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Novel Thermoplastic Elastomer of Reactive NR and PA6 Blends

M. SEADAN[*#], V. LUKSAMEEVANISH[**] AND S. RATTANAPANE[*]

Relevant developments in polymer blends based on immiscible polymers have shown how efficient the amphiphilic species are in improving mechanical properties and morphological stabilisation through reactive reaction and dynamic vulcanisation on successive processing steps. However, it appears that, in blends of immiscible polymers, the interfacial compatibilities of polymers are necessarily mixed before the dynamically vulcanised process to obtain good mechanical properties of thermoplastic elastomers. The induced reactivity in a single screw extrusion is based on a mixture of peroxide (Perkadox 14®), reactive monomer (maleic anhydride) and activators (ZnO and stearic acid). The results confirm that a good level of reciprocal grafting occurred between NR and PA6. Their morphology showed a good interfacial adhesion with finer continuous phase of PA6. Dynamically vulcanised processes were done using several vulcanising systems on a single screw extruder. It showed that the suitable vulcanising agent was a phenolic resin (SP-1045). The produced thermoplastic elastomer showed a fine crosslinked dispersed phase NR, which corresponded to good mechanical properties of high tensile strength and elongation at break. The PA6/NR reactive blend TPE containing PA6 40% and NR 60% had a tensile strength level about 12 MPa with the elongation at break about 135%. It also showed very good oil resistance at an ultra-high temperature of 200ºC.

Key words: thermoplastic elastomer; reactive blends; dynamic vulcanisation; PA6; NR; morphology; vulcanising systems; crosslinking; mechanical properties

Elastomer-thermoplastic blends have become technologically useful as thermoplastic elastomers in recent years[1]. A good thermoplastic elastomer has blended properties comprising vulcanised rubber particles in thermoplastic matrices which are due to a method called dynamic vulcanisation. Thus dynamic vulcanisation is a route to create a new class of thermoplastic elastomers, namely thermoplastic vulcanisates (TPV). The improved properties resulting from dynamic vulcanisates are reduced permanent set, improved mechanical properties and greater stability of phase morphology. The original investigation on the dynamic vulcanisation of TPVs were performed on polypropylene and different rubber compositions, initiated by Coran and co-workers[2,3]. Well-known commercial TPVs are blends of polypropylene (PP) and ethylene-propylene-diene terpolymer rubber (EPDM).

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[*] Faculty of Science and Technology, Prince of Songkla University, Pattani, 94000, Thailand
[**] Faculty of Science and Technology, Chiang Mai Rajabhat University, Chiang Mai, 50300, Thailand.
Corresponding author: (e-mail: mseadan@bunga.pn.psu.ac.th)

TPV preparation steps originally begin with a mixing of PP and EPDM in molten stage. Due to the compatibility of PP and EPDM, a fine co-continuous phase morphology is formed. Subsequently a vulcanising agent (phenolic resin or peroxide) is added to crosslink the rubber phase. At the end of the dynamic vulcanisation process, the rubber phase will be finely dispersed in the thermoplastic matrix. However, these type of TPVs can only be used at a limited temperature range and have low oil resistance. Hot oil resistance and fairly good strength TPVs can be produced by a dynamic vulcanisate of NBR-Nylon blend with dimethylol phenolic resin, as the curing agent[4,5]. In the case of thermoplastic/rubber combinations of high interfacial tension, their compatibility is necessary for the blend in order to generate a fine dispersion of the rubber phase[6,7].

So far, there has not been much available information on such TPE or TPVs created from thermoplastic (polyamide or polyester) and NR blends[8]. The difficulty of preparing such TPE is due to the high interfacial energy between the two components and the high degradation of NR during high temperature mixing. However, by using a suitable compatibiliser and dynamic vulcanising agent, it would be possible to develop nylon 6/NR TPE. The maleated rubbers are successful examples of compatible blends with Nylon. The anhydride groups of these rubbers can react with polyamide amine end groups and form a graft copolymer at the rubber-matrix interface. However only a little amount of anhydride groups grafted on NR and a lot of gel was contained in the grafting process. The maleated NR/PA6 blends of TPV were not successful in yielding good elastic and mechanical properties, due to a coarse morphology.

Recent developments in polyamide-polyolefin blends have shown the possibility to create a high amount of amphiphilic species by *in situ* reactivity at the interface[9–11]. The reactive blends were carried out in the molten process, focused on the combination of radical and condensation reactivity of peroxide and maleic anhydride, leading to a high level of reciprocal grafting at the interface[9–11].

The development of PA6/NR TPE presented here is divided into two steps of mixing and dynamic vulcanisation. The first stage is aimed at studying the compatibility in a small bath mixer by using the *in situ* combined free radical and condensation reactivity of PA6/NR blends. These complex reaction systems consist of peroxide, maleic anhydride and activators (stearic acid and ZnO). The correct level of reactivity is examined in order to obtain a fine morphology of blends which will then be mixed *in situ* in a single screw extruder. The second step of PA6/NR blend dynamic vulcanisation takes place in the same single screw extruder with various types of vulcanised systems. The standard tension samples are then injected from the final blends. The static mechanical properties, DSC properties and morphology of the PA 6/NR TPE blends are finally characterised.

MATERIALS AND METHODS

The thermoplastic used was the extrusion grade polyamide 6 (Ultramid B4®) produced by the BASF company while man-made air dried sheet natural rubber from the local area was selected for study. The used peroxide, namely Perkadox 14-40P® [1,3-bis(1-tert-butyldioxy-1-methyl)benzene], was supplied by Akzo company. This peroxide has a half life time of 2.5 min at 180ºC and has a benzene group which is lightly soluble in natural rubber. Therefore, it can be left at the interface and/or it can be solubilised in the PA6 phase. Maleic anhydride was used as a bifunctional monomer.

It is well known as an unsaturated monomer that can be reacted with PA and is frequently used in free radical grafting reactions. Stearic acid and ZnO are activators for reactive blends. Four curing systems of sulphur, phenolic resin (SP-1045), peroxide Perkadox 14®, and bismaleimide agents were studied. Toluene and formic acid were used as solvents for NR and PA6, respectively, whereas acetone and water were the main solvents for the relative precipitation.

The rubber was masticated and then mixed with the peroxide, the monomer and the activator on a two roll-mill at 80ºC. When a well distributed mixer was obtained, the PA6 was added. A further reaction of NR/PA6 compound was carried out using a 80 cm^3 Brablender mixer at 240ºC. The properties and morphology of the blends were characterised by using solvent extraction technique and using SEM image for fracture surface study. The right level of reaction ingredients of NR/PA6 compounds were mixed *in situ* in a single screw extruder at 240ºC and a 5 kg/hr flow rate. The extrudate was quickly cooled with water as soon as it came out of the extruder die and cut to granulate form. The granules of NR/PA6 reactive blends were dried under vacuum at 50ºC for 24 h. The dried reactive blend was physically mixed with the vulcanisation agents and then dynamically vulcanised *in situ* in the single screw extruder under the same conditions. The product was dried and was injected to the standard tensile sample by using the plastic injection machine. The mechanical, thermal and solvent extraction properties were investigated and its morphology was characterised using SEM.

RESULTS AND DISCUSSION

Mixed Processing Characteristics

The *in situ* reactive blends of two systems; maleated natural rubbers (MNR) / PA6 blends and the interfacial reaction of complex mixed Perkadox 14® (peroxide) and maleic anhydride, were performed in a Brablender mixer at a rotor speed of 60 r.p.m., blending time 10 min and temperature about 240ºC. All blends contained PA6, approximately 80% and the formulae are shown in *Table 1*. The first formulation (*Formulation 1.1*) is a physical blend wherelse *Formulation 1.2* and *Formulation 1.3* are *in situ* reactive blends of PA6 with MNR, prepared in the Brablender at 120ºC, 10 min of reaction time and at a rotor speed of 60 r.p.m. The MNR (1) and MNR (2) consist of 1 p.h.r. of MA and 0 or 0.1 p.h.r. of Perkadox 14®, respectively.

TABLE 1. FIVE FORMULATIONS FOR THE STUDY OF PA6/NR REACTIVE BLEND

Ingredients	Formulation 1.1	Formulation 1.2	Formulation 1.3	Formulation 1.4	Formulation 1.5
PA6	80	80	80	80	80
NR	20	–	–	20	20
MNR (1)		20			
MNR (2)			20		
Maleic anhydride				0.5	1.0
Perkadox 14®				0.1	0.1

The amount of anhydride groups grafted on MNR (1) and MNR (2) are about 0.70 p.h.r. and 0.68 p.h.r., respectively. The MNR (1) and MNR (2) are used as crude products, so they may have some non-grafted maleic anhydride left. The latter 2 formulations (*Formulation 1.4* and *Formulation 1.5*) are complex reaction systems. The blend's morphologies of the samples' fracture, solidly frozen by liquid nitrogen, were studied using SEM, and shown in *Figure 1*. *Figure 1.1* shows the non-compatible physical blends of PA6 and NR. A rough surface and non-effective bind to matrix of NR were clearly seen. The reactive blends of MNR and PA6 (*Figures 1.2* and *1.3*) show a good improvement in morphologies. A fine rubber dispersion phase and interfacial adhesion seems to be better than that of the physical blend. However, when we compare the morphology of the complex reactive blends (*Formulation 1.4* and *Formulation 1.5*) with those of the reactive blends (*Formulation 1.2* and *Formulation 1.3*), a better, finer rubber dispersion phase and a higher interfacial adhesion can be clearly seen.

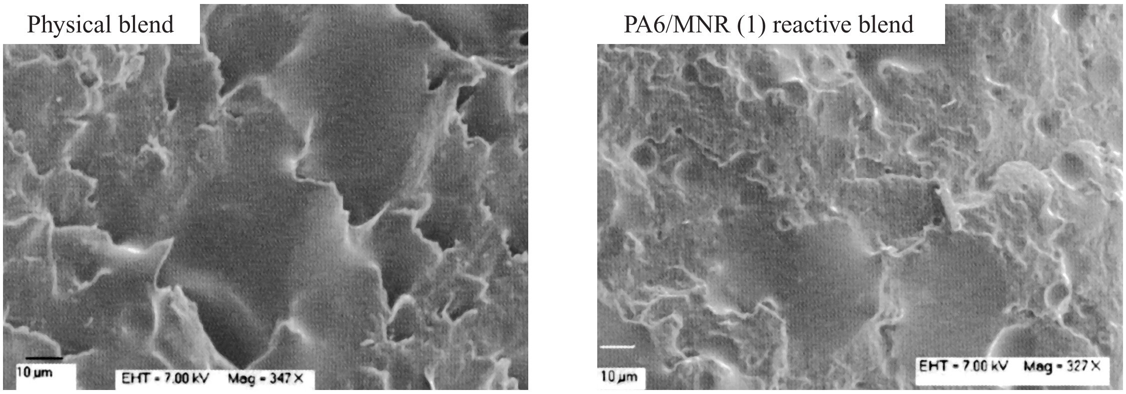
Therefore, the complex reactivity of peroxide and maleic anhydride was the most suitable method for NR and PA6 blends in one step processing and this condition was employed throughout this study.

Reactive Blends in a Single Screw Extruder

Here the aim was to study the possibility of the NR/PA6 blend in a single screw extruder. *Table 2* presents all the formulations of the blends, containing the same fraction of PA6/NR (40/60). Three systems of the physical blend (*Formulation 2.1*), the reactive blend (*Formulation 2.2*) and the complex reactive blends (*Formulation 2.3* and *Formulation 2.4*) were prepared in the single screw extruder using a one-step process. The extrusion was carried out at 240ºC (both barrel and die temperatures), the screw speed was 30 r.p.m. and the output rate was 5 kg/hr. The extrudate was granulated, dried and then injected as a standard dumbbell tensile test sample, using the thermoplastic injection machine. The tensile strength and elongation at break are reported in *Table 2*. The physical blend (*Formulation 2.1*) gave the highest tensile strength but indicated an extremely low value of 20% elongation at break. This was due to non-compatible blend characteristics. The reactive blends of *Formulation 2.2* and *Formulation 2.3* showed higher values of elongation at break than that of the physical blend, whilst the complex reactive blend with the activation agents ZnO and stearic acid (*Formulation 2.4*) had a better elongation at break (90%) with a similar value of tensile strength of previous formulations. It also provided an easy operation in extrusion. Thus, this complex reactive formulation of 40/60 - PA6/NR could be further examined for suitable curing systems in dynamic vulcanisation.

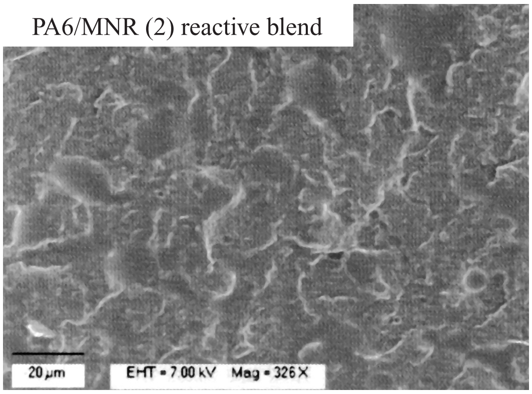
Dynamic Vulcanisation Systems

Four curing systems of sulphur, phenolic resin, peroxide, and bismaleimide were used to study dynamic vulcanisation of the 40/60-PA6/NR blends. The blends were mixed with vulcanising agents on a two roll-mill at 80ºC for 5 min. Dynamic vulcanisation occured in the single screw extruder at the same condition of mixing. *Table 3* presents the vulcanising ingredients and the mechanical properties of blends. It showed that the conventional sulphur vulcanising system did not give better values of tensile strength and elongation at break. This could be caused by a fast curing rate and a high conversion cure at the dynamic vulcanisation temperature of 240ºC. Thus, there would not have been enough time to modify the morphology during vulcanisation. The peroxide and bismaleimide systems gave slightly higher

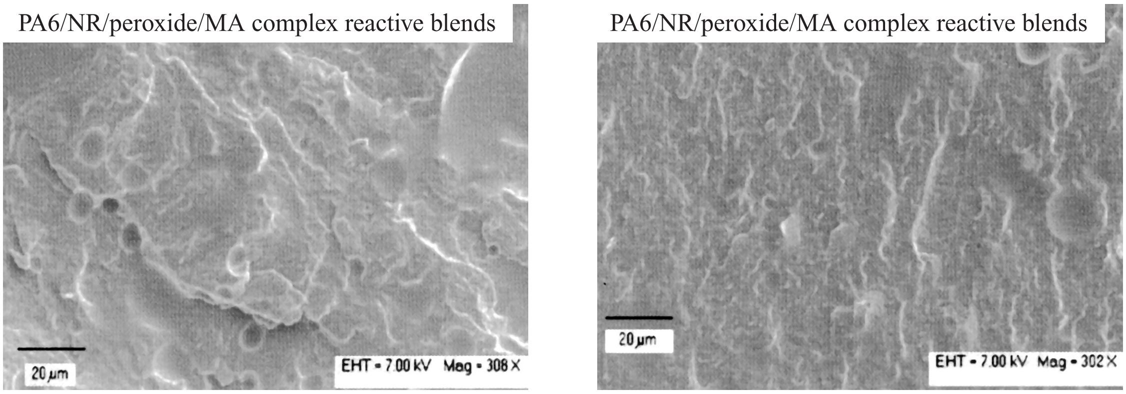


(a) Formulation 1.1

(b) Formulation 1.2



(c) Formulation 1.3



(d) Formulation 1.4

(e) Formulation 1.5

Figure 1. Morphology of (a) Physical blend, (b) PA6/MNR (1) reactive blend, (c) PA6/MNR (2) reactive blend, (d) and (e) PA6/NR/peroxide/MA complex reactive blends.

TABLE 2. FORMULATION AND PHYSICAL PROPERTIES OF PHYSICAL (2.1), REACTIVE (2.2) AND COMPLEX REACTIVE BLENDS (2.3 AND 2.4) (WITH AND WITHOUT ACTIVATORS; ZnO + STEARIC ACID)

Ingredients	Formulation 2.1	Formulation 2.2	Formulation 2.3	Formulation 2.4
Polyamide 6	40	40	40	40
Natural Rubber	60		60	60
MNR (2) (MA 1 p.h.r., Perkadox® 0.1 p.h.r.)		60		
Perkadox 14®			0.1	0.1
Maleic anhydride			1.0	1.0
Zinc oxide				1.0
Stearic acid				1.0
Tensile strength (MPa)	11.62	8.81	9.63	8.22
Elongation at break (%)	20	75	40	90

TABLE 3. DYNAMIC VULCANISATION FORMULATION OF FOUR CURING SYSTEMS.

	Formulation 3.1	Formulation 3.2	Formulation 3.3	Formulation 3.4
CBS	0.3			
Sulphur	0.8			
Perkadox 14®		0.1		
Maleic anhydride		2.0		
Phenolic resin (SP-1045)			2.5	
Bismaleimide				1.5
Tensile strength (MPa)	6.98	12.61	14.1	12.42
Elongation at break (%)	50	70	100	75

values of tensile strength. The most attractive dynamic vulcanising system, presented here, is the phenolic resin curing system. Both the tensile strength and elongation at break improved. This system had a low curing rate, indicating a suitable cure time with the extrusion operating time at an extremely high temperature of 240ºC. There was enough time for the blend to modify conversion phase processing to obtain a fine vulcanised rubber by dispersion phase morphology. The inversion phase morphology of blend provides a thermoplastic-like material. Therefore, it can be transformed easily in a commercial thermoplastic equipment.

Dynamic Vulcanisation of PA6/NR Blend with Phenolic Resin

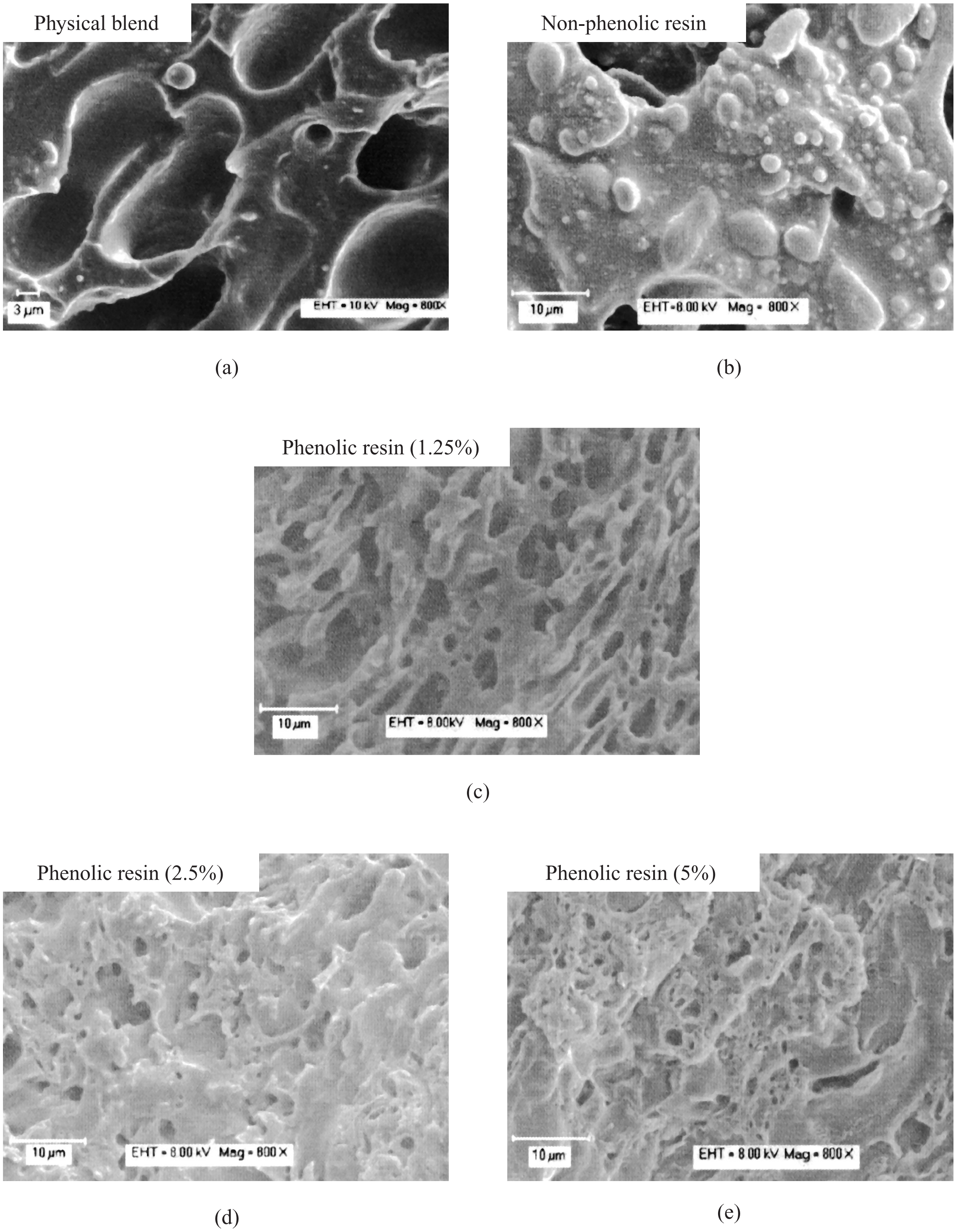
Figure 2 shows the SEM of the surface fracture after the rubber phase was extracted with toluene at 110ºC for 4 h. It also shows the dynamic vulcanisation complex of the reactive blends of the 40/60-PA6/NR morphology. *Figure 2(a)* presents large holes of the non-compatible physical blend. *Figure 2(b)* consists of a large co-continuous phase with some holes of unvulcanised rubber in PA6 continuous phase and some particles of PA6 in rubber phase. The dynamic vulcanisation step of the 40/60-PA6/NR blend morphology using various amount of phenolic resin are shown in *Figures 2(c)* to *Figures 2(e)*. The morphology of the PA6/NR blends changed to the fine co-continuous phase (*Figure 2(c)*) after dynamic vulcanisation with 1.25 p.h.r. of phenolic resin. The inverse phase took place after dynamic vulcanisation with 2.5 p.h.r. phenolic resin, indicated by small holes in the rubber phase morphology [*Figure 2(d)*]. This converse phase phenomenon was confirmed from dynamic vulcanisation with 5 p.h.r. phenolic resin as shown in *Figure 2(e)*. These two latter figures show the rubber particles distributed in the PA6 phase. The complete inverse phase appears at about 2.5 p.h.r. phenolic resin. The solvent extraction of NR phase with toluene for 8 h at 110ºC and extraction PA6 phase with formic acid for 24 h at room temperature are showed in *Table 4*. The toluene soluble fraction of the complex reactive PA6/NR (40/60) blend is approximately 44.3%. This means that most of NR phase is extracted with toluene. The formic acid soluble fraction is about 31.5%, that means that there is about 8.5% of PA6 left in the insoluble toluene, corresponding to the continuous rubber matrix phase. As the degree of dynamic vulcanisation increases, the toluene soluble fraction rapidly declines from 44.3% to 7.01% while the formic acid soluble fraction increases from 31.5% to 40%. The solvent extraction effect corresponds to inverse phase phenomena during dynamic vulcanisation. In the case of dynamic vulcanisation, the non-soluble toluene and formic acid fractions are the fraction of rubber vulcanised. The majority of the rubber phase is vulcanised and rubber particles formed with very small particle sizes.

The dynamic vulcanisation process not only affects the inverse phase morphology or the improvement of the blend morphology but it also improves it's physical properties. The tensile strength values increased from 8.22 MPa to 14.1 MPa while the elongation at break also improved (see *Table 4*).

Thermoplastic Elastomer PA6/NR Blend Characteristics

The four types of blends, the physical blend (*Formulation 2.1*), complex reactive blend (*Formulation 2.4*), dynamically vulcanised reactive blend (*Formulation 4.3*) and dynamically vulcanised reactive blend mixed with carbon black were characterised. They were named as *Formulation A, B, C* and *D*, respectively. *Formulation D* consisted of 15% carbon black added in the first step, and 0.6% antioxident [N-phenyl-N-1,3 dimethylbutyl-*p*-phenylenediamine (6PPD)] added in the dynamic vulcanisation step. The stress-strain relationship of these four formulations are shown in *Figure 3*. It is clearly shown that the reactive blend (*Formulation B*) is softer than that of the physical blend. This might be caused by the change of the reactive blend morphology and the activator (ZnO and stearic acid) effect on the rubber phase. The dynamic vulcanisate did not improve only the tensile strength and elongation at break, it also made the blend stiffer. Unusually, the carbon black contained in *Formulation D* make the material soft compared with the dynamically vulcanised blends (*Formulation C*). This might be caused by the incompatibility of PA and carbon black.

Figure 4 shows solvent extraction of *Formulations A* to *D*. It is composed of three



(a) (b)

(c)

(d) (e)

Figure 2. Dynamic vulcanisation morphology of phenolic resins: (a) physical blend (b) unvulcanised reactive blend (c) to (e) reactive and dynamic vulcanisation of varying phenolic resins of 1.25%, 2.5%, 5%, respectively.

TABLE 4. EFFECT OF DYNAMIC VULCANISATION IN PHYSICAL AND SOLUTION EXTRACTION PROPERTIES

Formulation (Phenolic content%)	Tensile strength (MPa)	Elongation at break (%)	Solution in toluene (%)	Solution in Formic acid (%)	Non-solution (%)
Formulation 4.1 (0.0%)	8.22	90	44.30	31.51	24.19
Formulation 4.2 (1.25%)	11.2	60	23.92	31.58	44.50
Formulation 4.3 (2.5%)	14.1	100	7.06	37.63	55.31
Formulation 4.4 (5.0%)	13.7	100	2.15	40.11	57.74

TABLE 5. HARDNESS AND COMPRESSION SET OF REACTIVE PA6/NR (40/60) TPE

Formulation	Hardness (Shore A)	Compression set (%)
Formulation C	84	40
Formulation D	82	40

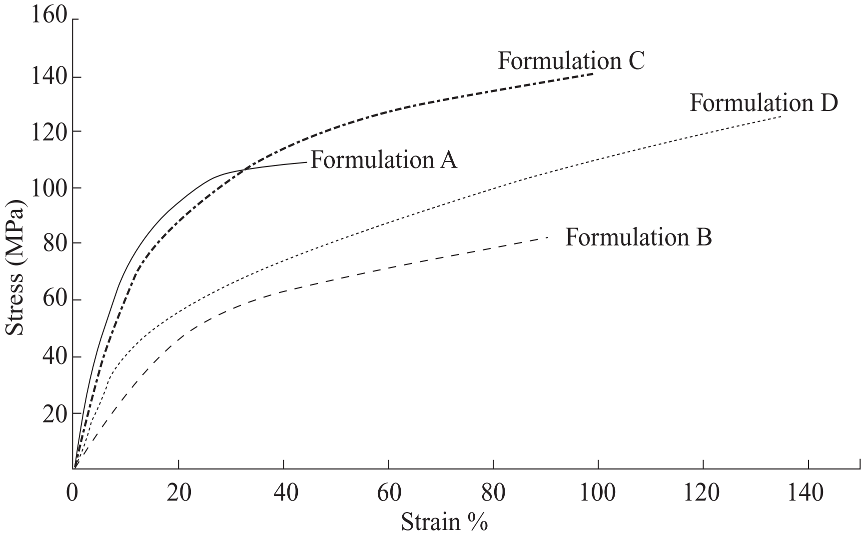


Figure 3. Stress-strain relationship of PA6/NR (40/60) blend for Formulation A *(physical blend)* Formulation B *(reactive blend),* Formulations C *and* D *(reactive and dynamic vulcanisation).*

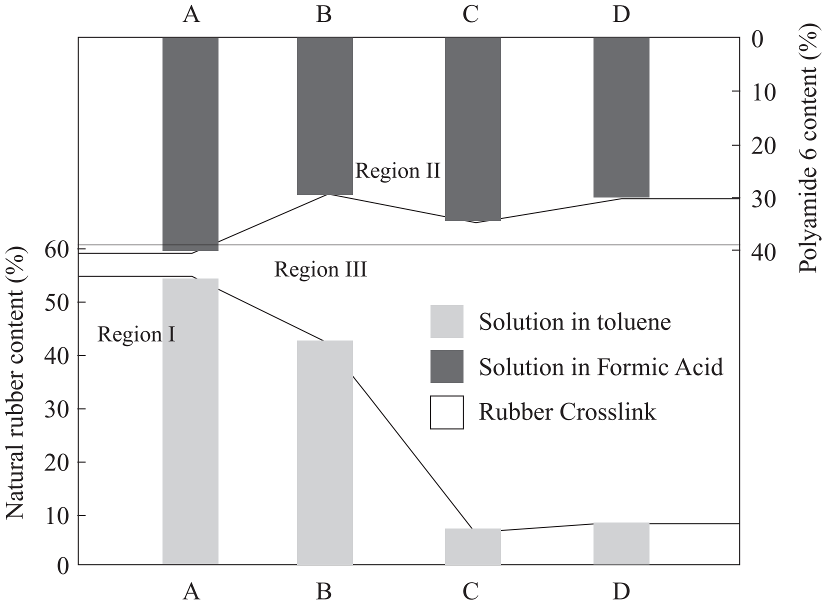


Figure 4. Solvent extraction properties of Formulations A, B, C *and* D.

regions of the solution in toluene (Region I), in formic acid (Region II) and the insoluble fraction (Region III). *Formulation A* indicated that nearly all of the NR and PA6 phases dissolved in the corresponding solvent. Only a tiny amount of NR gel content might be left. There was approximately 25% of PA6 phase that could not be dissolved in the case of the reactive blend and dynamically vulcanised blends (*Formulation B, C* and *D*). For this condition, the PA6 phase cannot be crosslinked, so that this 25% PA6 could be considered as the fraction of the NR-PA6 block copolymer, created from the complex reactive blends. This extremely high amount of created block copolymer was confirmed by the dramatic change in morphology of the complex reactive blend. Extremely high amounts of *Formulations C* and *D* rubber crosslinking are clearly indicated as the white area (Region III) in *Figure 4*. This is corresponding to the morphology shown in *Figure 2 (d)* which indicated the high amount of rubber crosslinked particles dispersed in the thermoplastic PA6 phase.

The examination of DSC thermal properties of these four formulations are presented in *Figure 5*. In case of the complex reactive blend (*Formulation B*), the molten and crystalline temperatures of the PA6 phase are slightly shifted to lower temperatures than those of the physical blend. This movement is not clearly seen in the case of the dynamically vulcanised TPE blends (*Formulations C* and *D*).

The results of solvent resistance examination, following *ASTM D 471-98* (the swelling standard method) are presented in *Table 6*. Very good solvent resistance is clearly seen compared with the vulcanised NR. The oil resistant values of the produced TPEs were three times lower than that of the NR.

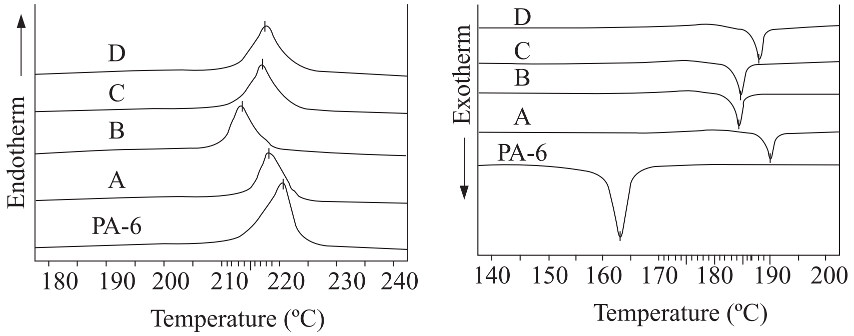


Figure 5. DSC of Formulations A, B, C *and* D.

TABLE 6. OIL RESISTANCE OF THE COMPLEX REACTIVE PA6/NR (40/60) TPE

Item	Swelling (%)		
	Formulation C	Formulation D	Reference (NR-Cure)*
Isooctane 100	25.54	24.69	56.09
Isooctane + toluene; 50+50	46.39	41.58	128.00
Toluene 100	54.17	47.90	178.57
Diesel fuel 100	17.02	34.65	158.51

*NR: 100; ZnO: 5; Stearic Acid: 2.5; Oil (Deoflow S): 15; TBBS: 0.5; Wingstay L®: 1 and Sulphur: 2 p.h.r.

The white TPE (*Formulation C*) and the black TPE (*Formulation D*) had the hardness values of 84 and 82 (Shore A), respectively. The compression sets were about 40% of the 25% compression at 70ºC for 72 h (*ASTM D395-96*). This shows that these TPEs can be considered as a hard type and had a similar hardness and compression set values of the commercial TPE.

The dynamic mechanical properties were analysed by using dynamic mechanical thermal analyzer (Rheometric Scientific, DMTA V). Dual cantilever sample deformation was tested at a frequency of 1 Hz; strain control of 1% and the temperature ranged between 25ºC and 250ºC. The results are shown in *Figure 6* for the white and the black TPEs. It showed that the storage modulus was higher than the loss modulus, which confirms that the TPEs are of hard rubber material. The modulus was continuously constant during the temperature range of 25ºC and 200ºC and it dropped rapidly at temperatures above 200ºC. These results confirm that the provided material could be used up to the extremely high temperatures of 200ºC.

GENERAL DISCUSSION

The investigated blend confirms that the complex system of free-radical and conden-

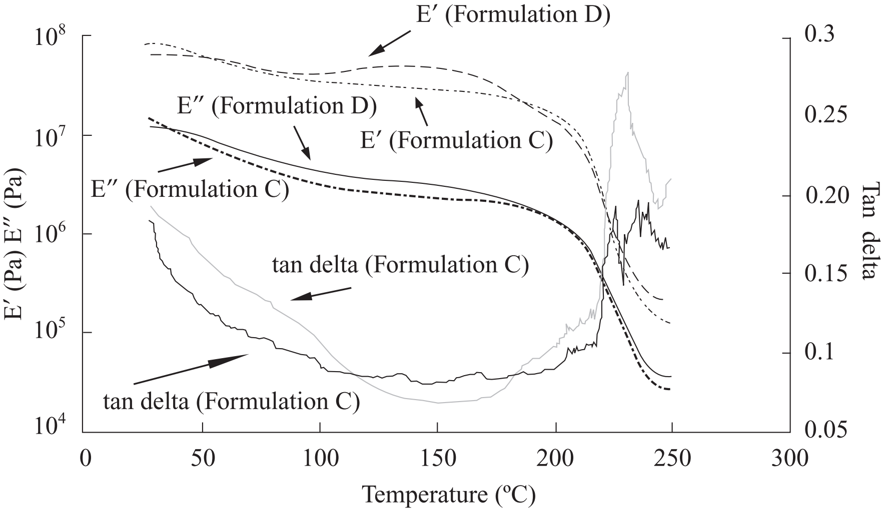


Figure 6. Dynamic properties of the reactive PA6/NR (40/60) TPE.

sation reaction could be an efficient way for interfacial grafting and co-crosslinking between Polyamide 6 and natural rubber. The changes in solubility characterised by solvent extraction techniques are able to confirm the high level of reciprocal grafting, which could signify an efficient reacting system limited to interfacial volume. Two kinds of reaction are involved. Firstly, we expect to obtain reciprocal termination processes between free-radical polymeric site on both polymers presented at the interface. Secondly, the condensation reaction between grafted maleic anhydride and primary-amine-terminated polyamide chain ends created the grafted copolymeric species as shown in *Scheme 1*. It is very difficult to define the specific contribution of free-radical reactivity and that of the condensation reaction to the total amount of grafting. Apparently the activators zinc oxide and stearic acid play an important role as interfacial lubricants to carry reactive agents to the interfacial volume between the two polymers. If the main complex reaction is carried out in the interfacial volume, the introduced concentrations of MA, peroxide, ZnO and stearic acid are quite high in the limited volume indicated as grey-coloured areas in *Figure 7*.

The dynamic vulcanisation step is important to identify the morphology and the mechanical properties of the investigated TPE. Phenolic resin cure system is most effective for this examined PA6/NR. Due to the very low curing rate, the operated temperature was very high. So, there was enough time to evaluate inverse phase phenomena and fine morphology. This phenolic resin cure reaction might be evaluated from *Scheme 2*.

CONCLUSIONS

The compatibility of NR/PA6 blends was conducted using induced reactivity in a single screw extruder based on a mixture of peroxide

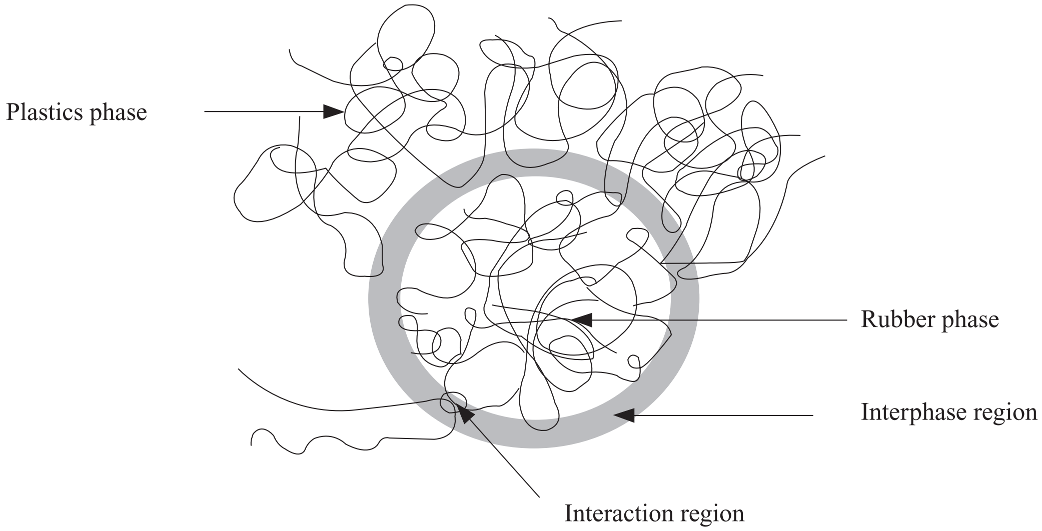
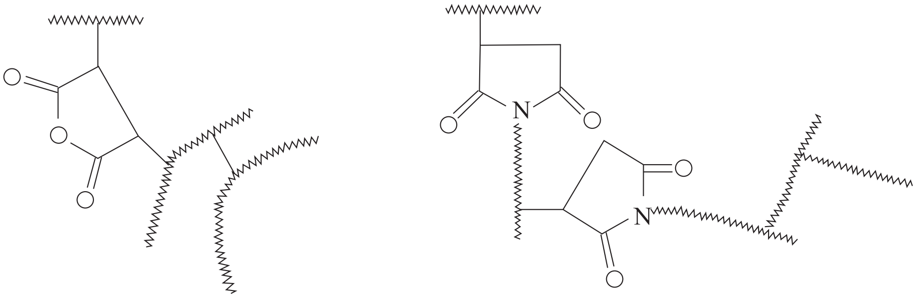
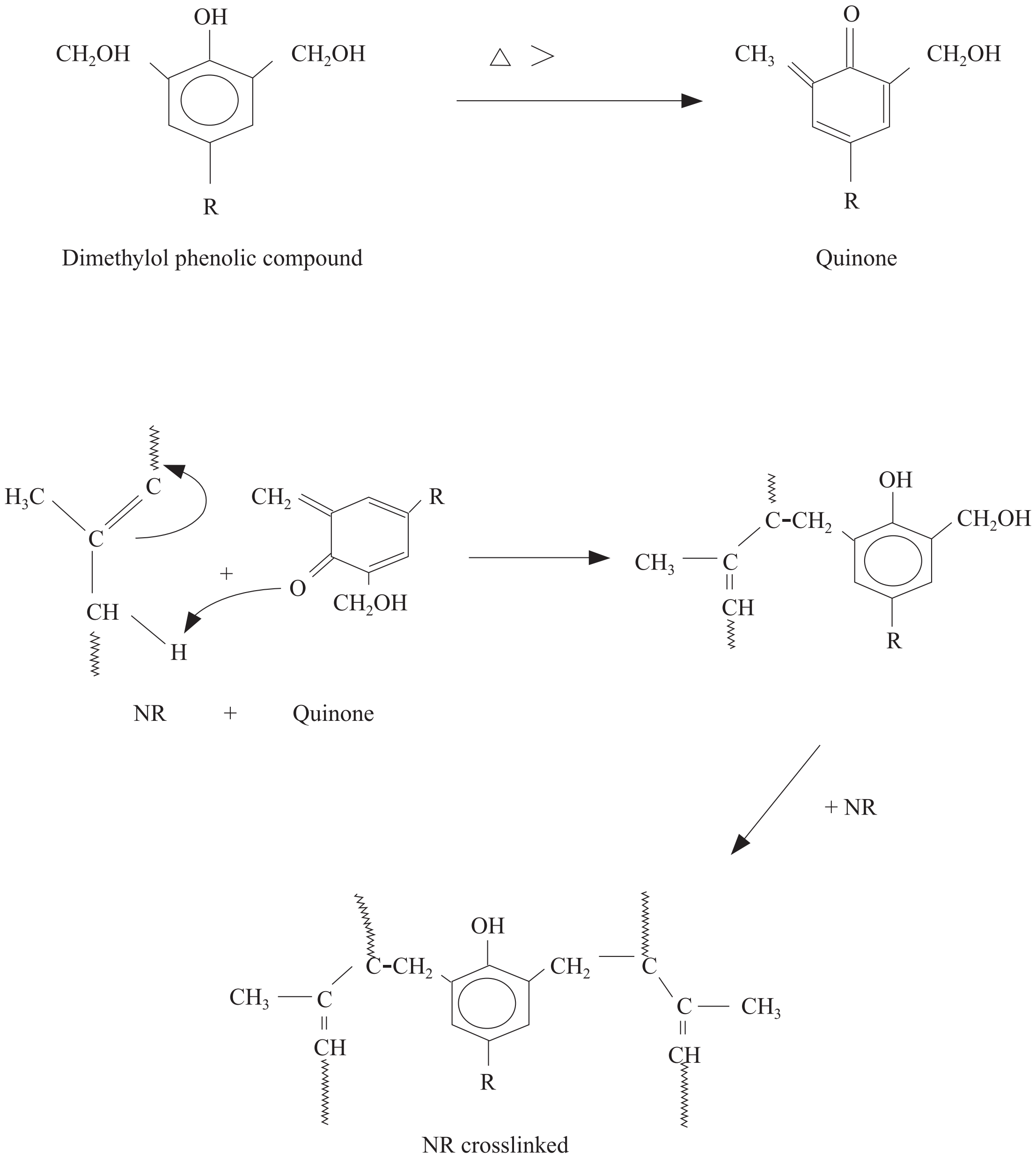


Figure 7. Schematic representation of the interfacial reactive area.



The reciprocal grafting between PA6 and NR by free radical and condensation reaction, respectively.

Scheme 1



Possible phenolic cure reactions of NR phase in the dynamic vulcanisation process.

Scheme 2

(Perkadox 14®), reactive monomer (maleic anhydride) and activators (ZnO and stearic acid). The results showed that a good level of reciprocal grafting occurred between NR and PA6. Theirs morphologies showed good interfacial adhesion with a fine continuous phase for PA6. The TPE was done by vulcanised rubber phase using the dynamic vulcanisation method in the secondary step.

Dynamic vulcanisation process was studied using several vulcanising systems on the single screw extruder. It showed that the suitable vulcanising agent is a phenolic resin (SP-1045). The thermoplastic elastomer produced showed a fine NR crosslinked dispersed phase. Good mechanical properties were obtained for the produced TPE. It's tensile strength and elongation at break were about 12 MPa and 135%, respectively. The TPE also showed very good oil resistance and could be used up to the very high temperature of 200ºC.

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