IJCRT.ORG ISSN : 2320-2882

INTERNATIONAL JOURNAL OF CREATIVE RESEARCH THOUGHTS (IJCRT)
An International Open Access, Peer-reviewed, Refereed Journal

Studies on Thermoplastic Elastomer Based On Linear Low Density Polyethylene And Latex Product Waste Modified with Thiocarbanilide

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Abstract

Thermoplastic elastomers are materials showing the properties of thermoplastics at processing temperatures and those of elastomers at service temperatures. At low temperatures, the thermoplastic phase acts as crosslinks or reinforcing filler particles in between the soft rubbery phase. Polyethylene- natural rubber blends, which are subjected to dynamic vulcanization, have promising properties like thermoplastic behavior. Latex product waste when replaces natural rubber in such blends, proves to be a potential substitute for producing several end products using thermoplastic elastomers. Also, recycling and reusing waste rubber is the need of the hour, which is being realized in this process. The mechanical and rheological studies of these blends are done in the present study.

Key Words

Thermoplastic elastomer, Polyethylene- natural rubber blends, Latex product waste, dynamic vulcanization, mechanical and rheological studies.

Introduction

Thermoplastic elastomers are materials showing the properties of thermoplastics at processing temperatures and those of elastomers at service temperatures (1-3). They contain a soft rubbery and a hard thermoplastic segment. They exhibit typical melt characteristics at high temperatures, which are attributed to the thermoplastic phase. The elastic behavior is resulted from the soft rubbery phase, at low temperatures (4-5). At low temperatures, the thermoplastic phase acts as crosslinks or reinforcing filler particles in between the soft rubbery phase (6). This blending of characteristics makes this category of polymer an easily processible one.

Over recent years, blends of Natural rubber with Polyolefines have widely been studied (7-9) and are found to be good thermoplastics. The effect of the nature of components and blend ratios on the properties of the resulting thermoplastic elastomers has been reported (10-11).

The present study aims to utilize Reclaimed Natural Rubber Product Waste to prepare a thermoplastic elastomer by blending with Linear Low Density Polyethylene (LLDPE). Powdered glove waste, modified with thiocarbanilide, hereafter mentioned as GW (P), is blended with LLDPE. Dynamic vulcanization (12-15) is applied to prepare the blends.

Materials and methodology

In this study, we have developed a thermoplastic elastomer based on linear low density polyethylene and powdered latex waste modified with thiocarbanilide, both unvulcanized and dynamically vulcanized. The mechanical and rheological evaluations were done and compared with those of PE/ natural rubber blends.

Preparation of blends

First, the latex product waste was modified as per the formulation given in Table 1. Weight of the modified waste was adjusted according to the rubber hydrocarbon content so as to maintain the proportion of rubber in the blend. Blending was done as per the procedure described. Measurements of mechanical and rheological properties were done.

Table 1 Formulation for modified waste

Ingredients	Phr
Powdered Glove waste, GW (P)	100.0
NR	20.0
ZNO	5.0
Stearic acid	2.0
Thiocarbanilide	3.0
CBS	0.6
Naphthenic oil	3.0
Hydroquionone	0.2

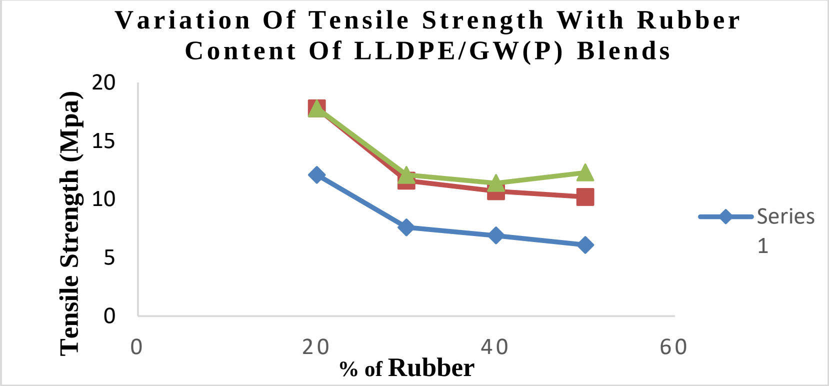
The blending procedure is as follows:

Mixing was done on a Brabender Plasticorder model PL 3S, at 150^{o} C and 50 rpm. LLDPE was melted in the mixer for 4 minutes and then GW (P) containing the additives was added. During the melt mixing, 2.5phr Sulphur was added to effect dynamic vulcanization. Mixing was continued for 6 more minutes. Then the mix was taken out and sheeted on a laboratory mixing mill at 20 mm nip gap setting. The sheeted material was then cut into small pieces and again mixed in the plastic coder at 150^{o} C for 4 minutes so as to get uniform dispersion of ingredients. This blend was compression molded in an electrically heated hydraulic press at 160^{o} C for 6 minutes. Specially fabricated mould with nuts and bolts was used for this purpose. The mould with sample was cooled by circulating cold water and the molded sheet was taken out and tested for the properties.

Results and Discussion

Fig 1 shows the variation of tensile strength with rubber content of uncross-linked and dynamically cross-linked LLDPE/GW (P) and uncross linked LLDPE/NR blends. In all the cases, tensile strength decreases with increase in the rubber content. LLDPE/GW (P) blends show higher tensile values than LLDPE/NR blends. Also the dynamically vulcanized LLDPE/GW (P) blends show the highest values when compared to vulcanized blends. The reasons is the presence of residual cross links in GW (P) (crosslink density 1.9 x 10^{-3}g mol/cc) and also the effect of dynamic vulcanization on mechanical properties. Advantage of dynamic vulcanization is more significant in the 50/50 LLDPE/GW (P) blend, as observed.

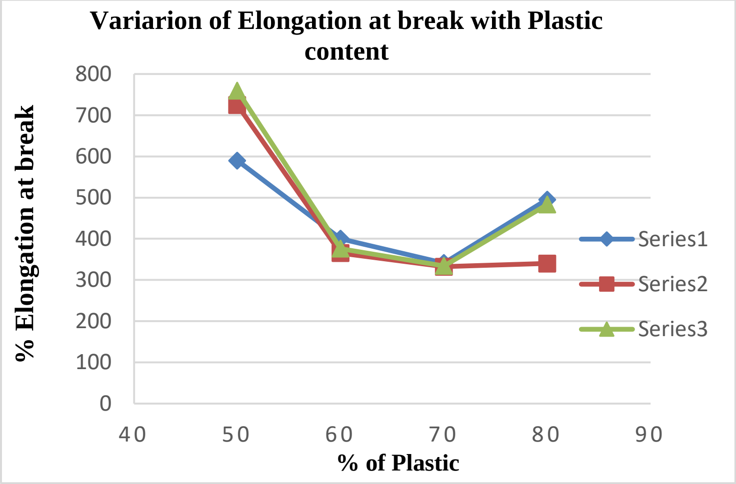
Fig 1



Series1- LLDPE/NR Series 2- LLDPE/GW(P) Uncrosslinked Series 3- LLDPE/GW(P) Dynamically vulcanized

Fig 2 shows the variation of elongation at break with plastic content. It can be seen that as the LLDPE content decreases, the elongation at break also decreases. The elongation value decreases up to 60/40 plastic/rubber ratio. At 50/50 plastic/rubber ratio, a slight increase in the elongation at break is observed. This is because of the higher proportion of rubber compared to other blends. On dynamic vulcanization of the LLDPE/GW (P) blends, the elongation at break still decrease due to the increase in the extent of crosslinking.

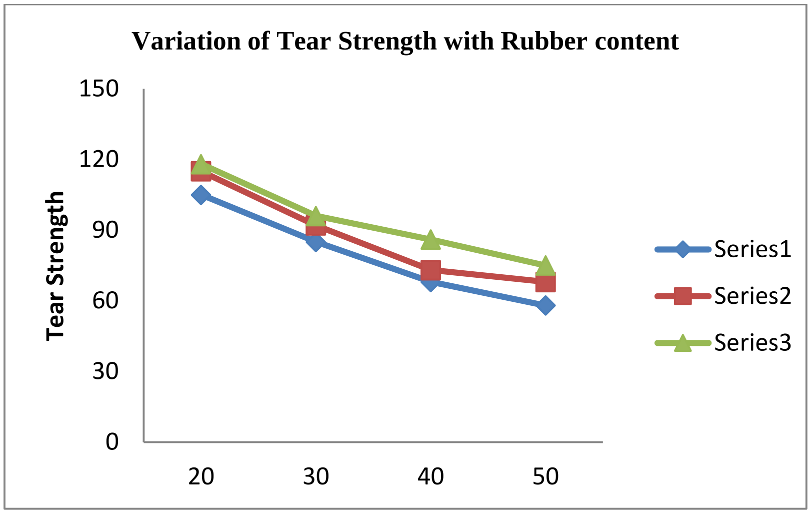
Fig 2



Series1- LLDPE/NR, Series 2- LLDPE/GW(P) Dynamically vulcanized, Series 3- LLDPE/GW(P) Uncrosslinked

Fig 3 shows the variation of tear strength with % of rubber. In all the cases, tear strength decrease with increase in % of rubber. Both the vulcanized and dynamically vulcanized LLDPE/GW (P) blends show higher tear strength than the LLDPE/NR blends. Again this is due to the slight crosslinking which is already present in GW. The highest values are exhibited by the dynamically vulcanized blends.

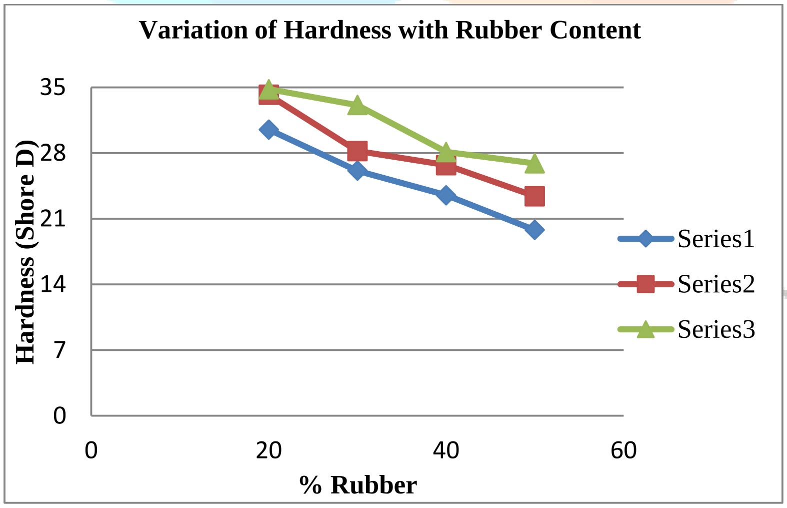
Fig 3



Series 1- LLDPE/NR, Series 2- LLDPE/GW(P) Uncrosslinked, Series 3- LLDPE/GW(P)Dynamically vulcanized

Fig 4 shows the relationship between Hardness and % of rubber. As the rubber content increases, hardness decreases. The cross-linked blends show hardness as expected.

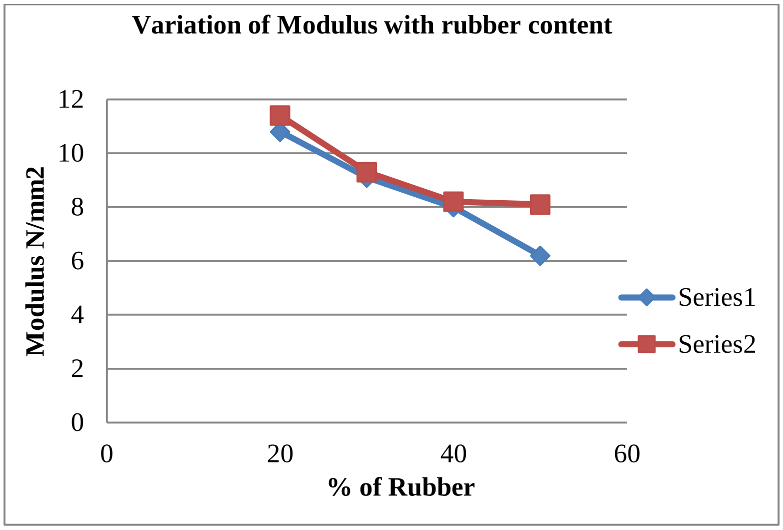
Fig 4



Series 1- LLDPE/NR, Series 2- LLDPE/GW(P) Uncrosslinked, Series 3- LLDPE/GW(P)Dynamically vulcanized

In fig 5, variation of modulus at 100% elongation of uncrosslinked and dynamically crosslinked LLDPE/GW (P) blends with rubber content is shown. As the plastic content increases modulus also increase. Slightly higher values are observed for dynamically vulcanized blends.

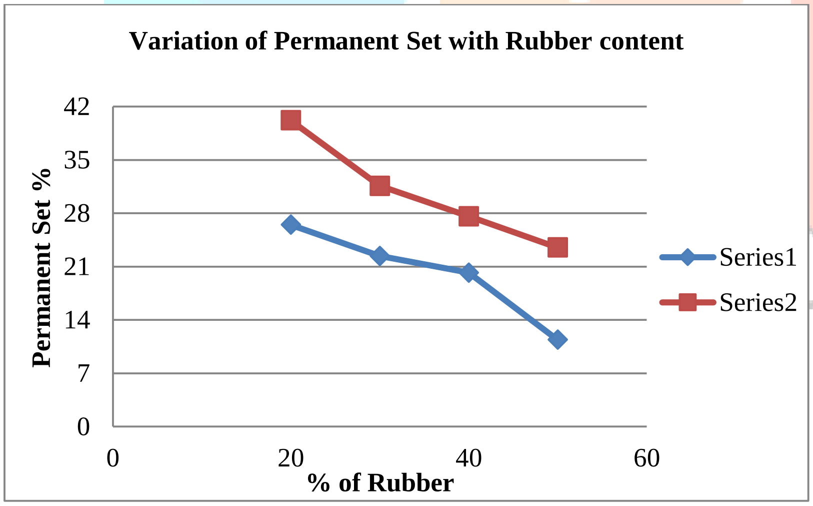
Fig 5



Series 1- LLDPE/GW(P) Uncrosslinked, Series 2- LLDPE/GW(P)Dynamically vulcanized

Fig 6 shows the relationship between permanent set and rubber content of LLDPE/GW (P) blends, both crosslinked and uncrosslinked. As the rubber content increases, permanent set decreases. The permanent set values decrease significantly on dynamic vulcanization of the rubber phase. When the crosslinking increases, Permanent set decreases as expected.

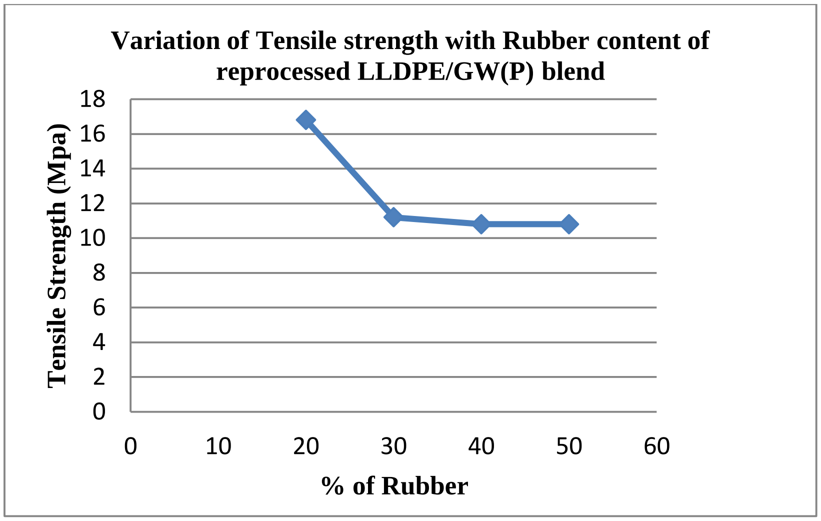
Fig 6



Series 1- LLDPE/GW(P) Dynamically vulcanized Series2- LLDPE/GW(P) Uncrosslinked

Fig 7 gives the variation of tensile strength values of dynamically vulcanized. remelted and remoulded samples,, with rubber content. The tensile strength is not much affected by remelting and the reason is dynamic vulcanization, which prevented the degradation of the rubber phase during remelting and remoulding.

Fig 7



In fig 8, the elongation at break of remelted samples is plotted against plastic content. The values are very close to the original ones because the extent of crosslinking of rubber phase is retained even after re-melting due to dynamic vulcanization.

Fig 8

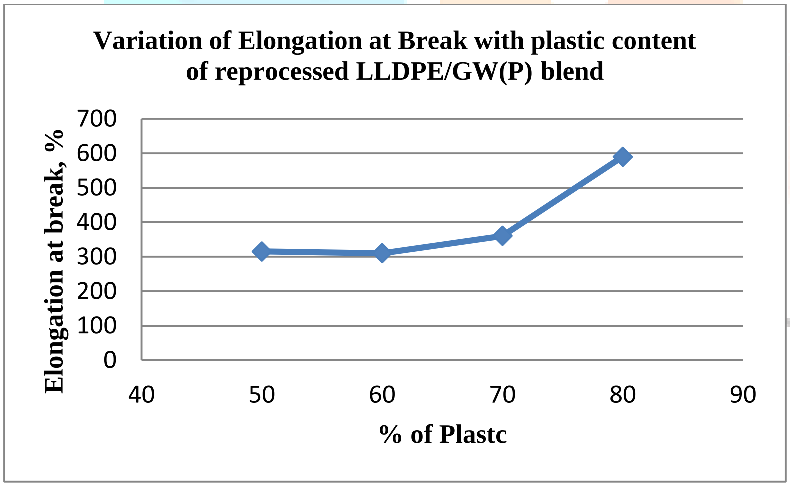


Fig 9 shows the variation of tear strength with rubber content. Again the values are comparable with those of the original ones.

The impact strength values of all the LLDPE/GW (P) beldns were found to be above 1 KJ/m. Presence of soft and elastomeric GW (P) along with highly flexible LLDPE leads to the absorption of increased amount of energy during fracture, which resulted in high impact resistance.

Fig 9

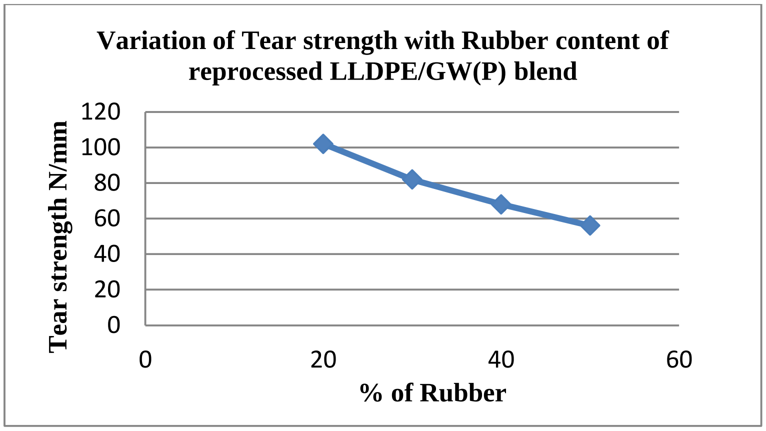
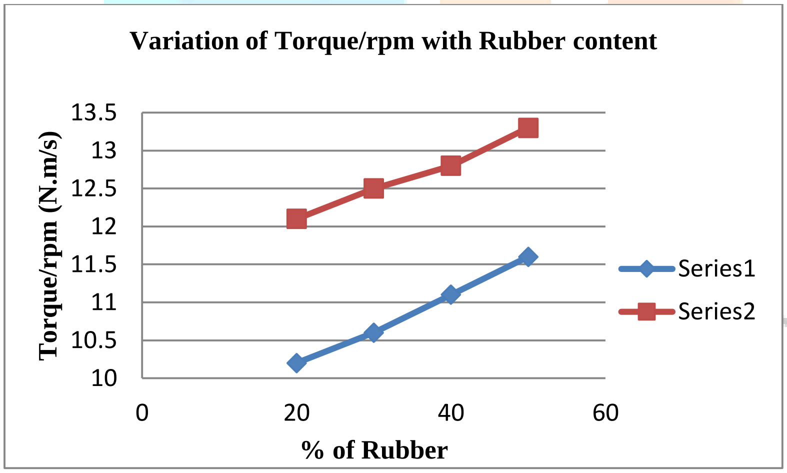


Fig 10 shows the variation of viscosity (torque/rpm) with rubber LLDPE/GW (P) blends, both uncrosslinked and dynamically crosslinked, measured on the Brabender Plasticorder at constant shear rate of 50 rpm. It is seen that as the rubber content, increase, viscosity also increases in both the cases. Viscosity values of dynamically Vulcanized blends are found to be higher than those of uncrosslinked blends. This is because of the higher torque developed during dynamic vulcanization. Crosslinked rubber has higher viscosity compared to uncrosslinked rubber.

Fig 10



Series 1- LLDPE/GW(P) Uncrosslinked, Series 2- LLDPE/GW(P) Dynamically vulcanized

In Fig 11, apparent viscosity is plotted against apparent shear rate of 50/50 LLDPE/GW (P) dynamically vulcanized blend, measured on HAAKE Rheoflixer V3. 53. It is seen that as the shear rate increases viscosity decreases.This shows that the blend is pseudoplastic in nature (19)

Fig 11

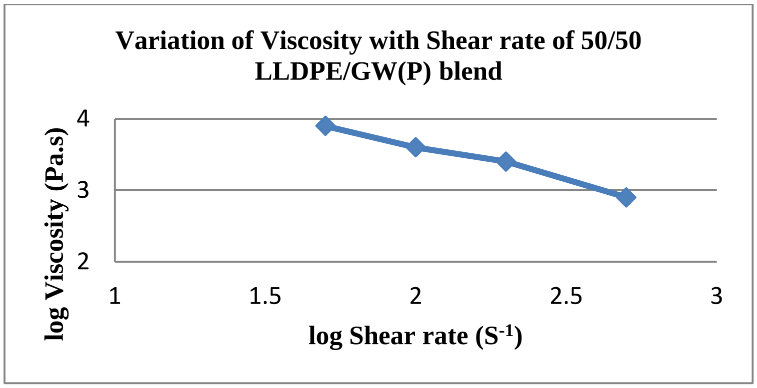


Fig 12 shows the variation of shear stress with shear rate of 50/50 LLDPE/GW (P) blend. As the shear rate increases, shear stress also increases as expected. This confirms the non-Newtonian behavior of the blend.

Fig 12

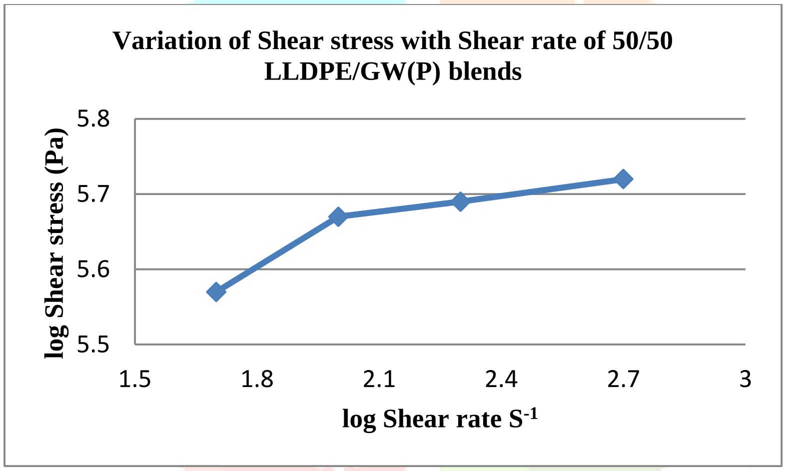


Fig 13 shows the variation of viscosity and shear stress with shear rate of 80/20 LLDPE/GW (P) dynamically vulcanized blend, measured on the Capillary Viscotester. The same trend as that of 50/50 blend is shown here also. That is, as the shear rate increases, viscosity decreases and shear stress increases confirming the non-Newtonian behavior of the blend.

Fig 13

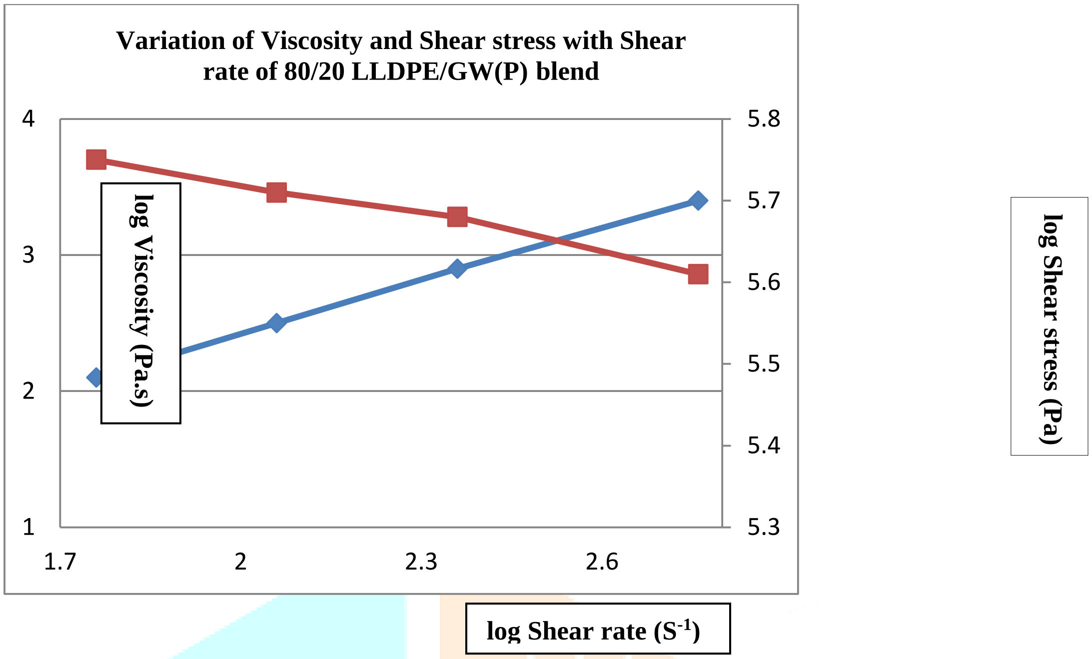


Table 2 shows the value of pseudo plasticity index (n) and the variation of die swell ration (de/dc) with shear rate. The increase in the die swell ratio with shear rate is very small that indicates the low deformation of the GW (P) phase. Again, the very low value of ‘n’ implies that the blend is pseudo plastic in nature.

Table 2 Variation of d_e/d_c with shear rate of LLDPE/GW (P)

Shear rate	Die swell ration	Pseudo plasticity Index (n)
50	1.224	0.02
100	1.269	
200	1.277	
300	1.296	
1000	1.297	

Conclusions of studies on LLPE/modified waste blends

1. Blends of good mechanical properties and rheological behavior can be developed from LLDPE and latex product waste modified with Thiocarbanilide.
2. Dynamic vulcanization of the rubber phase has enhanced the proprieties of the blends to a great extent. The peculiar elongation behavior shown by LLDPE has very much influenced the elongation at break of the blends.
3. Dynamically vulcanized 50/50 LLDPE/GW (P) blend is proposed as a novel thermoplastic elastomer that shows the properties of both thermoplastic and elastomer.

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