

BLENDING & TESTING OF FLAME RETARDED FLUXED NBR / PVC BLENDS

By

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Abstract :

Flame retarded fluxed Polyvinylchloride / Acrylonitrile Butadiene Rubber compositions can be prepared by (a) pre-stabilization of PVC, (b) blending pre-stabilized PVC with NBR to form a pre-stabilized NBR/PVC blend, (c) applying heat and shear to intimately blend said pre-stabilized NBR/PVC blend into fluxed NBR / PVC blend. Four different compositions of NBR/PVC blends, using stabilizer system including Ca Stearate, Zn Stearate and Ferric Oxide, were prepared and subjected to various thermal, mechanical and physical tests. Results reveal that the new compositions exhibit increased flame retardence, and improved physical, thermal and mechanical properties.

Keywords: PVC, NBR, Ca Stearate, Zn Stearate, Ferric Oxide, Tg.

1. INTRODUCTION

Blends of Acrylonitrile Butadiene Rubber (NBR) and Poly Vinyl Chloride (PVC) are commercially important and have a wide range of industrial applications.^[1,2] Acrylonitrile Butadiene Rubber/Poly Vinyl Chloride (NBR / PVC) is a miscible physical mixture of commercial importance. The NBR can act as a permanent plasticizer for PVC. The presence of PVC improves aging resistance of NBR as both PVC and NBR are polar and blending NBR with PVC increases the compatibility.^[1-4]

The aim in blending plastic and rubber is to improve the physical, thermal, and mechanical properties as well as to modify the processing characteristics and cost reduction of the final product.

Flame retarded NBR/PVC compositions are economical, have improved flame retardence, heat and light stability and reduced toxicity. Thermal stability of the blends is critically important to their performance when formulated into finished products. Flame retarded fluxed blends of NBR/PVC exhibit greatly enhanced thermal stability. This increased stability results from the process of coating the PVC with stabilizer prior to fluxing. The resulting fluxed blend demonstrates much improved color stability coupled with increased mixing time.^[5]

In addition, enhanced thermal stability will reduce the amount of off-grade material manufactured thereby reducing the production cost and increasing the product manufacturing efficiency.^[5]

2. EXPERIMENTAL

2.1. Materials

Materials used in these experiments were PVC (PolyvinylChloride), NBR (Acrylonitrile Butadiene Rubber), Ca Stearate, Zn Stearate and ferric Oxide. Suspension grade poly(vinyl chloride), Mecion HP65, with K-value 65 and degree of polymerization 920–1060 was supplied by Malayan Electro-Chemical Industry Co. Sdn. Bhd., Penang, Malaysia. Nitrile rubber (NBR) with 34% acrylonitrile content was purchased from Waters (M) Ltd. Ca Stearate, Zn Stearate and ferric Oxide was obtained from Descon Chemicals Private Limited, Lahore Pakistan.

2.2. Preparation of flame retarded fluxed NBR / PVC blends

Preparation of PVC/NBR blends consists of the following steps:

- a) Coating a PVC resin with stabilizer system to form pre-coated PVC
- b) Blending said pre-coated PVC with NBR to form a pre-stabilized NBR/PVC blend
- c) Applying heat and pressure to intimately blend said pre-stabilized NBR/PVC blend into a fluxed NBR/PVC blend

Pre-stabilization of PVC

PVC particulates were first coated with the stabilizer package such that PVC particulates were substantially covered by the stabilizer prior to blending and fluxing operation. The pre-stabilization process was carried out in a Brabender Plasticoder (PLE-330) to raise the temperature of the PVC particulate/stabilizer mixture to at least about 60° C but no higher than 80° C. At 80° C, the pre-stabilized PVC was removed from the mixer.

Blending and fluxing of PVC/NBR

The NBR rubber, in crushed form, was mixed with the pre stabilized PVC in a brabender mixer to a minimum temperature of 350° F up to a maximum temperature of 450° F, preferably 375 to 400° F. Alternatively, extruders of single or twin screw types may also be used to advantage to intimately blend and flux the PVC/NBR materials. [6]

The mixer was preheated to 175 degree prior to the NBR/PVC fluxing operation. A mixture of NBR and pre stabilized PVC in different ratios was introduced into the brabender mixer at a preset operating speed of 50 rpm, during processing the speed was increased to 60 rpm. When the NBR/PVC was completely loaded, the mixture speed was increased to 80 rpm for 1 min and then again reduced to 60 rpm until a temperature of 188 degree was reached. At 188 degree, the mixing speed was again reduced to 50 rpm and sample was withdrawn. Total mixing time was approximately 5 minutes.

The NBR/PVC blends were compression molded in an electrically heated hydraulic press at 210-220°C and at 10 MPa pressure to prepare circular test slabs. Aluminum foils were used to reduce the shrink marks on the molding surface. After 10 min of molding, the samples were cooled under pressure. This ensured the overall dimensional stability of the slabs. Table-1 shows different compositions of NBR / PVC blends with constant stabilizer package concentrations.

Table 1: PVC / NBR blend compositions

Sr #	A	B	C	D
PVC (g)	30	40	60	70
NBR (g)	70	60	40	30
Iron oxide (g)	5	5	5	5
Ca Stearate (g)	1.5	1.5	1.5	1.5
Zn Stearate (g)	2	2	2	2

Softening & degradation temperatures

Softening and degradation temperatures were measured with the help of Melting Point apparatus.

Differential Scanning Calorimetry (DSC) Analysis

Thermograms were obtained at a heating rate of 10°C min⁻¹ in Shimadzu DSC 60-A apparatus. NBR / PVC samples of different compositions were analyzed against aluminum as reference material. The temperature range for experiment was selected to be 0- 300°C.

Mechanical Testing

Impact test

Impact strength was determined with the help of Tubular Impact tester. The tests were performed according to ASTM D 2794. The weight of indenter was 1.8 kg. The thickness of the samples was in the range of 0.4-0.8 mm.

Hardness test

Durometer hardness (ASTM D 2240) is an industry standard test method for rubbery materials, covering two types of durometers, A and D. The *durometer* is the hardness measuring apparatus; and the term *durometer hardness* is often used with Shore hardness values.^[7] The thickness of the samples was in the range of 0.4-0.8 mm.

Swelling index

For determination of the swelling percentage of the blends, the test pieces with dimension 2 mm×5 mm×30 mm were weighed according to ASTM D 1817 and this was considered to be the original weight. The test pieces were immersed in toluene at room temperature for 46 hours. After removal from the toluene, they were wiped with tissue paper to remove excess toluene from the surface and weighed (swollen weight). The swelling index of the blends was calculated as follows:^[8]

$$\text{SWELLING INDEX} = \frac{\text{Swollen Weight}}{\text{Original Weight}}$$

Plastograph studies

Processing characteristics of the samples were studied by time-torque graph obtained from Brabender plasticoder (PLE-330).

Results and discussions

Softening and degradation temperatures

	A	B	C	D
Softening temperature	160-180	180-200	196-206	170-183
Degradation temperature	220-225	240-250	210-215	230-240

Table 2: Softening and degradation temperatures

Flexible PVC can stay for longer period at a temperature of 110° F or 43° C without degradation but this degradation temperature has increased up to 250° C by the use of thermal stabilizers e.g. calcium stearate, zinc stearate, ferric oxide.

Hardness test

As the concentration of PVC in the blend increases, shore D increases because of an increase in hardness and shore A decreases as elasticity decreases. Within the sample, if the concentration of PVC is greater than NBR then shore D will be greater than shore A. Thus as the concentration of NBR in the blend increases, sheet becomes more flexible and has greater shore A than shore D. Table 3 shows different values of Shore A, Shore D hardness for different blend compositions.

	A	B	C	D
Shore A	41.6	35.3	28.55	21.3
Shore D	17.3	21	31.32	34.7

Table 3: Shore A, Shore D hardness values

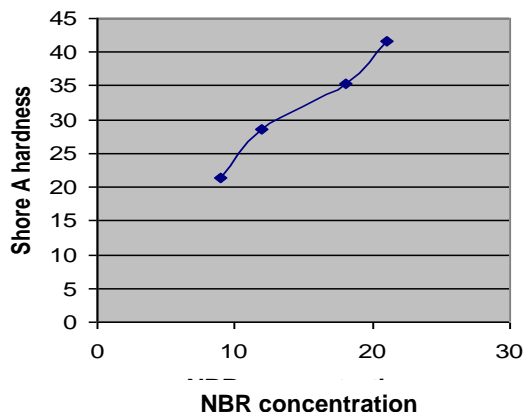
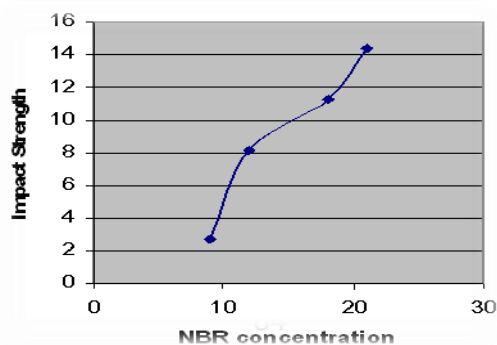


Figure 1: Shore A, Shore D hardness values for different blend compositions

Swelling index

For determination of the swelling percentage of the blends, the test pieces were weighed and this was considered to be the original weight. The original weight was kept constant 1.013 g. The test pieces were immersed in toluene at room temperature for 46 h. After removal from the toluene, they were wiped with tissue paper to remove excess toluene from the surface and weighed (swollen weight). The swelling index of the blends was calculated as follows :

$$\text{SWELLING INDEX} = \frac{\text{Swollen Weight}}{\text{Original Weight}}$$



NBR concentration

Figure 2: Swelling index of different compositions of NBR / PVC blend

Swelling index should be greater if the interfacial adhesion is greater which is proportional to the rheometric torque and indicates good NBR/PVC mixing or blending. [8, 9]

Thus if interfacial adhesion or cross linking is greater in case of higher concentration of NBR, then blending will be more proper and swelling index will increase.

Impact Strength

The impact properties of the polymeric materials are directly related to the overall toughness of the material, which is believed to increase with increase in cross-link density. [10]

Figure 3 shows the changes in the impact strength of PVC/NBR blends for different concentrations. In general, the impact strength of the PVC/NBR blends shows an increase with increased NBR content. As the NBR content in the blend increases, cross link density also increases which is responsible for such observations.

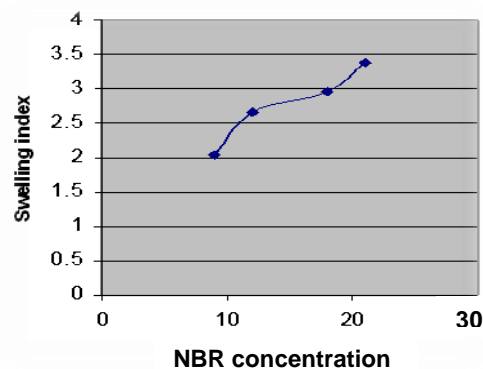


Figure 3: Impact strength of different compositions of NBR / PVC blend

As impact strength of PVC (both rigid and flexible) is significantly lower than the impact strength of PVC/NBR blend so by mixing the PVC with NBR we can increase impact strength about 10 times more. Moreover, as the concentration of NBR in the sample increases, impact strength also increases due to increase in flexibility of the sheet.

Differential Scanning Calorimeter (DSC)

Figure 4 shows thermograms of pure PVC, NBR and different compositions of NBR/PVC blends. PVC is a crystalline material and NBR is an elastomer. PVC/NBR blend can be obtained as a thermoplastic elastomer having reduced degree of crystallinity with the increased concentration of NBR in the blend.

Thermograms show that PVC has highest Tg and as the maximum concentration shifts to NBR, it progressively decreases. NBR rubber shows the lowest Tg since it is an elastomer. NBR / PVC blend has a lower Tg being the consequence of the fact that NBR/PVC blend is a miscible system.

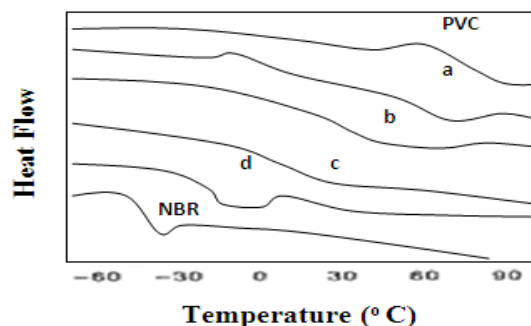


Figure 4 : DSC curves of pure PVC (a) 70:30 PVC/NBR (b) 60:40 PVC / NBR (c) 40:60 PVC / NBR (d) 30:70 PVC / NBR and NBR system

Plastograph Studies

Processing characteristics of the samples were studied by time-torque graph obtained from plasticoder. During processing, after the prestabilization of PVC, NBR in crushed form was charged in the brabender plasticoder mixer. It was observed that as NBR was charged, greater stabilization torque was required because of high viscosity of NBR. After the application of shear and heat, the viscosity of NBR reduced thus reducing the torque requirement. As compared to the 21/9 and 18/12 blends, the 9/21 NBR/PVC blend showed the lowest increase in torque at 0-2 min, because for this blend in zero time; PVC powder was charged into the mixing chamber together with other additives, but for 21/9 and 18/12 blends, in zero time; NBR was charged that has higher stiffness. After adding the second polymer, as viscosity decreased until equilibrium torque was achieved when the blend became homogenized.

For all blend compositions, the stabilization torque increased with increasing PVC fraction as expected after 2 mins mixing interval. That was due to the fact that blend viscosity was increased when the PVC content in the blend increased.

As the NBR content in the blends increases, torque difference (difference between the maximum torque and the minimum torque) also increases, because of high NBR content in the blend; requirement torque for oscillating movement is lower and after vulcanization process, it requires higher torque for movement.

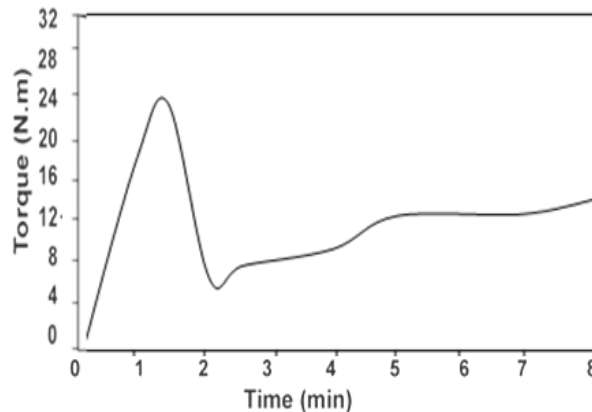


Figure 5: Torque Vs time behaviour of NBR / PVC blends having greater NBR content

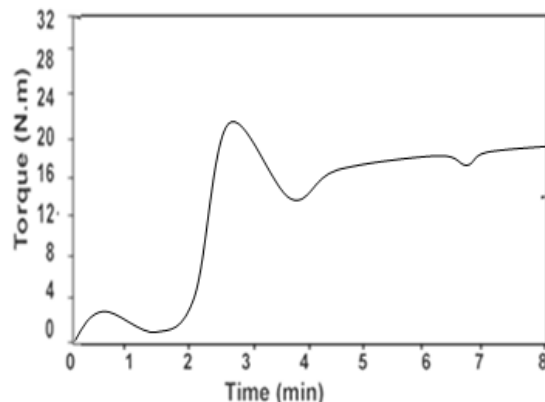


Figure 6: Torque Vs time behaviour of NBR/PVC blends having greater PVC content

For a similar blend composition, blends that are prepared with NBR powder have higher stabilization torque than those prepared with NBR bale. This is because by using NBR powder, owing to fine particle size (high surface area) of NBR; interaction between NBR and PVC are induced in the blends and results in higher stabilization torque.^[9]

Conclusion

Flame retarded compositions exhibit increased flame retardency when the Ca stearate, Zn stearate and Ferric oxide stabilizer package is employed. Moreover, these blends also exhibit improved mechanical and thermal properties.

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