base polymer and LIR is used as an oligomeric reactive toughener which also serves as plasticizer during the initial stage of mixing, and DCP serves as crosslinking agent.

Dynamic Vulcanization

Dynamic vulcanization is the process of blending thermoplastic and rubbery material followed by crosslinking using a curative and dispersing the rubbery phase in the plastic matrix. This procedure was carried out using rheo-mixer (Torque rheometer Haake rheocord, Thermo electron corporation, Haake RC 300P, Germany). Four compositions of SAN/LIR viz., 85/15, 80/20, 75/25 and 70/30 were developed. The compositions were regarded as LIR15, LIR20, LIR25 and LIR30 respectively. To crosslink the LIR phase, 5 parts per hundred rubber (phr) of DCP was incorporated. The mixer was set to 180 ºC and maintained same during the entire course of mixing. Firstly, the weighed quantity of SAN was introduced into the mixer to attain homogenized melt state at a constant rotor speed of 40 rpm. It was followed by addition of LIR, DCP, and mixed till the completion of crosslinking. The average time for complete process was about 12 minutes.

Specimen preparation and characterisation of blends

To evaluate the effect of LIR content on the mechanical properties of SAN, the test specimens were molded using hydraulic injection moulding machine (PIM1HDS, 4-ton clamping force, Tex Shine, Coimbatore) at 180 0C and 8 bars. The blends were also characterised for their morphology and thermal properties. The results obtained were compared with that of the virgin SAN (also referred as LIR0).

Mechanical properties

Hardness of the samples were determined as per ASTM D2240 using a Shore-D durometer. Tensile and flexural properties of the blends were determined using universal testing machine (UTM-servo, International Equipments, Mumbai) as per ASTM D638 and ASTM D790 respectively. The izod impact strength of all the specimens were determined as per ASTM D256 using Izod/Charpy impact tester (International Equipments, Mumbai).

Thermal and microscopic analysis

The glass transition temperature (Tg), loss / storage modulus and tan delta of the compositions were determined using dynamic mechanical analyzer (DMA, Q800, TA Instruments, USA) under tensile mode at 1 Hz, at a strain of 0.01%, and temperature ranging from -60 to 150 °C with a heating rate of 2 °C/min.

The phase morphology was assessed using a scanning electron microscope (SEM, JSM –IT300LV, USA) for which the tensile fractured specimens were used after gold sputtering.

III. RESULTS AND DISCUSSIONS

Effect of dynamic vulcanization on viscosity of the blend

During melt blending, the torque versus time was recorded to understand the effect of dynamic vulcanization on the viscosity of the blend. The rheograph pertaining to the dynamic vulcanization of LIR30 is shown in Figure 1. It can be observed from the figure that, initially when the SAN in charged into the mixer the torque is high and as the shearing happens under melting temperature, the viscosity of SAN drops down from 13 to 1 Nm. After the homogenization of melt (indicated by torque stabilization) at sixth minute, the LIR and DCP were added. Instantaneously, the graph shows a small decrease in the torque due to instant lubricating effect. A similar observation was reported by Ismail et. al. during the dynamic vulcanization of PS/SBR [38]. Then, as the crosslinking of LIR starts, the viscosity builds up and the torque is increased to a peak maximum of 10.8 Nm. Later, the crosslinked rubber particles get dispersed and distributed in SAN matrix wherein which the torque gets again stabilized by reaching 9.5 Nm at around 12th minute. Similar trend was noticed for other compositions (viz. LIR15, LIR20 and LIR25) except for the change in peak torque and equilibrium torque (Table 2). The effect of LIR content on peak torque and equilibrium torque is shown in Figure 2. From the figure it can be observed that, there is an increase in the peak torque and equilibrium torque with increase in LIR content. Which indicates that the increased crosslinking during dynamic vulcanization exerts more resistance on rotors of the rheomixer. Similar results are also reported by Ismail et. al. during the dynamic vulcanization PP/NR blends [39].

It was observed by Ahn et. al. that, by blending solid elastomer with SAN, the blend's melt viscosity was increased [15]. Further, if the solid elastomer is dynamically vulcanized then, the melt viscosity of the blend would also increase [39], and which in turn may affect the processability of the resultant blend. Ismail et. al. also reported the increased torque of PS/SBR during its dynamic vulcanization, which was more than 20 Nm [40]. SAN being even more viscous than PS [41], if a solid elastomer had been used for blending followed by its dynamic vulcanization then, that would have been resulted in much higher torque. However, in the present case, the addition of LIR is not having significant effect on the melt viscosity at the initial stage, but during its dynamic vulcanization, though there is an increase in torque, it is lower than what would be expected when solid elastomer was used. Hence, the liquid rubber is intended to offer energy efficient mixing and processing.

Effect of LIR content on mechanical properties of SAN

The mechanical test results of the TPV compositions and the neat SAN (LIR0) are tabulated in Table 3. As expected, with the inclusion of soft rubbery phase, the hardness of SAN reduced (from 80 shore-D for virgin SAN to 42 shore-D for 30% LIR). The tensile strength, tensile modulus, flexural strength and flexural modulus of the compositions containing LIR was lower than the virgin SAN. However, from the values mentioned in the table, an interesting trend can be observed among the compositions containing LIR. That is, the tensile modulus, tensile strength and flexural strength increases up-until 20% LIR content and further decreases. Conversely, when the percentage elongation at break (Figure 3) and the impact strength values are observed (Figure 4), all the compositions show higher values than virgin SAN in an increasing order till 20% LIR content and then decreases with further LIR addition. From the foregone discussions, it can be inferred that, with the addition of 20 parts of LIR, there is a promising increase in impact strength and elongation at break of SAN, which is about 45% and 5% respectively. Also, the other properties that are mentioned earlier are better at 20% LIR content than the remaining blend compositions. Such decrement in tensile and flexural strength with increased rubber content was also reported by Hwang et. al. in their investigation with blend of SAN/EPDM/CPE [16]. The further investigations on thermal and morphological analysis were confined to three compositions, viz. LIR0 (that is neat SAN), LIR20 (which offered better properties) and LIR30 (which showed reduced properties). The above variations in mechanical properties do correlate with the microscopic phase morphology which is discussed in the subsequent section.

Dynamic mechanical analysis

The dynamic mechanical properties of the blends are usually evaluated to study its miscibility and effect on visco-elastic behaviour of base polymer. The temperature corresponding to the maxima of tan delta is usually related to the glass transition temperature (Tg). The DMA analysis assists the miscibility studies of blends by observing this Tg. The increase in elasticity or plasticity is clearly sensed by DMA based on decrease or increase in peak value of tan delta (respectively) [42,43]. The storage modulus and Tg of LIR0, LIR20 and LIR30 obtained from DMA are given in Table 4. From the table, it can be observed that, as expected, the inclusion of soft rubbery phase resulted in decrease of storage modulus and Tg of the blends. However, the Tan delta has also slightly reduced from 2.3 for neat SAN to 1.7 for LIR30, which should have otherwise been increased as there is an increase in viscous component due to the presence of excess LIR, but, as the rubber gets cross linked, it contributes to increase in elastic component and hence, the reduction in loss tangent is of lower order than expected [42,43].

Phase morphology

Characteristics of blend is very much governed by its phase morphology. Immiscible blends are gaining industrial significance and its properties depend on the fineness of the phase morphology that gets formed during its melt-mixing. Further, during its shaping and service life, due to variation in thermodynamic parameters, the morphology tends to get altered in some cases. For this reason, it appears that results reported in many articles are contradictory. Hence, deeper

investigations in this particular aspect is ongoing. The main mechanism governing such blend morphology is a result of breaking up of droplet domain due to applied shear force and its coalescence over thermodynamic conditions. For the blends containing higher concentrations of the minor phase, such coalescence effects are predominant. Further, it is also true that, blending a highly viscous polymer with a low viscous molecule would affect quiescent phase coarsening [44]. In the present case, if liquid rubber would not have been vulcanized, then it would easily flow and coalesce back, and with increase in liquid rubber concentration, the coalescence would have been much more predominant leading to ineffective toughening. Mazidi et. al. investigated about such unstable phase morphologies leading to unstable fracture behavior in rubber toughened SAN. In which, it has been reported that the improvement of the toughness is a function of number of factors, such as type of rubber, rubber content, its particle size, extent of cross-linking, its adhesion with the base matrix phase, etc. So, there is always a greater challenge in predicting the fracture behavior of such systems or its toughening mechanism [45].

The SEM micrographs of SAN and the TPV compositions LIR20 and LIR30 is shown in Figure 5. From the micrographs it can be observed that, pure SAN depicts rough fracture surfaces which is indicative of brittle fracture behaviour. With the addition of 20% LIR, the blend phase morphology begins to show the globular rubber domains been dispersed in the major SAN matrix. Also, due to the presence of rubber phase, the fracture surface is relatively smooth, which means that the brittle fracture is transforming to ductile fracture mode. Further, with 30% addition of LIR, the blend phase morphology becomes co-continuous in nature, also the fracture surface is even smoother.

The morphology pertaining to LIR20 (Figure 5b) justifies the increased impact strength and elongation at break, which is due to energy absorption offered by the dispersed rubber phase in the SAN matrix. Further, the reduction of all the properties at 30% LIR content (as discussed earlier) could be attributed to the dramatic decrease in hardness of SAN by 50 % (Table 3). Even though there is a formation of co-continuous phase in the present case, which is also known to increase the mechanical properties, the blend failed to withstand the applied mechanical forces at interface. Such a behaviour in the present case may be attributed to absence of stronger forces of interaction between the components. Similar trends have been observed in an investigation pertaining to blends of SAN and HIPS [3, 46].

IV. CONCLUSIONS

From the present investigation, a newer approach in developing thermoplastic vulcanizate (TPV) using liquid isoprene rubber (LIR) and styrene acrylonitrile copolymer (SAN) is reported. Melt blending the polar SAN with non-polar LIR in presence of curing agent (DCP) in a rheo-mixer produced the dynamically vulcanized rubber blend. This makes the LIR non-blooming unlike other liquid plasticizers.

There is a considerable increase in izod impact strength (~45%) and elongation at break (~5%) at 20% LIR incorporation. Further increase in LIR content decreases the hardness, tensile / flexural strength and modulus. Thus, the 20% of LIR-50 imparts toughness into the SAN matrix through TPV approach along with facilitating energy efficient blending and processing over TPVs developed using solid elastomers.

VII. REFERENCES

1. M. Yokouchi, S. Seto, Y. Kobayashi, "Comparison of polystyrene, poly (styrene/acrylonitrile), high-impact polystryrene, and poly (acrylonitrile/butadiene/styrene) with respect to tensile and impact properties," *Journal of Applied Polymer Science,* Vol.28, No.7, 1983, pp.2209-16.

2. M. Gilbert, "editor. Brydson's plastics materials," *William Andrew,* 2016.

3. S. Li, X.J. Zhang, "Toughening mechanism of SAN resin," *Journal of Polymer Research,* Vol.2, No.4, 1995, pp.239-45.

4. L.W. McKeen, "The effect of sterilization on plastics and elastomers," *William Andrew,* 2018.

5. J.D. Moore, "Acrylonitrile-butadiene-styrene (ABS)-a review," *Composites,* Vol.4, No.3, 1973, pp.118-30.

6. M. Colella, B. Marcoulier, "inventors; Novacor Chemicals International SA, assignee. Highly transparent tough polymer blends," *United States patent US 5,344,878,* 1994.

7. M. Quaresimin, K. Schulte, M. Zappalorto, S. Chandrasekaran, "Toughening mechanisms in polymer nanocomposites: From experiments to modelling," *Composites Science and Technology,* 2016, pp. 123:187-204.

8. A.H. Gilbert, C.B. Bucknall, "Epoxy resin toughened with thermoplastic. InMakromolekulare Chemie," *Macromolecular Symposia,* Vol. 45, No. 1, 1991, pp. 289-298.

9. H. Kang, Y. Li, M. Gong, Y. Guo, Z. Guo, Q. Fang, X. Li, "An environmentally sustainable plasticizer toughened polylactide," *RSC advances,* Vol.8, No.21, 2018, pp. 11643-51.

10. H. Keskkula, D.R. Paul, "Toughening agents for engineering polymers," *In Rubber Toughened Engineering Plastics,* 1994, pp. 136-164.

11. M. Wang, Y. Wu, Y.D. Li, J.B. Zeng, "Progress in toughening poly (lactic acid) with renewable polymers," *Polymer Reviews,* Vol.57, No.4, 2017, pp.557-93.

12. E.B. Caldona, A.C. De Leon, B.B. Pajarito, R.C. Advincula, "A review on rubber-enhanced polymeric materials," *Polymer Reviews,* Vol.57, No.2, 2017, pp. 311-38.

13. J.Z. Liang, R.K. Li, "Rubber toughening in polypropylene: A review," *Journal of Applied Polymer Science,* Vol.77, No.2, 2000, pp.409-17.

14. M.P. Chandresh, C.D. Ani Dechamma, M. Bhavana, N. Rameshwara, S. Roopa, "Toughening of unsaturated polyester resin by solid elastomers and liquid rubbers: A review," *International Research Journal of Engineering and Technology,* Vol. 8, No.4, 2021, pp. 4885-4891.

15. S.J. Ahn, K.H. Lee, B.K. Kim, H.M. Jeong, "Morphology and physical properties of SAN/NBR blends: The effect of AN content in NBR," *Journal of applied polymer science,* Vol.78, No.11, 2000, pp.1861-8.

16. I.J. Hwang, M.H. Lee, B.K. Kim, "Preparation and properties of SAN/EPDM/CPE ternary blends," *European polymer journal,* Vol.34, No.5-6, 1998, pp. 671-5.

17. W. Liu, L. Wang, J. Mai, A. Zhang, "Synthesis of EPDM-g-MAN by suspension graft copolymerization and its toughening effect on SAN resin," *Polymer bulletin.,* Vol.71, No.12, 2014, pp.3111-29.

18. J. Mai, J. Zhu, L. Wang, "Toughening Effect of Ethylene Propylene DieneTerpolymer-Graft-Styrene-Acrylonitrile Copolymer (EPDM-g-SAN) on SAN Resin," *Journal of Macromolecular Science, Part B.,* Vol.53, No.3, 2014, pp.513-28.

19. H. Keskkula, H. Kim, D.R. Paul, "Impact modification of styrene-acrylonitrile copolymers by methyl methacrylate grafted rubbers," *Polymer Engineering & Science,* Vol.30, No.21, 1990, pp.1373-81.

20. M. Schneider, T. Pith, M. Lambla, "Structured latex particles as impact modifiers for poly (styrene–co-acrylonitrile) blends," *Polymers for Advanced Technologies,* Vol.7, No.7, 1996, pp.577-88.

21. Z. Zeng, L. Wang, T. Cai, X. Zeng, "Synthesis of high rubber styrene–EPDM–acrylonitrile graft copolymer and its toughening effect on SAN," *Journal of applied polymer science,* Vol.94, No.2, 2004, pp.416-23.

22. K. Xiong, L. Wang, A. Zhang, "Suspension grafting copolymerization of EPM-g-MAN and its toughening effect on SAN resin," *Journal of Elastomers & Plastics,* Vol.43, No.1, 2011, pp.49-63.

23. K. Xiong, Y. Zhu, L. Wang, T. Cai, A. Zhang, X. Zeng, "Graft Polymerization of Methyl Methacrylate-Acrylonitrile onto Poly (ethene-co-1-butene) and Its Toughening Effect on SAN Resin," *Journal of Macromolecular Science, Part B.*, Vol.51, No.7, 2012, pp.1351-69.

24. R. Asaletha, M.G. Kumaran, S. Thomas, "Thermoplastic elastomers from blends of polystyrene and natural rubber: morphology and mechanical properties," *European Polymer Journal,* Vol.35, No.2, 1999, pp.253-71.

25. S. Anandhan, P.P. De, A.K. Bhowmick, S.K. De, S. Bandyopadhyay, "Thermoplastic elastomeric blend of nitrile rubber and poly (styrene-co-acrylonitrile). II. Replacement of nitrile rubber by its vulcanizate powder," *Journal of Applied Polymer Science*, Vol.90, No.9, 2003, pp.2348-57.

26. K. Naskar, J.W. Noordermeer, "Thermoplastic elastomers by dynamic vulcanization," *Progress in Rubber Plastics and Recycling Technology,* Vol.21, No.1, 2005, pp.1-26.

27. M. TAHERI, J. Morshedian, M. Esfandeh, A. Vahidi, "Reactive compatibilization of SAN/EPDM blend and study of the parameters affecting its properties".

28. S. Anandhan, P.P. De, S.K. De, A.K. Bhowmick, "Thermoplastic elastomeric blend of nitrile rubber and poly (styrene-co-acrylonitrile). I. Effect of mixing sequence and dynamic vulcanization on mechanical properties," *Journal of applied polymer science,* Vol.88, No.8, 2003, pp.1976-87.

29. J. Patel, M. Maiti, K. Naskar, A.K. Bhowmick, "Nanocomposites based on thermoplastic elastomeric blends of styrene acrylonitrile and ethylene vinyl acetate: Effect of nature and loading of nanoclays and dynamic vulcanization," *Polymers and Polymer Composites,* Vol.14, No.5, 2006, pp.515-25.

30. Z. Wang, X. Zhang, Y. Zhang, "Impact properties of dynamically vulcanized nylon/styrene–acrylonitrile copolymer/nitrile rubber blends," *Polymer testing,* Vol.21, No.5, 2002, pp.577-82.

31. Z. Wang, X. Zhang, Y. Zhang, Y. Zhang, W. Zhou, "Effect of dynamic vulcanization on properties and morphology of Nylon/SAN/NBR blends: A new compatibilization method of Nylon/ABS blends," *Journal of applied polymer science,* Vol.87, No.13, 2003, pp.2057-62.

32. M.P. Chandresh, S. Roopa, Siddaramaiah, "Liquid isoprene rubber as a safe processing aid in natural rubber compounds," *Rubber Science,* Vol.34, No.1, 2021, pp. 91-100.

33. K. Sando, S. Kohjiya, Y. Ikeda, S. Yamashita, N. Kawabata, "Liquid rubber as a reactive softener for 1-chlorobutadiene–butadiene rubber," *Journal of applied polymer science,* Vol.62, No.7, 1996, pp.1093-8.

34. D. Gunwant, P.L. Sah, M.G. Zaidi, "Morphology and micromechanics of liquid rubber toughened epoxies," *e-Polymers*, Vol.18, No.6, 2018, pp.511-27.

35. G.M. Shashidhara, K.G. Pradeepa, "Preparation and characterization of polyamide 6/liquid natural rubber blends," *Journal of Applied Polymer Science,* Vol.131, No.2, 2014.

36. G.J. Salomons, M.A. Singh, L.G. Hiltz, L.H. Pan, W.R. Newson, "SAXS study of deformation mechanisms in liquid rubber-toughened polystyrene," *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms.,* Vol.97, No.1+-4, 1995, pp.282-6.

37. J. Kruželák, R. Sýkora, I. Hudec, "Sulphur and peroxide vulcanisation of rubber compounds–overview," *Chemical Papers,* Vol.70, No.12, 2016, pp.1533-55.

38. H. Ismail, Z. Mohamad, B.A. ABU, "The effect of dynamic vulcanization on properties of rice husk powder filled polystyrene/styrene butadiene rubber blends".

39. H. Ismail, M.N. Salmah, "Dynamic vulcanization of rubberwood-filled polypropylene/natural rubber blends," *Polymer testing,* Vol.20, No.7, 2001, pp.819-23.

40. M. Zurina, H. Ismail, A.A. Bakar, "Rice husk powder–filled polystyrene/styrene butadiene rubber blends," *Journal of applied polymer science,* Vol.92, No.5, 2004, pp.3320-32.

41. K. Satterthwaite, "Plastics Based on Styrene," *InBrydson's Plastics Materials,* 2017, pp. 311-328.

42. X.Y. Shi, W.N. Bi, S.G. Zhao, "DMA analysis of the damping of ethylene–vinyl acetate/acrylonitrile butadiene rubber blends," *Journal of Applied Polymer Science,* Vol.124, No.3, 2012, pp.2234-9.

43. D.G. Dikobe, A.S. Luyt, "Morphology and properties of polypropylene/ethylene vinyl acetate copolymer/wood powder blend composites," *Express Polymer Letters,* Vol.3, No.3, 2009, pp.190-9.

44. V. Everaert, L. Aerts, G. Groeninckx, "Phase morphology development in immiscible PP/(PS/PPE) blends influence of the melt-viscosity ratio and blend composition," *Polymer,* Vol.40, No.24, 1999, pp.6627-44.

45. M.M. Mazidi, M.K. Razavi Aghjeh, F. Abbasi, "Unstable fracture behavior of rubber toughened poly (styrene-co-acrylonitrile)," *Journal of Macromolecular Science, Part B.,* Vol.52, No.8, 2013, pp.1158-82.

46. Z. Wang, H. Zhao, J. Zhao, X. Wang, "Rheological, mechanical and morphological properties of thermoplastic vulcanizates based on high impact polystyrene and styrene-butadiene rubber," *Journal of applied polymer science,* Vol.117, No.5, 2010, pp.2523-9.

Table 1: Details of Materials Used

| Material	Manufacturer/ Supplier	Specifications/ Remarks	
Styrene acrylonitrile copolymer: Lustran Sparkle **SAN**	Monsanto, St. Louis, MO	ACN content:	27%
		Specific Gravity	1.07
		Melt Flow Index (at 230 ^{0}C, 3.8 kg)	12 g/10 min
Liquid isoprene rubber: **LIR-50**	Kuraray Co. Ltd., Japan	Specific Gravity	0.91
		Molar mass	54,000 g/mole
		Viscosity (at 38 ºC)	500 Pa.s
Di cumyl peroxide: **DCP**	Aldrich, Milwaukee, WI	Purity	98%

Table 2: Effect of LIR content on Torque during blending

LIR content (%)	Peak Torque (Nm)	Equilibrium Torque at 14th minute (Nm)
0	_	1.2
15	6.9	6.3
20	7.4	6.7
25	8.4	7.0
30	10.8	9.5

Table 3: Effect of LIR content on mechanical properties of SAN

Composition	LIR0	LIR15	LIR20	LIR25	LIR30
Hardness (shore-D)	80	65	56	51	42
Tensile Modulus (MPa)	928	305	452	400	329
Tensile Strength (MPa)	52	17	28	22	19
Flexural Strength (MPa)	89	24	39	37	25
Flexural Modulus (MPa)	4077	2512	2572	2550	2107
Elongation at break (%)	14.2	16.3	20.6	18.1	17.6
Impact Strength (J/m)	166	205	240	189	148

Table 4: Effect of LIR on storage modulus,Tan Delta and T$_g$

Properties	SAN	LIR20	LIR30
E$^{'}$ at 70ºC (MPa)	1917	1101	929
E$^{'}$ at 80ºC (MPa)	1812	1028	858
E$^{'}$ at 90ºC (MPa)	1636	914	758
Tan Delta	2.3	1.9	1.7
T$_g$ (^{0}C) (from Tan Delta)	116	111	110
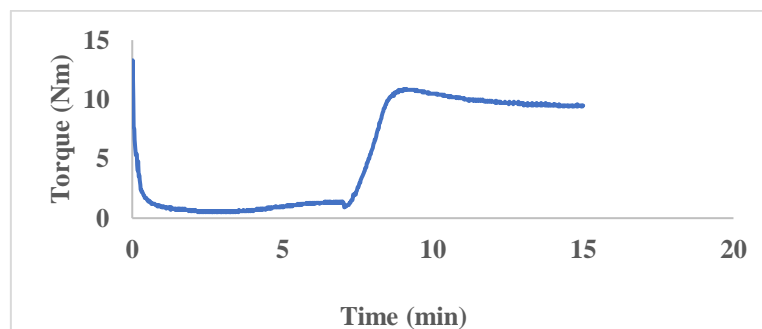
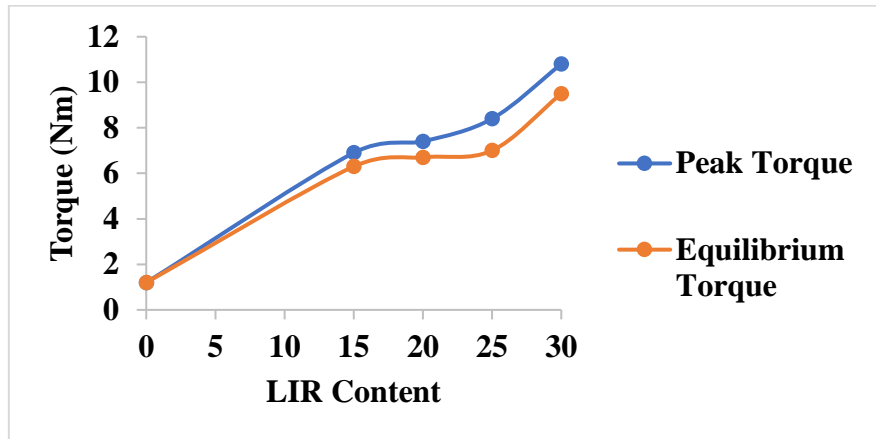**Figure 1: Rheograph of dynamically vulcanized LIR30 blend**

Figure 2: Effect of LIR content on Peak Torque and Equilibrium Torque
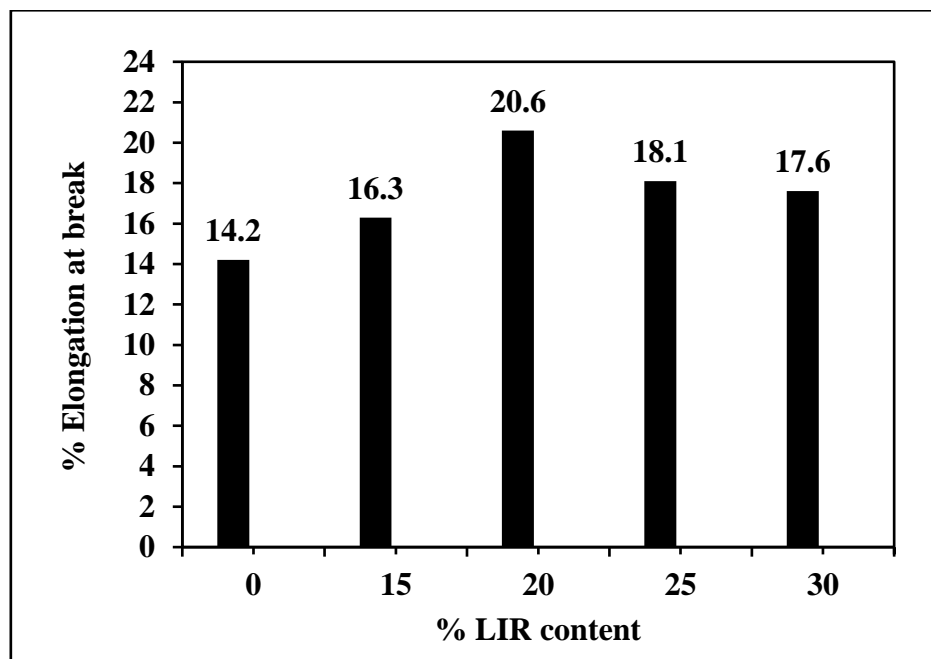

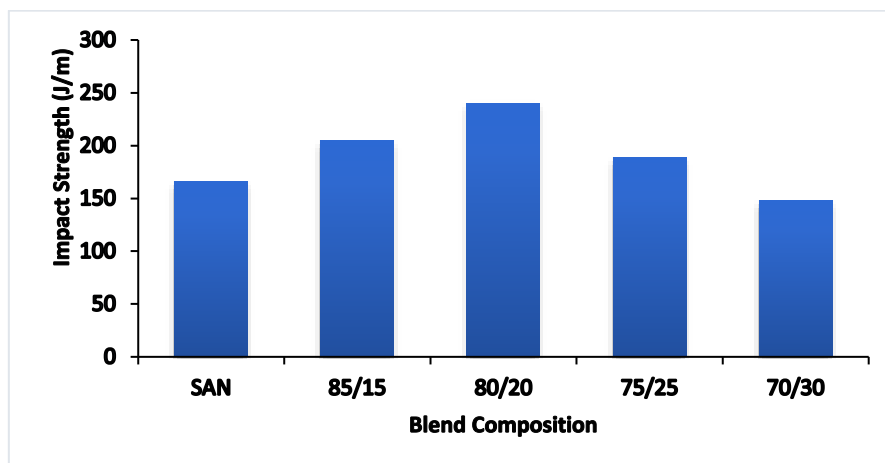**Figure 3: Effect of LIR content on elongation at break**

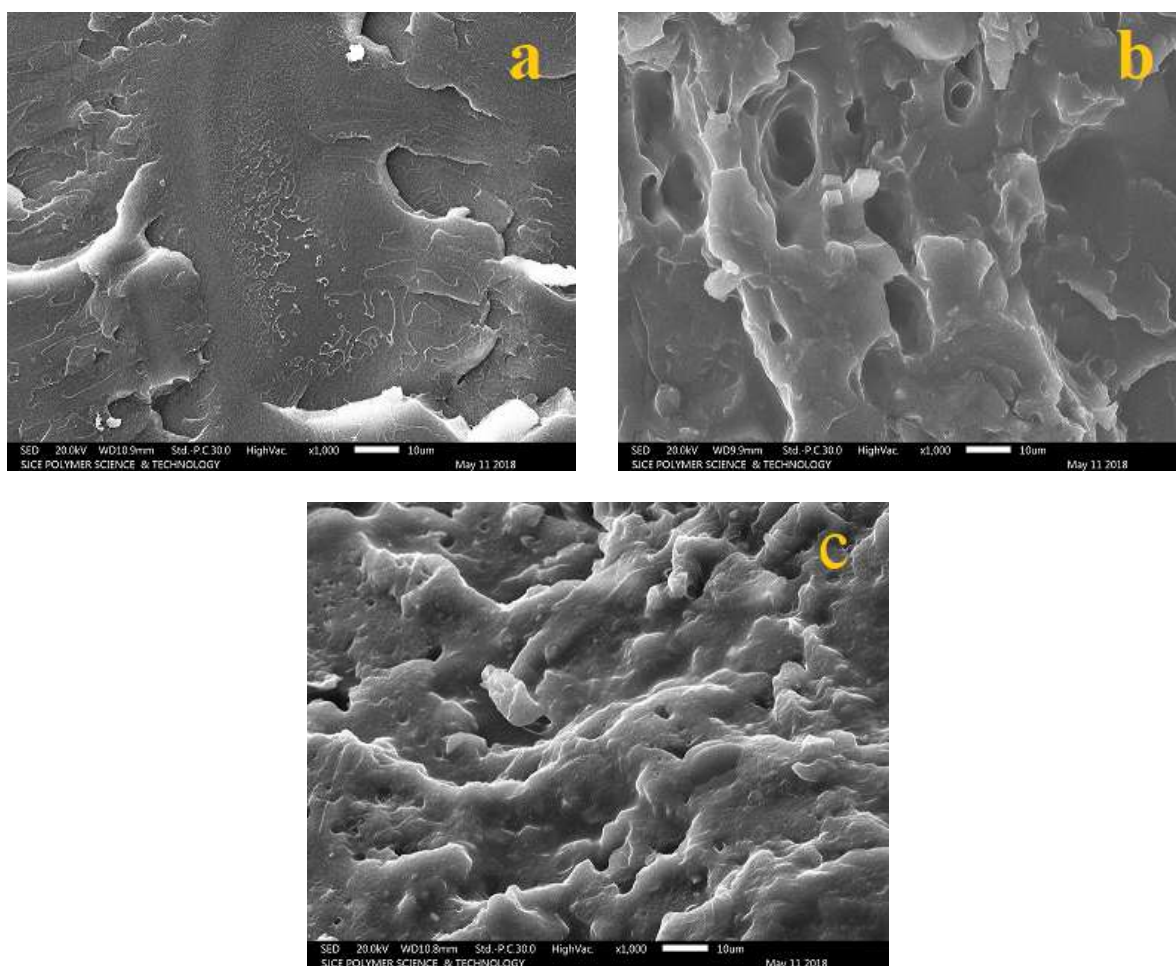**Figure 4: Effect of LIR content on impact strength of SAN**

Figure 5: Effect of LIR on phase morphology- a) SAN b) LIR20 c) LIR30