

# Preparation and Characterization of Blends Containing Natural and Some Synthetic Rubbers with Synthesized Aromatic Polyester

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**ABSTRACT:** This work deals with the synthesis of aromatic polyester (AP) from polyarylate [Bisphenol A (BPA)/dimethyl terephthalate (DMT)/ethylene glycol (EG)] and maleic anhydride (MA) in presence of dibutyl tin oxide (DBTO) as a catalyst. Blends were prepared from candicated AP (10–30 phr) with different types of rubber [natural rubber (NR), acrylonitrile butadiene rubber (NBR), styrene butadiene rubber (SBR) and ethylene-propylene diene monomer (EPDM)]. The obtained blends were subjected to physicomechanical measurements to evaluate their properties as efficient blends for economic industrial applications. In case of AP blended with rubber, better properties were obtained than that of rubber vulcanizates. The fatigue life values decreases by increasing the AP contents for all types of the tested blends. The equilibrium swelling (%) for the prepared blends exhibits different

behavior in solvents like toluene and motor oil. The addition of *N*-isopropyl-*N'*-phenyl-*p*-phenylene diamine (IPPD), as antioxidant, affects the properties of all the prepared products. These properties were in consequent with the data of the initial shear modulus, which is calculated from the Mooney-Rivlin equation and the percentage of the equilibrium swelling. Scanning electron microscope (SEM) was used to study the morphological structure; the SEM results show the changes in surface of the rubber before and after being blended with AP. The investigated blends are considered a new trend in giving products with variable physicomechanical characteristics. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2823–2835, 2008

**Key words:** aromatic polyester; rubbers; physicomechanical properties

## INTRODUCTION

Recently polymer blending is considered one of the most economical techniques that plays a special role to improve the physical and mechanical properties of the new finished product.<sup>1,2</sup> Thermoplastic elastomers have the characteristics of the thermoplastic materials at processing temperature and those for elastomers at service temperature.<sup>3</sup> They contain a soft rubbery phase and a hard thermoplastic phase. Thermoplasticity results from the melting characteristics of the hard thermoplastic at the high temperatures of processing, whereas the elastic properties arise from the soft rubbery phase at low temperatures.<sup>4</sup> At these temperatures, the hard thermoplastic acts as crosslinks or as reinforcing filler particles between the soft rubbery phases.<sup>5</sup>

As a result of blending, the physical properties can be altered to produce useful materials with a wide range of applications and possess a combination of physical and rheological properties that are

unavailable in a single polymer.<sup>6–8</sup> This type of blending is considered as a convenient route for obtaining materials with improved properties and low cost performance.<sup>9–11</sup> Because of the fact that aromatic polyester offer a high heat distortion temperature, an inherent UV stability, and excellent mechanical properties, in addition, can exhibit transesterification upon mixing; blends of polyarylates with other polymers have been studied for both industrial applications and academic interest.<sup>12–15</sup>

Polyarylate is thermoplastic aromatic polyester derived from 2,2'bis(4 hydroxy phenyl)propane, Bisphenol A (BPA), and a mixture of isophthalic acid (IA) and terephthalic acid (TA).<sup>16–18</sup> Various synthesizing routes as acidolysis, phenolysis, alcoholysis, and esterolysis have been investigated to produce polyarylate.<sup>19,20</sup> Mahajan et al. used three-step processes to synthesize aromatic polyesters polyarylate by transesterification of dimethylterephthalate (DMT)/dimethylisophthalate (DMI)/BPA using alcoholysis in the presence of different catalysts.<sup>21,22</sup>

This work aims to prepare aromatic polyester (AP) from the polyarylate (BPA/DMT/EG) and maleic anhydride (MA) in the presence of dibutyl tin oxide (DBTO) as catalyst. Different blends containing AP with different types of rubber as natural rubber

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TABLE I  
Some Specifications of the Rubbers Used

Specifications	Type of rubber			
	NR	NBR	SBR	EPDM
Density (g/cm <sup>3</sup> )	0.913	1.170	0.945	0.860
Mooney viscosity ML (1+4) at 100 °C	41 ± 2	45 ± 5	52 ± 3	85
Average molecular weight <sup>a</sup>	174,189	163,376	140,326	–

<sup>a</sup> Calculated according to Huggins equation.<sup>23</sup>

(NR), acrylonitrile butadiene rubber (NBR), styrene butadiene rubber (SBR), and ethylene-propylene-diene monomer (EPDM) were prepared and evaluate the physical and mechanical properties of the obtained blends.

## EXPERIMENTAL WORK

### Materials

2,2-Bis(4 hydroxy phenyl)propane, Bisphenol A (BPA), and dibutyl tin oxide (DBTO) were supplied by Aldrich Company.

Dimethyl terephthalate (DMT), ethylene glycol (EG), and maleic anhydride (MA) were obtained from Merck Chemical Company (Germany). All reagent-grade were used without further purification.

Dicumyl peroxide (DCP), bis(1-methyl-1-phenyl-ethyl) peroxide as catalyst with active oxygen 5.87%, and *N*-isopropyl-*N'*-phenyl-*p*-phenylene diamine (IPPD) were purchased from Bayer.

- Natural rubber (NR), the ribbed smoked sheets of NR (RSS-1).
- Styrene-butadiene rubber 1502 (SBR) with 23.5% styrene content.
- Nitrile butadiene rubber (NBR) was a Bayer product, Perbunan that is a butadiene-acrylonitrile copolymer with 32% acrylonitrile content.
- Ethylene-propylene-diene monomer (EPDM) with an ethylene weight content of 70%, an unsaturated ratio NB/100, and 8 and 22% propylene. Some specifications of the different types of rubber used are given in Table I.

### Methods

#### Preparation of prepolymer based on polyarylate

The preparation of the prepolymer was carried out in 250-mL round-bottomed flask with a magnetic stirring bar, a nitrogen inlet, and a reflux condenser. The reaction flask was charged with 0.1 mol (19.42 g) of DMT, 0.1 mol (22.84 g) of BPA, 0.1 mol (6.2 g) of EG, and 0.126 g (0.55 wt % based on BPA) of DBTO. The system was purged with dry nitrogen

for 15 min at room temperature (25 ± 2)°C. The reactants were heated till 200°C in a dry nitrogen atmosphere until methyl alcohol as a by-product start to distill out. Since methanol is a low boiling compound, it can be removed conveniently and efficiently from the reaction medium. The temperature is maintained till methanol is removed completely. The reaction flask is then let to cool to ambient temperature.

#### Preparation of the aromatic polyester (AP)

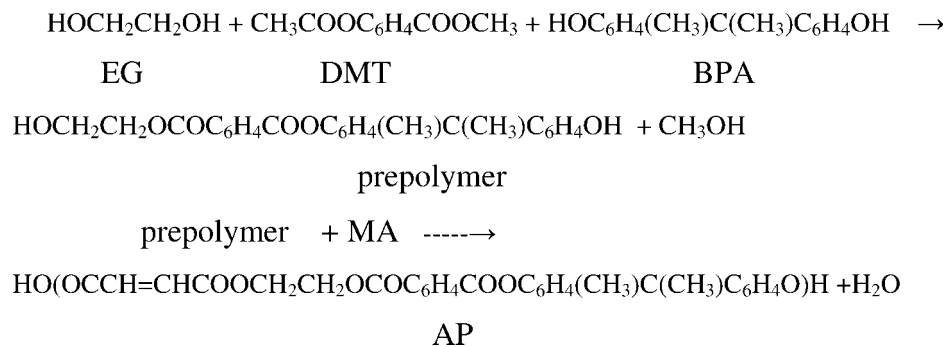
The prepared prepolymer was heated with MA at a molar ratio 1.1/1.0 (mol/mol) of hydroxyl to carboxyl and 0.5% of DBTO, wt/wt of prepolymer. The temperature was raised to 150°C and then increased step wisely at intervals of 10°C per hour to 240°C until the products became very viscous. The reaction course was followed by determining the acid number every hour until it reached 50 ± 2 mg KOH/g. The unreacted monomers were removed from the reaction mixture by vacuum distillation at 200°C for 45 min, and then the (AP) was purified by dissolving in chloroform, precipitating with petroleum ether. The process of purification was repeated twice and then the product was dried under reduced pressure.

#### Preparation of the blends

The blending of the components was carried out according to [ASTM (D15-72)] in a Brabender plastimeter at 150°C and a rotor speed 30 rpm. The mixing was continued for 5 min at room temperature, and then the peroxide (DCP) was added to the mix on a laboratory two-roll mill (470-mm diameter, 300-mm working distance). The speed of the slow roll was 24 rpm with a gear ratio of 1 : 1.4. The obtained blends were left overnight before vulcanization.

#### Vulcanization

Vulcanization was carried out in a single-daylight electrically heated auto controlled hydraulic press at (152 ± 1)°C and pressure 4 MPa.



Scheme 1

**Evaluation of the aromatic polyester and the blends**

The IR spectra were recorded on a JASCO FTIR 300E Fourier transform infrared spectrometer.

<sup>1</sup>H NMR spectra were obtained at 260 MHz using a JEOL-EX-270 NMR spectrometer.

The rubbers and their blends were conducted to many tests at room temperature (25 ± 2)°C and at atmospheric pressure according to the following standard methods, namely,

- a. The physicomechanical properties [ASTM D 412 (1998)]; Tensile strength, Young’s modulus (E), was measured using Zwick tensile testing machine (model-1425).
- b. Thermal oxidative aging was measured according to [ASTM D 573 (1994)].

- c. Hardness [ASTM D 2240-97 (1997)] using a Shore A type durometer. The term degree shore represents the resistance against the penetration of a truncated cone into the sample.
- d. Tear resistance was determined on a Zwick tensile testing machine (model-1425) [ASTM D 624 (1998)].
- e. Fatigue property was performed using a Monsanto Fatigue Failure Testing machine, according to [ASTM D 3629 (1998)]. The specimens had a gauge length of 89.0-mm (3.5 in.), width of 25.4-mm (1.0 in) thickness of 2.0-mm (0.079 in). The specimens were subjected to tension-tension fatigue in a displacement-controlled machine.
- f. Swelling equilibrium [ASTM method D 471-97 (1998)]. A test piece weighing about 0.2 g. was immersed for 24 h in pure toluene at room tem-

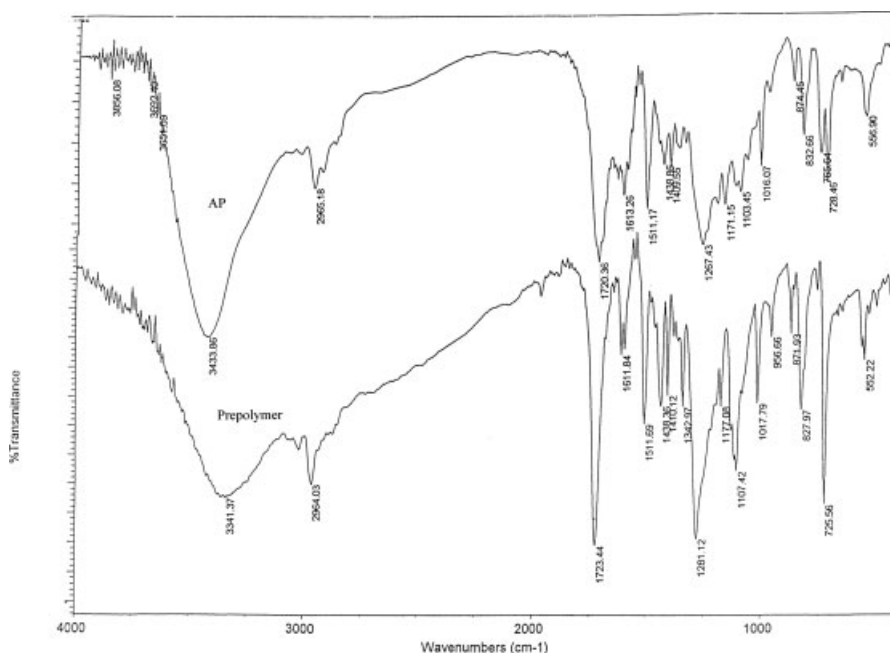
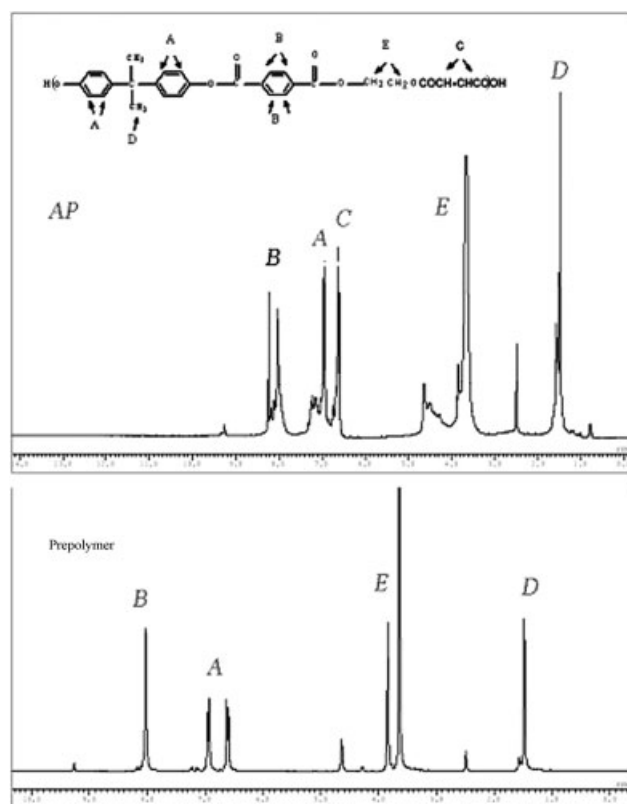


Figure 1 IR spectra of prepolymer and aromatic polyester (AP).



**Figure 2**  $^1\text{H}$  NMR spectra of prepolymer and aromatic polyester (AP) based on polyarylate.

perature. At the end of this period the test piece was taken out, the adhered liquid was rapidly removed by blotting with filter paper, and the swollen weight was measured immediately. The equilibrium swelling is defined as

$$Q = (W_1 - W_0)/W_0 \times 100 \quad (1)$$

where  $W_0$  is the weight of the test piece before swelling and  $W_1$  is the weight of the swollen test piece after 24 h of immersion. A similar test procedure was used in motor oil for 70 h at room temperature.

- a. Permanent set (tension set), is measured after 15 min from rupture of the sample [ASTM D 395 (1998)].

**TABLE II**  
Some Physicomechanical Characteristics of Natural Rubber/Aromatic Polyester (NR/AP) Blends

NR	100	90	80	80	70
PA	–	10	20	20	30
IPPD	–	–	–	1	–
Peroxide (DCP)	3	3	3	3	3
Permanent set, %	10	12.5	15	19	24
Equilibrium swelling, in toluene %	500	447	489	644	459
Equilibrium swelling, in motor oil %	66	53	50	59	39

- b. A Jeol JXA-840A Electron Probe Microanalyzer Scanning electron microscope (Japan) was employed to observe and study the morphology of the blends. The actual pretreatment of preparation consisted only of the gold plating of the samples in S150A Sputter Coater Edwards (England).

## RESULTS AND DISCUSSIONS

Scheme 1 illustrates the synthesis of the AP sample

### Characterizations of the prepolymer and the aromatic polyester

The process of AP synthesis involves two stages process, the first started with the reaction of DMT, EG, and BPA at 200°C in the presence of DBTO as a catalyst under mechanical stirring. The catalyst selected for this study is known to be effective for aliphatic transesterification reactions.<sup>21</sup> The presence of catalyst during the transesterification reaction is necessary, as no distillation of methanol was observed when transesterification was carried out without catalyst. The catalyst employed is a derivative of the group IV-A metals in the periodic table, such as dibutyl tin oxide. The use of tin derivatives exhibited good conversions and color among all other catalysts.<sup>21</sup> The second step consists of reacting the prepolymer products with MA as described in the preparation section. The obtained AP is hard resin soluble in acetone, chloroform and insoluble in ethanol, benzene, toluene, and xylene.

The IR spectra of the prepolymer and AP are represented in Figure 1 and characterized by strong

**TABLE III**  
Some Physicomechanical Characteristics of Styrene-Butadiene Rubber/Aromatic Polyester (SBR/AP) Blends

SBR	100	90	80	80	70
AP	–	10	20	20	30
IPPD	–	–	–	1	–
Peroxide (DCP)	3	3	3	3	3
Permanent set, %	5	5	7.5	7.5	8.5
Equilibrium swelling, in toluene %	329	296	361	462	410
Equilibrium swelling, in motor oil %	16.4	15	14.27	16.26	12.93

TABLE IV  
Some Physicomechanical Characteristics of Acrylonitrile-Butadiene Rubber/Aromatic Polyester (NBR/AP) Blends

NBR	100	90	80	70	80
AP	–	10	20	20	30
IPPD	–	–	–	1	–
Peroxide (DCP)	3	3	3	3	3
Permanent set, %	17	16	15	14.1	18.78
Equilibrium swelling, in toluene %	119	114	122	141	118
Equilibrium swelling, in motor oil %	1.34	0.304	0.246	0.303	0.217

bands at the vicinity of  $3341\text{--}3433\text{ cm}^{-1}$  that is attributed to stretching frequencies of OH groups in both prepolymer and AP, respectively. It is worth-mentioning that, the relative increase in the intensity of band near  $3430\text{ cm}^{-1}$  is for AP spectrogram Figure 1, may refer to the hydroxyl group of  $\text{--COOH}$  of MA added to prepolymer to form AP. The intense sharp band near  $1723\text{ cm}^{-1}$  in prepolymer spectrum is quite characteristic for the stretching frequency of the carbonyl groups. The smaller shift of the carbonyl stretching in AP spectrum to  $1720\text{ cm}^{-1}$  and its splitting may also be attributed to the adding of  $\text{--COOH}$  group through the MA addition.

This result was confirmed by  $^1\text{H}$  NMR spectra for both prepolymer and AP. In the region  $7.9\text{--}8.3\text{ ppm}$ , closed to terephthalic structure, the NMR spectrum of the AP, (Fig. 2) which, shows also four additional peaks between 8 and  $8.3\text{ ppm}$ , due to the symmetrical aromatic ester substituted terephthalic unit [B]. The symmetrical aromatic ester substituted BPA moiety shows [A] aromatic proton shifts in the region  $6.5\text{--}7\text{ ppm}$  for prepolymer and  $6.8\text{--}7.4\text{ ppm}$  for AP, (Fig. 2), besides the aliphatic proton singlet at  $1.4\text{--}1.6\text{ ppm}$  [D]. In addition to these shifts, additional peaks are observed at higher field in both the regions. It is well known that phenolic OH group is strong electron donor and exhibits shielding effect on ortho, meta, and para protons of the aromatic nucleus, causing up field shifts. A group of signals [E] from  $3.5\text{ to }4.7\text{ ppm}$  seem to be due to the methylene proton of EG. The  $^1\text{H}$  NMR spectrum of the AP. Figure 2 indicates the participation of MA in the reaction as proved by the two unsymmetrical signals [C] at  $6.5\text{--}6.8\text{ ppm}$  characteristic of the olefinic protons in the MA-fumaric acid residue  $\text{--CH=CH--}$ .

#### Evaluation of the physical properties of the investigated blends

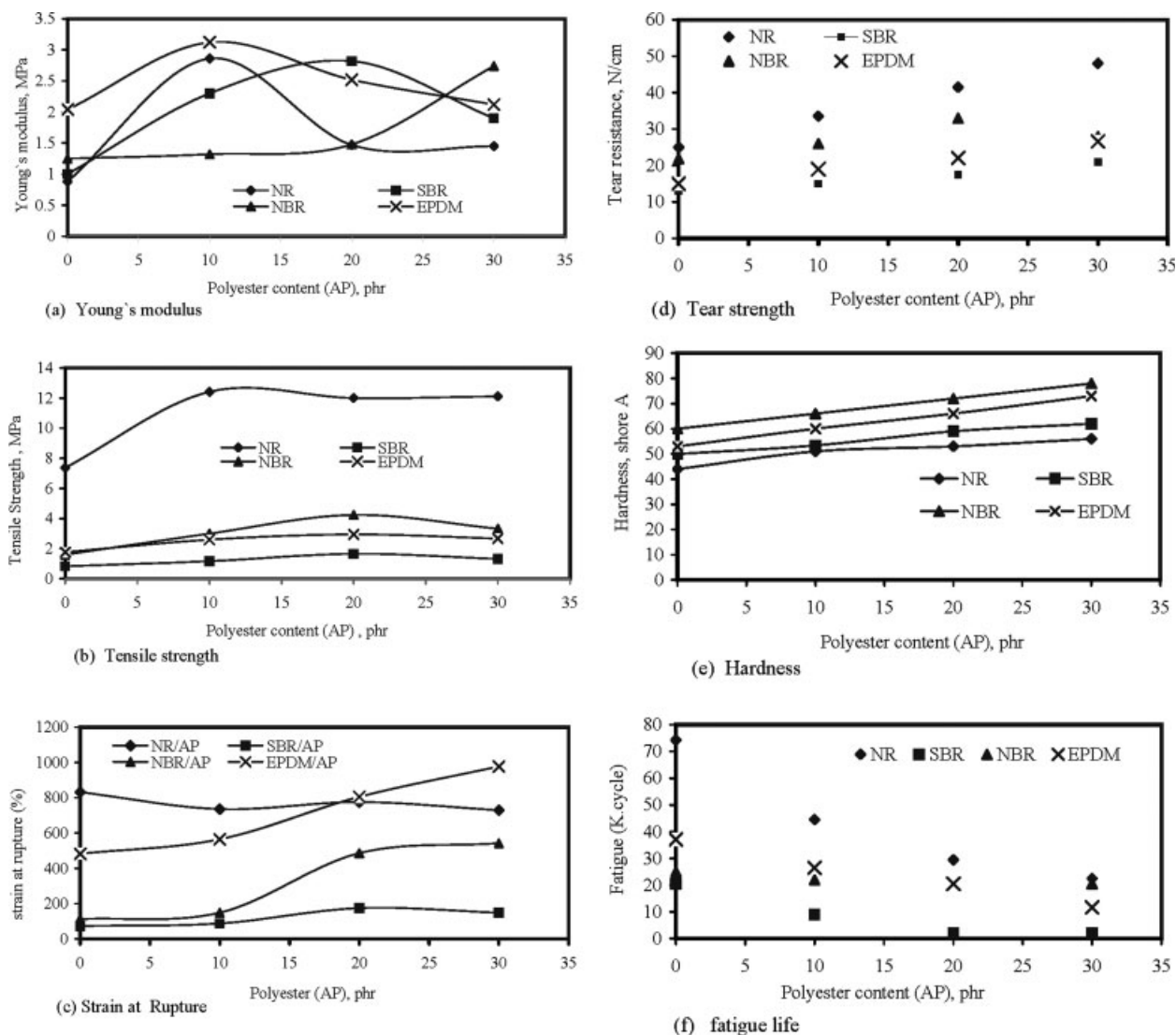
This section reveals to study the physicomechanical properties of natural and some synthetic rubbers such as SBR, NBR, and EPDM blended with the prepared aromatic polyester (AP). The ratios of rubber/AP blends are (100/0, 90/10, 80/20, and 70/30). NR, SBR, and EPDM are non polar types, whereas NBR is a polar one. The physicomechanical properties of

the investigated blends were determined at room temperature ( $25 \pm 2$ ) $^\circ\text{C}$  and at atmospheric pressure. The data obtain are illustrated in Tables II–V and represented in Figure 3. The Young's modulus curve for the different blends is given in Figure 3(a). The presence of 10 phr AP improves the Young's modulus of the NR/AP blends by 223% while at 30 phr the improvement reaches 65% only.

Similar trend was observed when SBR is blended with different content of AP where the values of the improvement of Young's modulus were 130, 182, and 90%, respectively, for the three loadings of AP (10–30 phr). For the blend of NBR/AP, containing 30 phr of AP, the Young's modulus recorded 119% according to high polarity of NBR, while EPDM blend shows about 4% only at the same AP content. The interaction between rubber and AP plays an important role in the improvement of modulus, due to the difference in plasticity of AP and different types of rubber.<sup>24</sup> Figure 3(b) shows the tensile strength of the chosen blends with various contents of AP. It is clear that, the tensile strength increased with increasing AP content for 10 and 20 phr in the blends NBR/AP, SBR/AP and EPDM/AP. The higher concentration of AP (30 phr) results in lowering the tensile strength values, but still higher than, the value obtained for rubber formulation alone (without AP). The (NR/AP) blends has different pattern of behavior [(Fig. 3(b)], where the tensile strength value obtained in case of 10 phr AP is significantly high compared to that of NR alone, this is due to the formation of large aggregates resulting from interpenetrating polymers networks. Also, the presence of maleic acid in the backbone of AP induce some double

TABLE V  
Some Physicomechanical Characteristics of Ethylene-Propylene-Diene Monomer Rubber/Aromatic Polyester (EPDM/AP) Blends

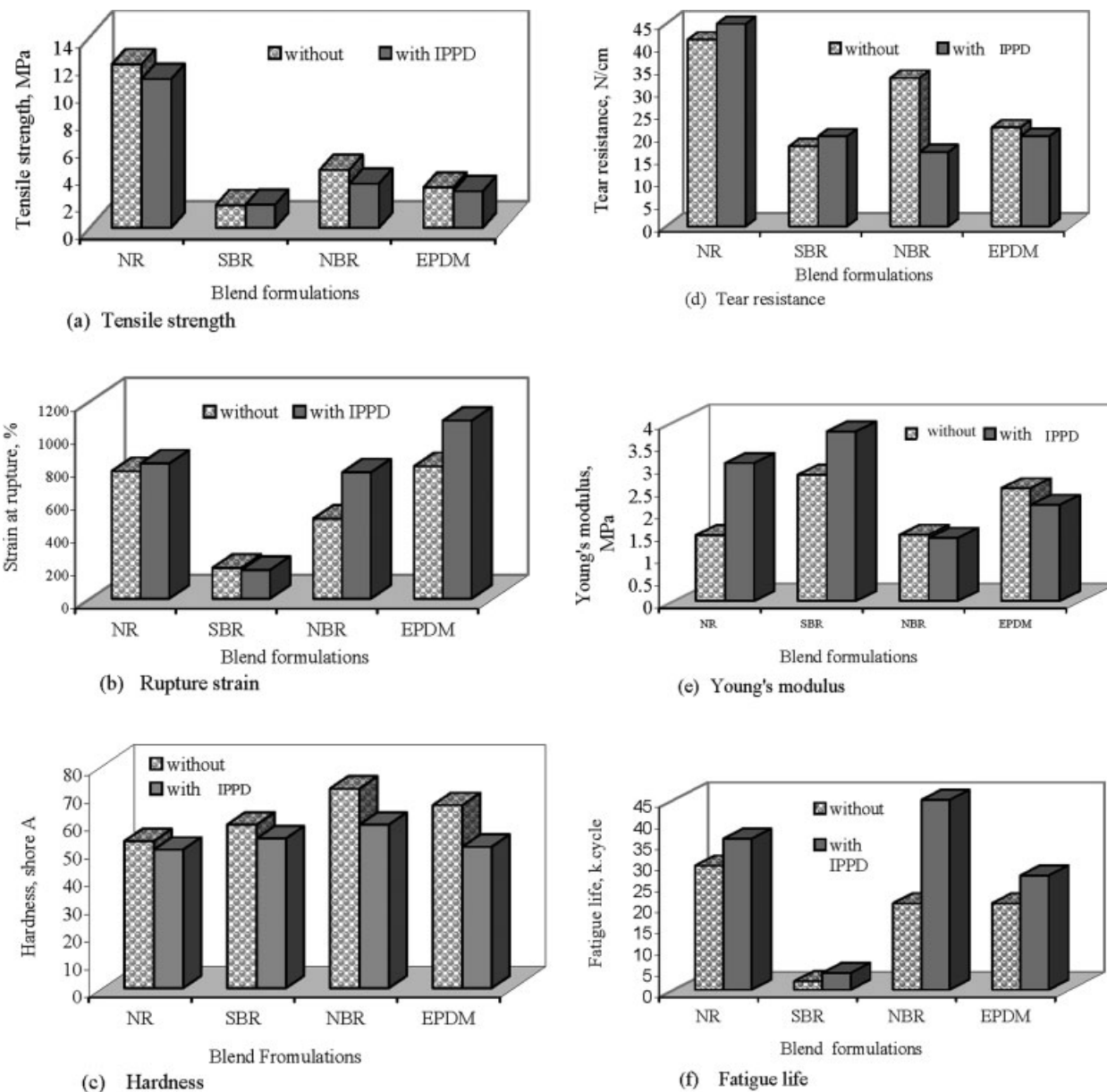
EPDM	100	90	80	70	80
AP	–	10	20	20	30
IPPD	–	–	–	1	–
Peroxide (DCP)	3	3	3	3	3
Permanent set, %	30	31.6	30	34	32.5
Equilibrium swelling, in toluene %	622	436	481	668	471
Equilibrium swelling, in motor oil %	26	47.9	97	102.8	187.6



**Figure 3** Mechanical properties of the blends as a function of different ratios of AP with NR, SBR, NBR and EPDM. (a) Young's modulus, (b) Tensile strength, (c) Rupture strain, (d) Tear strength, (e) Hardness, (f) Fatigue life.

bonds in the blend, and the presence of DCP (peroxide) these double bonds can help to construct crosslinks between the two phases (AP and rubber). The tensile strength remains nearly constant for the blends containing 20 and 30 phr AP. Therefore, the AP with different ratios in the blends of natural and synthetic rubber plays an important role in enhancing the tensile strength characters even at the addition 30 phr of AP. The strain at rupture (%) curve (3c) showed an improvement for EPDM blend containing 30 phr AP reaches 102%, while for NBR blend the improvement records  $\sim 385\%$ . The SBR blend exhibits a similar pattern for improvement nearly reaches 105%. The NR blend shows different behavior, where the strain at rupture decreases with increasing AP content, because NR tends to crystallize on stretching.

Figure 3(d,e) illustrate the variations in tear and hardness strength versus AP content for the different blends. Tear strength and hardness increases with increasing AP content for all blend types, due to the rigidity of AP,<sup>25</sup> as well as the unsaturation sites of polyester which can react with some double bonds of rubber in the presence of DCP and consequently increasing the degree of crosslinking.<sup>26</sup> The tear strength of NBR blended with 30 phr AP shows insignificant decrease. Permanent set (*P*) values, showed in Tables II–V, also exhibit similar trend, and observe an increase with increasing AP content for all blend types. Fatigue life (as number of cycles) for various rubber blends with different AP contents is represented in Figure 3(f). It is clear that, lowering the fatigue life by increasing AP content for all types of blends can be attributed to the hard nature of AP.



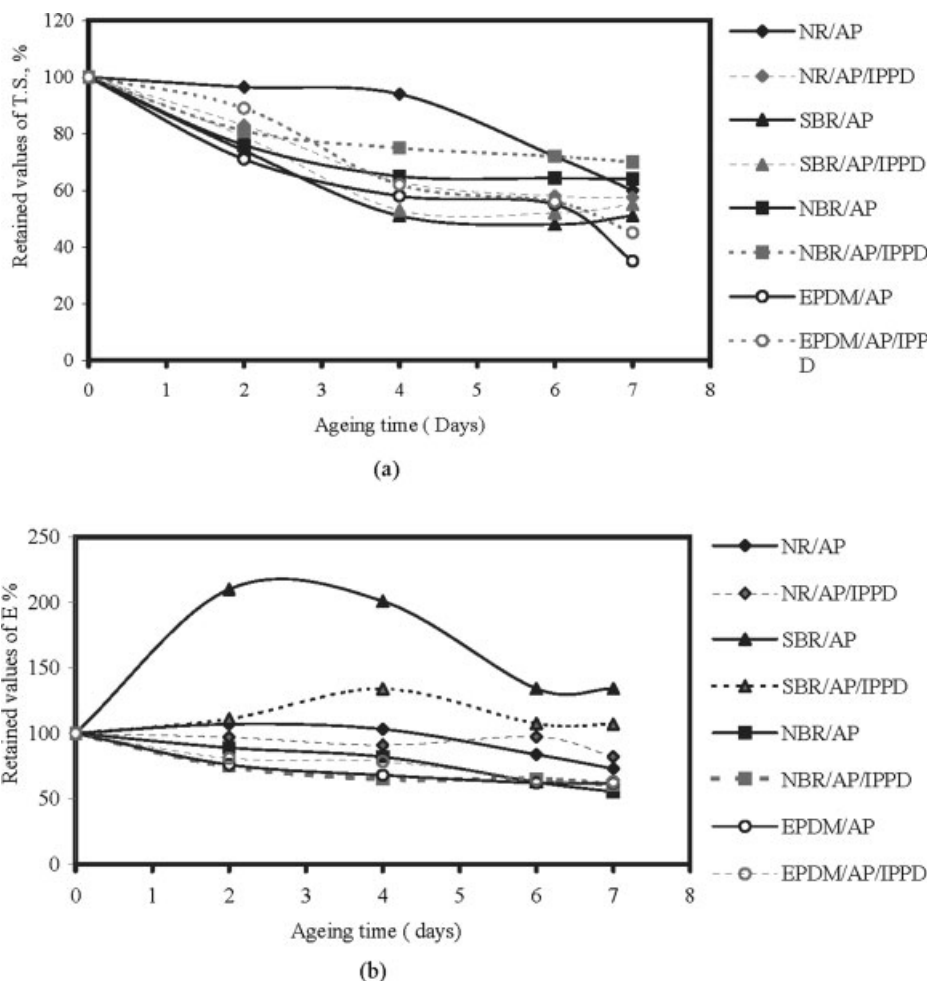
**Figure 4** The mechanical properties of the blends as a function of IPPD. (a) Tensile strength, (b) Rupture strain, (c) Hardness, (d) Tear strength, (e) Young's modulus, (f) Fatigue life.

The NBR/AP blend shows lower decrease in the fatigue life values.

The equilibrium swelling (%) in toluene for all blends are represented in Tables II–V. The presence of 10 phr AP decreases the equilibrium swelling of SBR. Further increasing of AP content (20 and 30 phr) results in increasing the equilibrium swelling of SBR in toluene which can be attributed to the polar nature of AP, while it remains nearly constant for NBR blends and this may be attributed to the polarity of both NBR and AP and their different solubilities in toluene. The degree of equilibrium swelling for rubber vulcanizates depends on the flexibility and mobility of the network structure, relatively

high flexibility polymer network tends to swell more.<sup>27</sup> Swelling of NR has been influenced by various factors, e.g., crosslink type, density, type of elastomers, amount, and type of filler.<sup>28</sup> NR/AP and EPDM/AP blends have the same trend of equilibrium swelling in toluene. The addition of 10 phr AP improves equilibrium swelling of the blends. The same effect exists for the other ratios of AP. Therefore, the presence of AP help in improving the resistance of the blends NR/AP and EPDM/AP to the solvent (toluene) through uniform distribution and dispersion of the solvent in the rubber matrix.

The oil resistance is an important property for rubber/AP blends which are exposed to oil during



**Figure 5** Retained values of (a) tensile strength and (b) elongation at break versus ageing time of rubber/AP blends in presence and without IPPD.

service. The prepared vulcanizates were immersed in motor oil at room temperature for 70 h. The results obtained are shown in Tables II–V. It is clear that, from the data of the blend swelling in motor oil that it decreases as the polyester content increases.

#### Evaluation the effect of IPPD antioxidant in the properties of the investigated blends

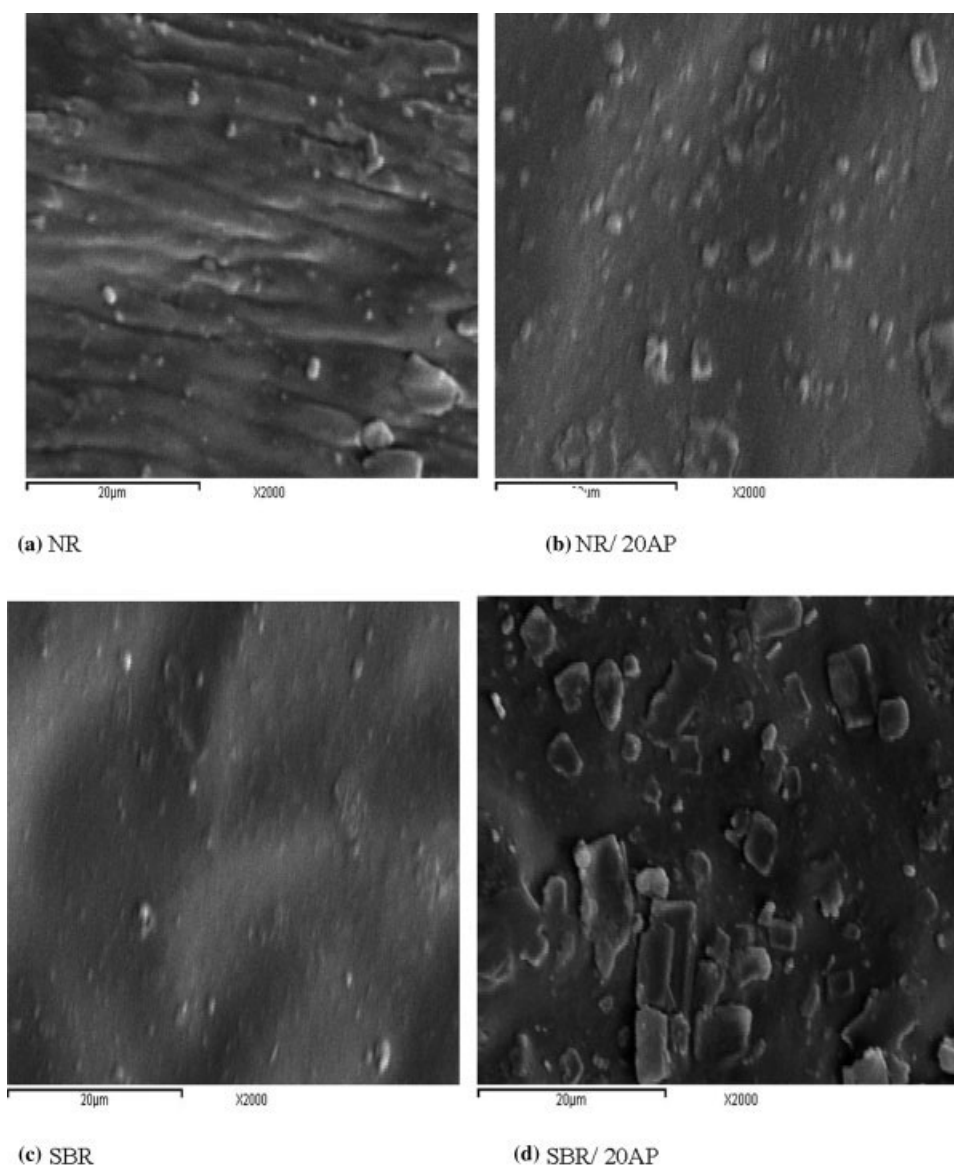
Studying the effect of the addition of IPPD is very interesting, as the addition of an antioxidant for rubber affects the properties of the final products. The chosen formulation for this study is rubber/AP blend (80/20). One phr of IPPD is added during mixing process and the physicochemical properties of the blends were measured. The data is represented in Figure 4 and Tables II–V which illustrated that, the tensile strength and hardness decrease due to the presence of IPPD in all investigated blends. This may be due to the fact that; the presence of IPPD increases the elasticity of the blend resulting from lower degree of crosslinking which is achieved

due to the scavenging effect of the antioxidant (IPPD) against the peroxide. The above results were confirmed by the decrease in permanent set for all investigated blends, and also increase in the equilibrium swelling, Tables II–V. The strain at rupture, fatigue life [Fig. 4(b,f)] increases with the addition of IPPD to the blends. The mechanical shear occur during fatigue process generates macroalkyl radicals, small fraction of them react with oxygen to form alkylperoxy radicals, leaving behind high concentration of macroalkyl radicals scavenging by IPPD.<sup>29</sup> Tear strength and Young's modulus [Fig. 4(d,e)] show improved properties for NR/AP and SBR/AP blends, but deteriorated for NBR/AP and EPDM/AP.

#### Thermal oxidative aging

The 80/20 rubber/AP blends in the presence and absence of IPPD were subjected to thermal oxidative aging. The change of the mechanical properties were



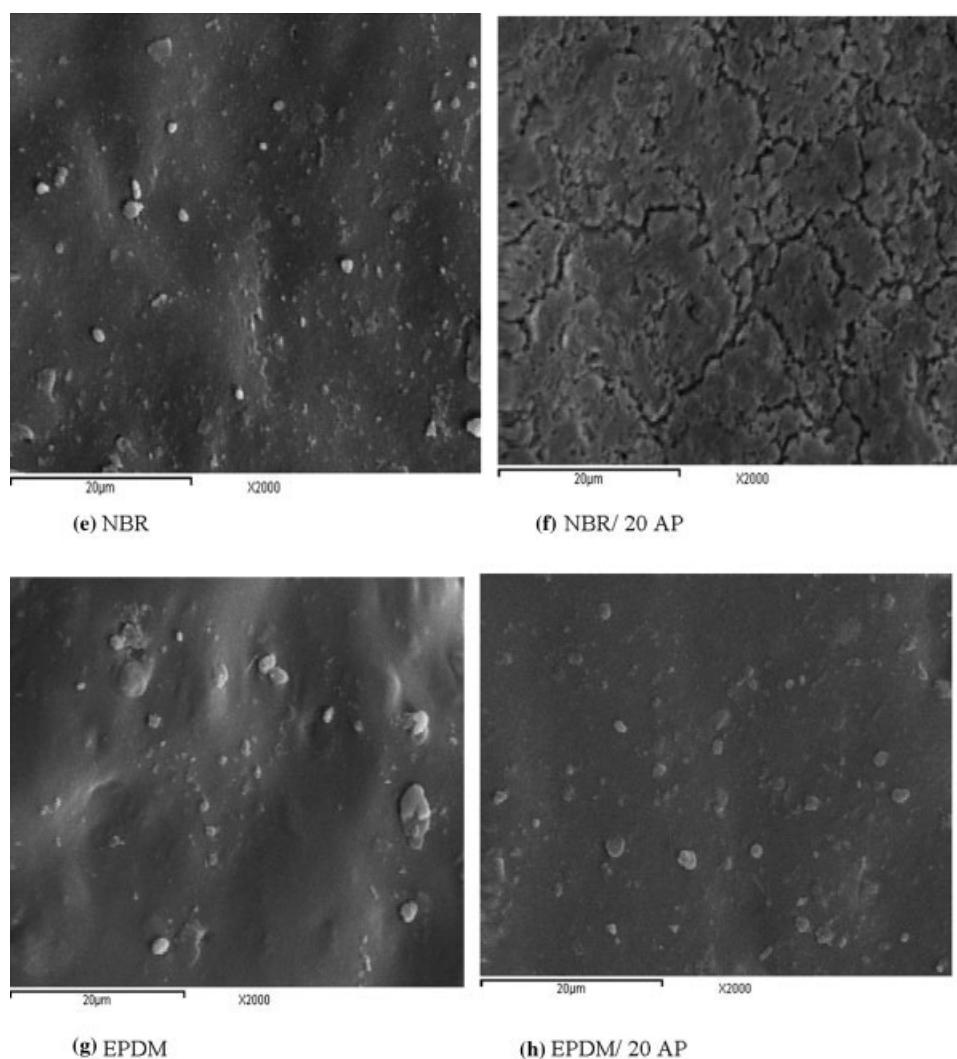


**Figure 6** Scanning electron micrograph of natural rubber and some types of synthetic rubber and their blends with 20 phr AP.

monitored as a function of various aging time and the percentage of retained values were calculated and plotted against aging time as illustrated in Figure 5(a,b). The retained tensile strength indicate that, the NBR, SBR and EPDM blended with AP in the presence of IPPD can tolerate thermal oxidative aging more than NR/AP/IPPD. On the other hand, adding IPPD to NBR, SBR and EPDM blended with AP improve the value of retained tensile strength. While excellent retention value of elongation at break was observed for EPDM/AP/IPPD. The presence of IPPD with NBR/AP and SBR/AP decreases the retained value of elongation at break while in case of NR/AP/IPPD the value of E% was improved after 4 days.

### Morphology of the blends

Scanning electron microscope was used to study the morphology of different rubbers and its blends with 20% AP. Figure 6(a) shows the morphology of the 100% NR, no significant etching is apparent and the surface of the micrograph specialized by dark and bright region. From Figure 6(b), it can be deduced that incorporation of 20 phr AP shows good dispersion and distribution of the particles of AP in NR matrix. Figure 6(c) and d show the morphology of 100% SBR and the blend of SBR/20 phr AP. The inspection of Figure 6(d) micrograph indicates two phases with irregular domain size and shape; this means that SBR/AP blend is immiscible, where large



**Figure 6** (Continued from the previous page)

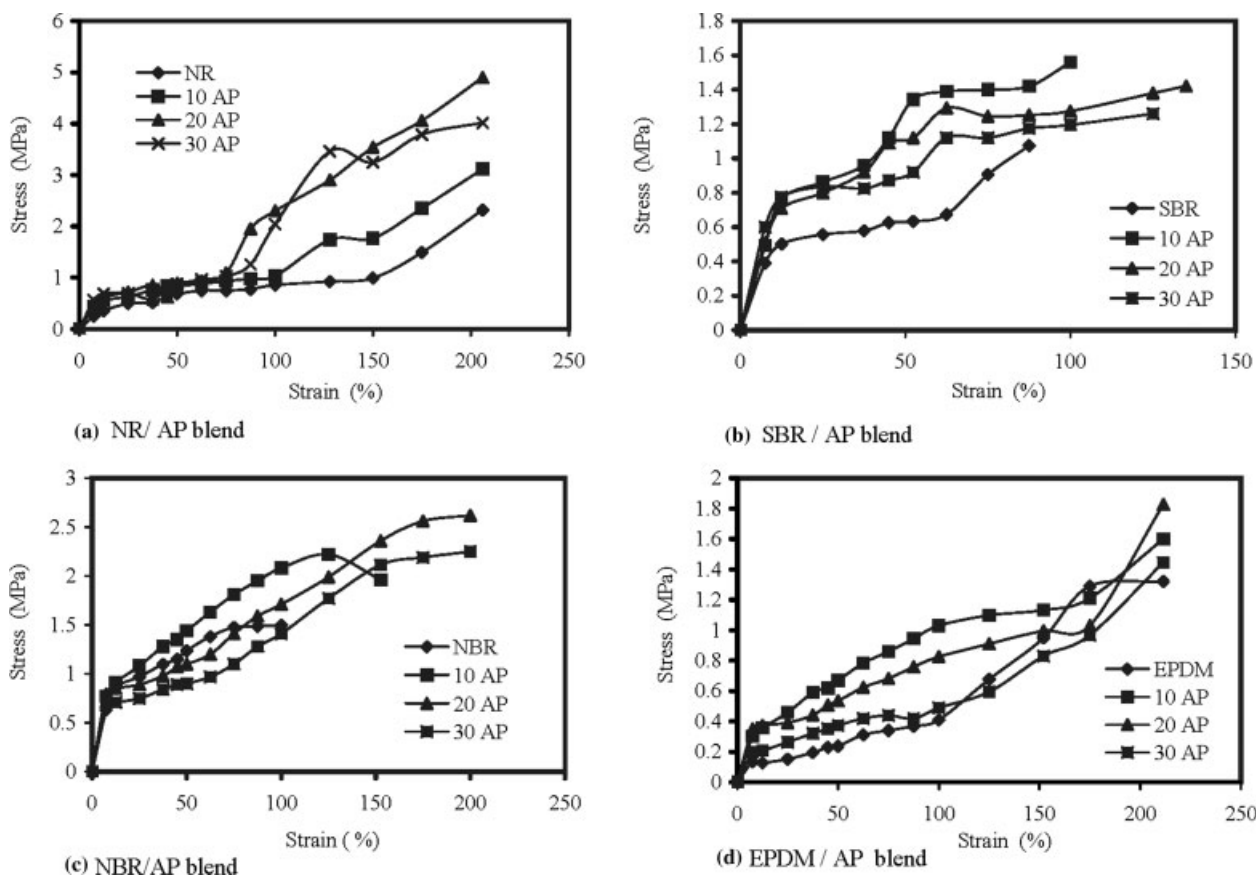
AP domains are dispersed in the SBR matrix. The micrograph of Figure 6(e) showed that, dispersion of the particles encased within the matrix; the particles have irregular shape and vary in size (spheroid in shape but some are elongated). On the other hand, in case of addition of AP to NBR the micrograph exhibits good blending of NBR/AP, where the AP (thermoplastic) particles are dispersed in the continuous phase of rubber component [Fig. 6(f)]. The morphology of EPDM/AP blend shows smooth surface and uniform diameter of dispersed phase. As a result of uniformly dispersed domains obtained due to the reduced interfacial energy between the two phases [Fig. 6(g,h)].

#### Evaluation of Mooney-Rivlin plots of the investigated blends

The behavior of blends and vulcanizates at large deformations can be conveniently described by the

Mooney-Rivlin equation. Each of its curves shows a linear relation over a range from low to moderate extensions, a true Mooney-Rivlin material gives a straight line. The straight line obtained by fitting the experimented points with a least-squares analysis that can be extrapolated to infinite deformation ( $\lambda^{-1} = 0$ ) and the value of the reduced stress is then  $\approx 2C_1$ , i.e., phantom limit. In a similar manner, extrapolation to zero deformation ( $\lambda^{-1} = 1$ ) leads to  $2(C_1 + C_2)$  which is not far from the modulus recorded by measurements at small deformations, i.e., the affine limit. The constant  $2C_2$  is the slope of the straight line obtained,<sup>30</sup>  $C_2$  reflects the concentration of physical properties and also the unstable crosslinks<sup>30</sup> (such as entanglements, filler/filler, and filler/polymer interaction).

One of the key properties of thermoplastic elastomers is their stress-strain behavior, which also yields the first information on the compatibility of the blends. The stress-strain curves for the blends in the

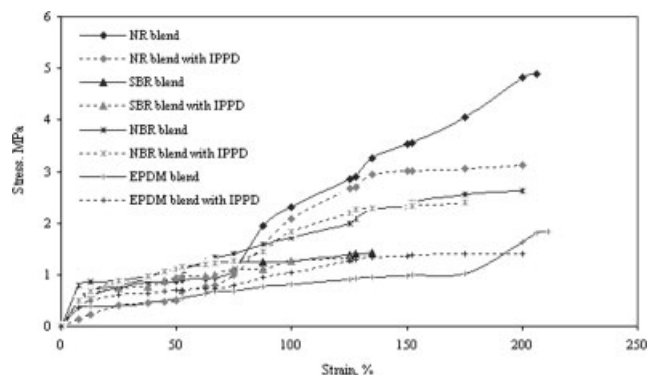


**Figure 7** Stress/strain curves of the different blends (a) NR/AP blend, (b) SBR/AP blend, (c) NBR/AP blend, (d) EPDM/AP blend.

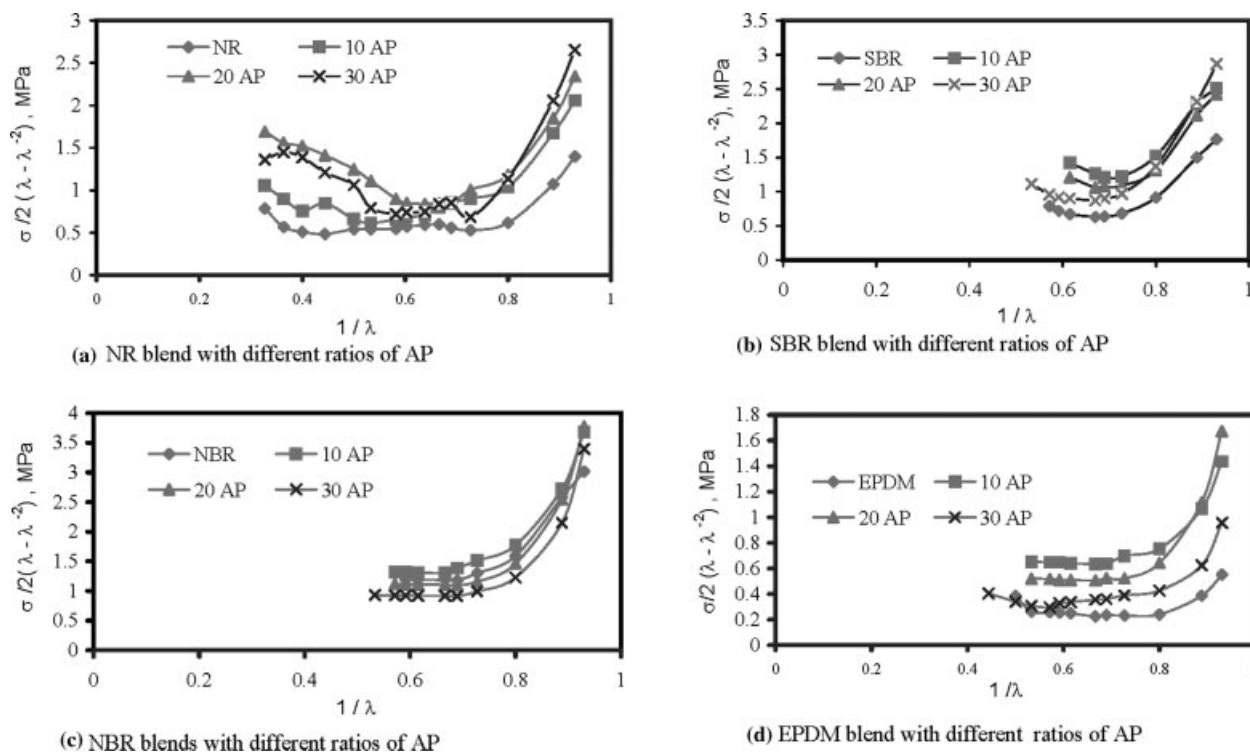
presence of different ratios of AP were represented in Figure 7. The increase in the stress of NR/AP upon adding the second phase (i.e., the addition of AP) may be due to the excellent elastic property imparted by the AP, Figure 7(a). However, there is also improvement in stress generally recorded for all NR/AP blend formulations. Figure 7(b) describes the stress–strain curve of SBR/AP blends and it is clear that for all formulations there is an increase in the strain up to 40%. The SBR/AP with the formulation 90/10 showed strain value up to 100%. Raising the AP content in SBR to 20 and 30 phr accompanied by an increase in the strain more than 100% at the stress 1.3 and 1.4 MPa, respectively, Figure 7(b). The decrease in stress–strain of SBR/AP compared to NR/AP may be attributed to the reduction in the adhesion between the two phases in SBR/AP blends and/or the decrease in the dispersion of the components in each other.<sup>31</sup> The stress–strain curves of NBR/AP and EPDM/AP blends exhibit nearly similar trends and are represented in Figure 7(c,d), respectively. Increasing the AP contents in the rubber matrix is accompanied by an increase in stress–strain values which may reach 200% strain at more than 1.5 MPa stress. However, the structural differ-

ences between the two polymers may prevent or delay the formation of intimate blends.<sup>24</sup>

Figure 8 summarized a comparative study between the formulation 80/20 of NR/AP, SBR/AP, NBR/AP, and EPDM/AP blends that contain one phr IPPD. The data show that, the mechanical properties of EPDM/AP blend in the presence of IPPD are better than the blend properties in its absence.



**Figure 8** Stress–strain curves for 80/20 formulations of NR/AP, SBR/AP, NBR/AP, and EPDM/AP blends in presence and absence of IPPD.



**Figure 9** The Mooney-Rivlin plot for different blends, (a) NR blend with different ratios of AP, (b) SBR blend with different ratios of AP, (c) NBR blend with different ratios of AP, (d) EPDM blend with different ratios of AP.

This improvement may be due to the toughening and stiffening characteristics of the investigated blends. The NBR/AP and SBR/AP blends show more or less similar trend in stress–strain curve, (Fig. 8), where there is no change detected in presence or absence of the IPPD.

Near the equilibrium stress–strain, measurements were carried out for all blend samples according to the Mooney-Rivlin equation<sup>32</sup> and the data obtained were presented in Figure 9. Accordingly the theoretical equation could be as follows:

$$\sigma = 2(C_1 + C_2/\lambda)(\lambda - \lambda^{-2}) \quad (2)$$

where  $\sigma$  is the stress,  $\lambda$  is the extension ratio which is defined as  $(1 + \varepsilon)$  where  $\varepsilon$  is the strain produced by stress  $\sigma$ ,  $C_1$  is a term which expressed departures from ideal elastic behavior,  $C_2$  is the slope of the straight line obtained.

Figure 9 describes the relation between extension ratio  $\lambda^{-1}$  and the “reduced stress”  $\sigma/2(\lambda - \lambda^{-2})$ . The intercept at  $\lambda^{-1} = 1$  gives  $(C_1 + C_2)$ . It is also reported that, the initial shear modulus ( $G$ ) could be related to the equation<sup>31</sup>:

$$G = 2(C_1 + C_2) \quad (3)$$

The  $G$  values for all blend formulations were given in Table VI. When adding AP to rubber, the highest value of  $G$  obtained reflect that this blend

became stiffening (rise in  $G$ ), while the lowest value of  $G$  means that this blend became softening (drop in  $G$ ). Therefore, these observations may be deduced from Figure 7; the blend of NBR with AP has the highest value of  $G/2$  while EPDM/AP has the lowest value. On other word, adding AP to NBR produced blend of shear modulus  $G$  of high cross-linking density, while the value of equilibrium swelling decreased. In case of adding AP to NR the value of  $G$  increases (i.e., the stiffness) and additional crosslinks formed may cause a decrease in equilibrium swelling. Also when adding the polyester (AP) to SBR the values of  $G$  increases and therefore the value of equilibrium swelling and hardness increases consequently.

Comparing the behavior of EPDM/AP and EPDM/AP/IPPD blends led to that, the presence of IPPD decreases the value of  $G$  and consequently crosslinks density decrease and as a result the

**TABLE VI**  
The Initial Shear modulus,  $G$ -Values, Calculated According to Mooney-Rivlin Equation for Various Blends Having Different Formulations

Mix code	100/0	90/10	80/20	80/20 +IPPD	70/30
NR/AP	1.133	1.430	2.166	1.40	2.233
SBR/AP	1.2	1.05	1.35	1.79	1.56
NBR/AP	2.35	2.55	2.30	2.120	2.42
EPDM/AP	0.53	0.58	0.63	0.525	0.78

swelling degree increases. The following features could be stated;

- Unsaturation only occur in the side chain
- Very low unsaturation just sufficient for vulcanization and
- Inherent resistance to swelling (drop in the value of equilibrium swelling before adding AP).

These observations coincide with Subramanian et al.<sup>33</sup>

### CONCLUSIONS

1. The synthesized unsaturated aromatic polyester (AP), based on polyarylate, could be used for the improvement of the properties of rubber (natural and some synthetic ones).
2. The presence of IPPD, as antioxidant, improves fatigue life, tear strength, and Young's modulus for natural rubber and styrene butadiene rubber, while its addition increases the elasticity of all the investigated blends based on shear modulus measurements.
3. In this research and according to various application requirements wide range of formulations of acceptable blends can be applied in different industrial applications.

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