

Natural Rubber/Epoxidised Natural Rubber and Thermoplastic Ternary Blends. 1. Effect of preparation techniques on the properties of blends.

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Abstract

Blending of natural rubber with thermoplastic is widely practised as the resultant blend exhibit properties typical of rubbery materials. The properties of the blends however is affected by the methods of preparation. In this paper emphasis has been laid on the method of preparations and its bearing on the final properties like tensile strength, modulus, elongation at break and hardness properties.

Properties with respect to the method of preparations for thermoplastic such as polypropylene high density polyethylene and polyvinyl chloride were investigated. Presented also the effect of sulphur vulcanisation on these blends.

Introduction

Polymers can be blended to form wide variety of materials with novel properties. Among these materials are blends which consist of natural rubber (NR) and thermoplastic which is referred as thermoplastic natural rubber (TPNR). Thermoplastic NR blends exhibit properties similar to vulcanised rubber at the used temperature and can be processed in the 'melt' at elevated temperature[1-2].

Blending of natural rubber and thermoplastic have gained considerable attention due to the simple method of preparation and easy attainment of the required technical properties. In natural rubber-polyolefin binary blends the effects of characteristics of the components, blend ratios and dynamic crosslinking of the elastomer phase on the technical properties, processing characteristics and failure mechanism of the resulting thermoplastic elastomers have been reported[3-10]. However, the effects of these properties on ternary blends of natural rubber is seldom reported. Chang Sik Ha et. al, have published the effect of mechanical properties and morphology on ternary blends based EPDM rubber[11]. Ternary rubber blend based on epoxidised natural rubber, have been reported by R.Alex and others[12-14], but no publications known, discussing about the effect of preparation technique on natural rubber based ternary blends.

In this study natural rubber based ternary blends of SMR5/ENR25/polyolefin were melt-mixed in an internal mixer with special reference to Brabender mixing to study the effect of preparation methods on the mechanical properties of the blends in the unvulcanised state and the vulcanised state. This effect is important since blend properties is not only dependent on parameters such as rotor speed, time, and temperature of processing but also the method of preparations.

Experimental.

Materials

Standard Malaysian Rubber (SMR 5) was supplied by Lee Rubber, Skudai, Johore, Epoxidised Natural Rubber (ENR 25) 25% epoxidation by Rubber Research Institute of Malaysia (RRIM), polyvinyl chloride (PVC) grade no. Riken TM 6019 was from Riken Vinyl Industry Co. Limited Japan, polypropylene (PP) type GCM (45) from ICI and High Density Polyethylene (HDPE) type HDBK 649 from Mobil. Other chemicals viz ZnO, stearic acid and sulfur from RDH and accelerator N-cyclohexylbenzothiozole-2-sulphenamide (CBS) obtained from RRIM.

Blending method

Blendings were carried out on a laboratory internal mixer Brabender Plasticorder PL2000 using cam-type blade with heated silicone oil circulation. Binary blends of SMR 5/ENR 25 was blended at a specific temperature to see the effect of blending parameter primarily. Actual study was on the method of blends preparation verses properties performance. Two methods were compared. First method, involved preparation of blends by charging the regular strip of rubber component (SMR 5/ENR 25) at the desired temperature followed by the thermoplastic component into the mixing chamber. The blending process was terminated after torque and stock temperature profiles become steady. In the second method, thermoplastic component was first

melted at the melting temperature followed by the addition of rubber strip. Termination of process as in method 1 (M1). Blending conditions used are shown in Table a.

Table a: Blending Conditions

Rubbery Component	Thermoplastic	Temperature	Speed	
			M1	M2
SMR5/ENR25	PP	175°C	80	40
	PVC	160°C	60	20
	HDPE	160°C	60	40

Composition: SMR5/ENR25/ THERMOPLASTIC(TP)
80:20:20 phr

PP - polypropylene , PVC - polyvinyl chloride ,
HDPE - high density polyethylene.

Crosslinking of blends were done dynamically on Brabender Plasticorder. For method 2 (M2) crosslinking agent was added after a stationary condition is reach and terminated after curing peak have subsided. Whereas crosslinking for M1, is by taking speed 40 rpm and temperature 80°C to stationary condition and dump. Curing was also done on Brabender at temperature 150°C and speed 40 rpm. Recipe for crosslinking process is as follows.

Table b: Recipe for crosslinking

Blend types	Sulphur*	Comments
SMR5/ENR25/HDPE	0.5 phr	Above 0.5, poor surface finished, 1 phr degraded
SMR5/ENR25/PP	0.25 phr	Above 0.25, poor surface finished, 0.5 phr degraded
SMR5/ENR25/PVC	0.0635 phr	Above 0.063, very poor surface finished 0.125 phr degraded.

*ZnO= 5 phr. , Stearic acid= 1 phr. , CBS= 1 phr .

Mechanical Testing

Crosslinked and uncrosslinked blends were moulded on hot press for 2 minutes and water cooled. Preparations and testing of specimens were in accordance to ASTM D412-87 crosshead speed of 500 mm/min. on Lloyd Instruments MTM (Model L1000R). Hardness test was done on Karl Frank Hardness Testing Instrument 38209 according to ASTM D 1415 .

Results and Discussion

Brabender torque and stock temperature

In all blends binary or ternary torque gradually reduces with mixing time until it reaches a steady values. This steady values after a certain period of mixing starts to drop sharply, perhaps due to morphology changes or degradation figure 1.

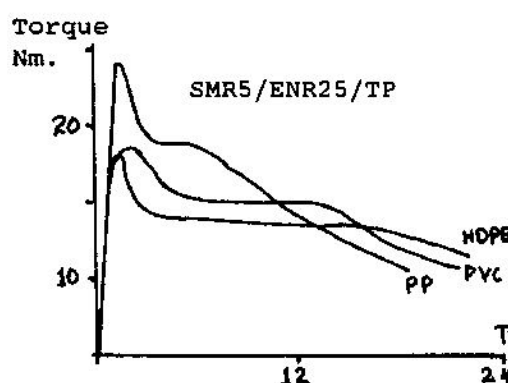


Fig. 1: Torque verses mixing time .

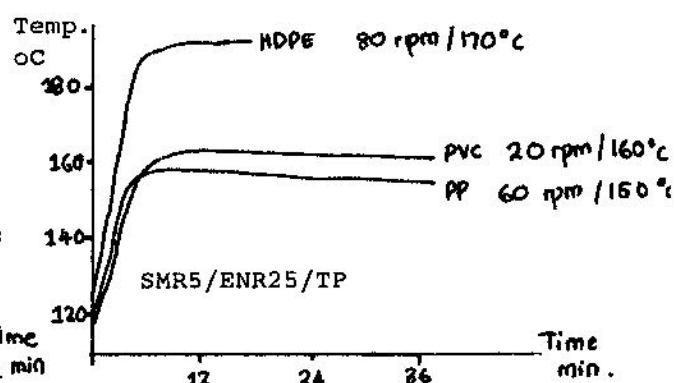


Fig.2: Temperature verses mixing time.

The progress of the stock temperature as a function of the mixing time is illustrated in figure 2. The observed lowering of stock temperature from the mixing temperature for all blends studied via M2 and M1 is due to the quick addition of the rubbery component (SMR5/ENR25) to the molten thermoplastic (PP,PVC,HDPE) for the former and the addition of the SMR5/ENR25/TP to the mixing chamber for the later. However, the vigorous shearing causes the stock temperature to rise steeply above the blending temperature and gradually rise until a final steady values is attained.

Effect of mixing parameters

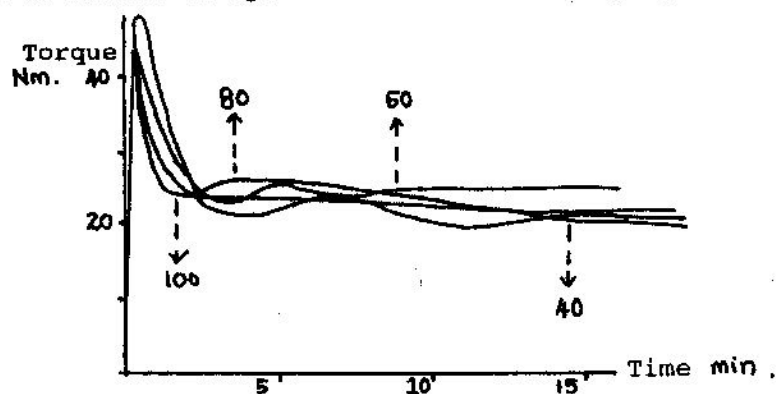
Blending parameters that may influence the physical properties of Brabender mixed products are rotor speed, blending time, blending temperature and total volume of the blending components[15-16]. However, when blending time for the blends are taken as the time for torque and stock temperature reach steady values (which indicate the completion of the exothermic mixing), physical properties seem to be independent of the rotor speed as shown in table 1, but varies with blending time after steady state attainment and before degradation (drop in mixing torque), table 2 for SMR5/ENR25 blends.

Table 1: Effect of time on blends tensile properties

Torque Nm.				
Time	5	10	20	30
Mod.10% MPa	0.028	-0.018	0.014	0.016
	±0.002	±0.003	±0.002	±0.000
Mod. 100% MPa	0.008	0.008	0.005	0.004
	±0.000	±0.001	±0.001	±0.001
Tensile strength MPa	0.177	0.156	0.131	0.116
% elong. at brk.	391.30	289.94	314.60	352.00

Composition: SMR5/ENR25 , 80:20

Table 2: Effect of speed on blends tensile properties



*Speed	40	50	80	100
Mod.10% MPa	0.012 ±0.006	0.015 ±0.001	0.013 ±0.002	0.014 ±0.003
Mod.100% MPa	0.004 ±0.001	0.005 ±0.001	0.004 ±0.000	0.005 ±0.001
Tensile strength MPa	0.127	0.147	0.138	0.153
% elong. at brk.	435	445	367	362

*All samples are taken 5 minutes after torque and stock temperature reaches constant value.

*Temperature 70°C

*total volume 60 cc.

Physical properties changes with time (after steady state attainment) could probably be due to changes in dispersion of the components in the blends. Some thermoplastic-rubber blends results in better properties with longer mixing times and some become worsens[17] due to the loss in thermoplasticity.

At low blending temperature , the resultant blends is coarse and some unmelted thermoplastic is observed embedded in it. Whereas too high the temperature causes the blends to degrade especially rubber which degraded above 200°C. Suitable blending temperature is near the melting range of the thermoplastic. Table 3 shows the physical observation on blends with respect to temperature.

Table 3 :Temperature effect on blends physically

Temperature °C	PP	PVC	HDPE
80	-	PVC granules	-
10	-	coarse blend	-
120	-	coarse blend	coarse blend
140	PP beads	smooth	smooth
160	smooth	fine and soft	smooth, soft
180	very soft	very fine and on long mixing - degraded	very fine and on long mixing -degraded

Effect of blending method

Using M1 it is observed that time to attain steady states depend on the rotor speed as depicted in figure 3 and temperature figure 4 for all blends including the ternary rubber-plastic blends.

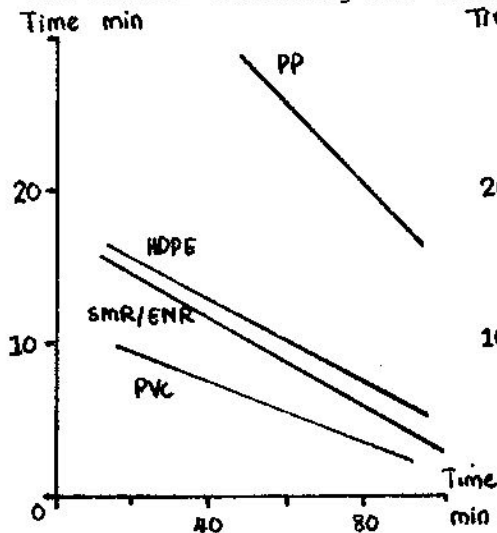


Fig.3:Effect of speed on time(steady state).

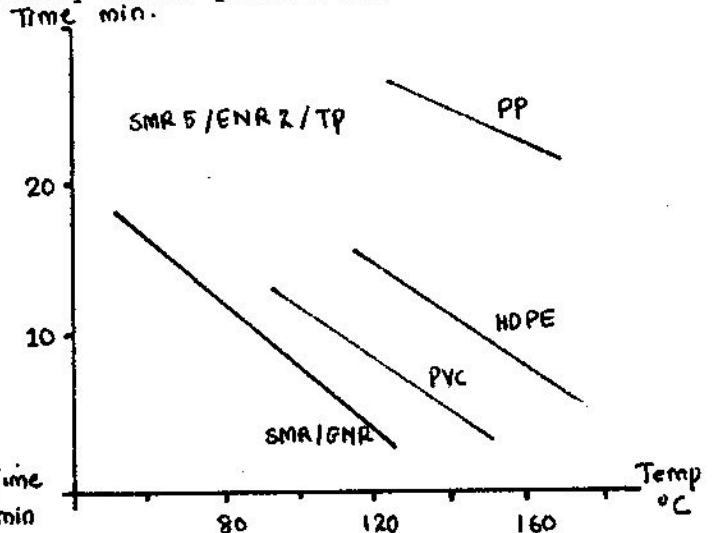


Fig.4:Effect of temperature on time(steady state).

As expected the faster the speed and the higher the temperature, thus the shorter will be the time to reach stationary conditions. However, the rotor speed limit, figure 5, is govern by the rise in temperature above the stock temperature as the blending proceeded until a final steady value is attained. This rise in temperature is due to the vigorous shearing, therefore rise in stock temperature (ΔT) increases with rotor speed. Hence 20°C or below, rise in temperature of the blends are allowed and recommended for obtaining good blends[18].

Blend composition : SMR5/ENR25/THERMOPLASTIC (80:20:20)

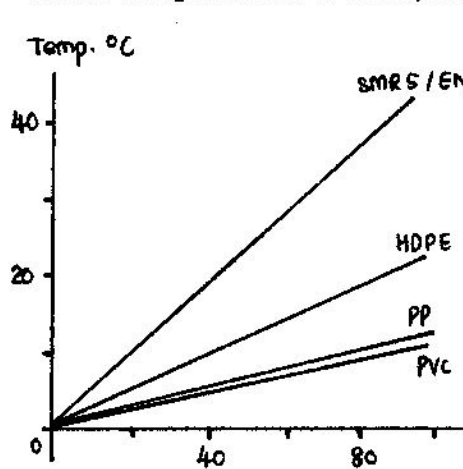


Fig.5:Temperature rise against speed.

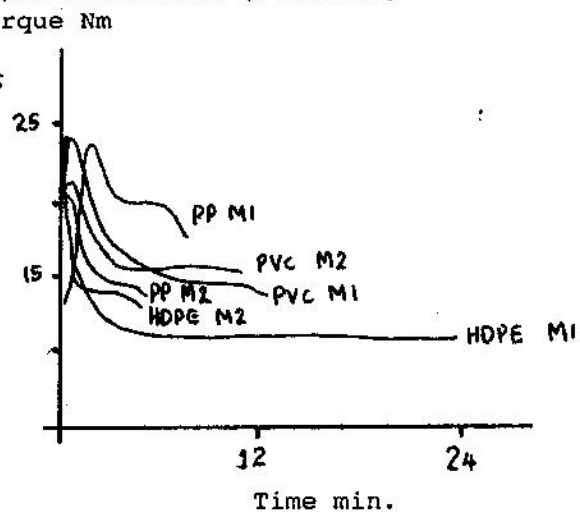


Fig.6:Torque against time.

The time for steady conditions attainment and temperature rise dependent is also observed in the second method. An advantage from

the second method is that time for completion of the exothermic mixing is shorter compared to the first method figure 6.

Physical properties obtained from second method is better than the first, figure 7 and table 4 . This could be due to the better dispersion in the blends component and the torque different observed at time of steady condition attainment.

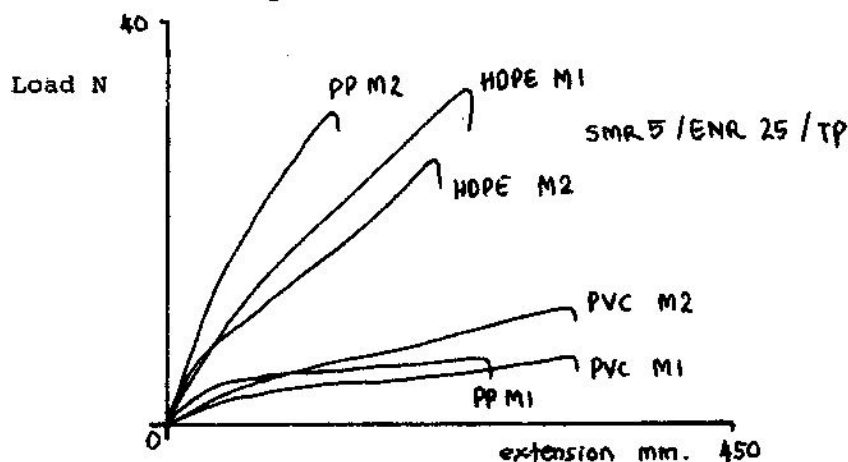


Fig.7: Load against extension of blends from M1 and M2.

Table 4: Properties of blends (M1 & M2)

	PVC		HDPE		PP	
	M1	M2	M1	M2	M1	M2
Mod. 10%	0.014	0.025	0.089	0.117	0.050	0.198
MPa	± 0.001	± 0.003	± 0.005	± 0.005	± 0.001	± 0.014
Mod. 100%	0.003	0.006	0.027	0.032	0.011	0.062
MPa	± 0.000	± 0.001	± 0.001	± 0.004	± 0.001	± 0.006
Tensile Strength	0.387	0.411	1.137	1.358	0.268	1.635
MPa						
% elong.	623.46	602.20	440.00	418.80	345.00	270.7
Tensile set. mm.	0.9	1.2	1.2	1.4	0.9	0.8
Hardness Shore A	4.7	5.3	18.6	23.1	21.4	33.5

Modulus at 10 % elongation and ultimate tensile strength from the unvulcanised blends shows a distinctive different whereby M2 shows higher values for all type of blends . However % elongation at break for M1 is higher than M2 for all type of blends, which could be due to the low viscosity of the rubber phase as compared to the thermoplastic and larger phase size of the thermoplastic component i.e ascribed to the morphological changes in the blends.

Hardness properties obtained for all blends from M1 is lower than from M2 for 80:20:20 blend composition. This is because M2 required less time in the mixer to achieve a complete exothermic mixing, since the thermoplastic component is first melted before blending, and

therefore less mastication on rubber component will occur (shown by the higher torque, figure 6) resulting in better properties observed for the unvulcanised blends. Whereas M1 required more time to complete the mixing process because the thermoplastic component needed to be melted before it can be well blended, and therefore more mastication on rubber occurs (shown by the low torque figure 6). This phenomena can be clearly explained in terms of blend morphology[19]. Furthermore it has been demonstrated that the morphology of a blend is a function of the relative viscosities of the constituent polymers[5]. Hence, from the properties analysis of the uncrosslinked soft blends M2 is a better technique to be used for blending.

Effect of curing on blending method

Blends obtained after curing from both methods show improvement in their mechanical properties figure 8. Table 4 shows the properties different between the two method for the various thermoplastic used.

Table 5: Mechanical properties of cured blends*.

SMR/ENR25/TP	Method 1			Method 2		
	PP	HDPE	PVC	PP	HDPE	PVC
Mod.10% elong.	0.121	0.137	0.012	0.101	0.154	0.025
MPa	± 0.010	± 0.053	± 0.002	± 0.012	± 0.031	± 0.004
Mod.100% elong.	0.038	0.060	0.004	0.054	0.062	0.011
MPa	± 0.006	± 0.033	± 0.000	± 0.006	± 0.018	± 0.002
Tensile	2.307	2.428	0.524	1.671	2.264	0.391
Strength MPa	± 0.340	± 0.219	± 0.246	± 0.471	± 0.671	± 0.030
% elong. at	516.0	252.3	664.0	157.1	296.1	219.4
break	± 14.7	± 21.2	± 19.3	± 9.6	± 15.5	± 46.6
Tensile set mm.	1.60	0.13	0.10	0.10	0.16	0.10
Hardness	22.30	31.75	v.soft	27.00	33.10	11.30
Shore A						

*Composition - SMR5/ENR25/THERMOPLASTIC
80:20:20

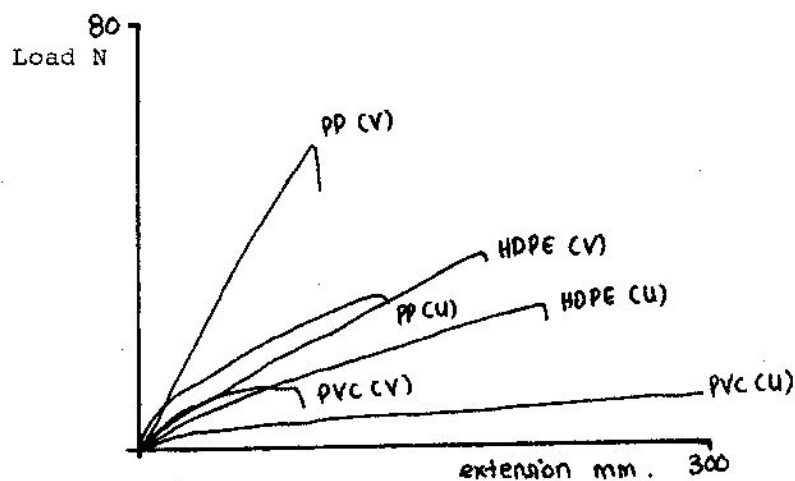


Fig.8: Load against extension of vulcanised & unvulcanised blends.

For SMR5/ENR25/PP and SMR5/ENR25/PVC blends at 80:20:20 composition, M1 shows a better tensile properties than M2. For example, these two blends exhibit higher tensile strength and % elongation at break. This perhaps can be deduced as, M1 for these blends give better homogeneity and degree of dispersion in the phases, since blends are first compounded before undergoing curing. However, for SMR5/ENR25/HDPE blend, M2 is preferred as shown, by the increase in tensile strength, modulus at 10% elongation and 100% elongation and elongation at break.

Hardness properties is higher in all blends via M2. This is consistent with the tensile test results, which shows a better elongation at break via M1, there is M1 gives product which is more rubbery than M2 and hence softer blends. The high elastomeric response shows in M1 could be due to the high continuity of the rubber phase. Continuity of a phase is favoured by both a high volume fraction and low viscosity relative to that of the other component [20-21]. M2 results in harder blends and lower elongation at break, perhaps as crosslinking proceeded the viscosity of the rubber phase increases causing the less viscous thermoplastic moving towards continuity. The results shown is consistent with that obtained for the unvulcanised blend. And also is supported by the trend high elongation at break correspond to the low hardness properties for the unvulcanised and vulcanised sample. Generally the presences of crosslinks in the rubbery phase enhances its modulus and strength while increasing its resilience.

Conclusion

From the above discussion and analyses, it is concluded that the melt-mixing on Brabender Plasticorder with cam-mixer, the time taken to reach a complete exothermic mixing is dependent on rotor speed and blending temperature. Tensile properties seem to be unaffected for SMR5/ENR25 blends by the rotor speed at this extent of mixing and the composition understudied. Method of blends preparation affect the mechanical properties of the vulcanised and the unvulcanised blends. It also proved that thermoplastic component contribute to the rigidity and the SMR5/ENR25 give the flexibility to the blends whereby different thermoplastic impart different rigidity. Curing further enhances the properties of the ternary blends.

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