Thermal, UV- and sunlight ageing of thermoplastic elastomeric natural rubber-polyethylene blends

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The ageing of a new family of thermoplastic elastomers from blends of natural rubber and polyethylene was studied using thermal treatments at 65°, 80° and 90°C. The effects of including various stabilizers and dynamic vulcanization were also investigated. The results of UV ageing in a weatherometer and sunlight ageing of the same samples were compared. Thermal ageing of the blends of two polymers caused the tensile properties to deteriorate, especially at longer times or higher temperatures of ageing. The tensile strength and modulus of dynamically vulcanized blends, which registered higher tensile properties, increased in the initial stage on thermal ageing before a final drop. When an antioxidant for rubber or heat or light stabilizer for polyethylene was added, thermooxidative stability was increased. Dynamic mechanical properties also indicated changes due to ageing. UV and sunlight ageing of the samples revealed that the antioxidant for rubber improved the properties. The results are explained in terms of crosslinking, degradation and crystallinity of the blends. No cracking was observed on the surfaces of the aged samples, even under prolonged periods of ageing and on extending the specimens under the microscope.
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1. Introduction

Thermoplastic elastomers present an attractive combination of properties, including ease of processing (by conventional thermoplastics methods), potential for scrap recycling, and the ease of property manipulation through composition change [1, 2]. Rubber-plastic blends form a class of thermoplastic elastomer with potential for many applications in engineering and consumer goods [2]. Initial problems with incompatibility of the rubber and plastic components have been largely overcome [3–5] but further development is required before they can compete as a low cost alternative for products such as automotive window seals, currently produced from ethylene-propylene-diene rubber (EPDM) [6].

A preliminary study of air ageing of natural rubber-polyethylene blends has been described previously [7]. The samples were aged for short times at different temperatures. Changes in tensile properties were mostly correlated to blend compositions including physical and chemical compatibilizers. It was concluded that the compatibilizers help in retention of strength properties. Elliott [8] also reported on the ageing behaviour of some natural rubber–polypropylene thermoplastic elas-

tomeric composites. However, the effect of stabilizers on the ageing of such blends has not been reported previously. As rubber and plastics are generally stabilized with different types of additives and these thermoplastic elastomeric compositions consist of continuous plastics matrix and dispersed rubber domains, it is worthwhile to investigate which type of antioxidant would be most efficient in protecting these materials. Also, it is interesting to understand the behaviour of these elastomers over long time ageing in actual atmosphere and simulated conditions, in addition to the elevated temperature performance in laboratory trials. Furthermore little attention has been paid to the role of morphology in determining the durability of these materials. The current paper describes a much more comprehensive study which includes an investigation of the effect of the presence of stabilizers and some morphological studies using X-ray diffraction and electron microscopy that assist the interpretation of the observed behaviour of the blends. Dynamic mechanical measurements have been used to complement the morphological studies. This work has been conducted on a family of compounds that has also been used in companion studies of photodegradation [9, 10].

2. Experimental
2.1. Materials and blend preparation
Natural rubber (NR) was supplied by Rubber Board, Kottayam, India. This had molecular mass 780×10^3, intrinsic viscosity (benzene 30°C m^3/kg $[\eta] = 0.44$) and Wallace Plasticity = 59.0. The polyethylene (PE) was Indothene 16 MA 400, supplied by IPCL, Baroda, India, and had Melt Flow Index (MFI) 40 g/10 min.. Some materials were prepared without any crosslinking system; others were crosslinked using either dicumyl peroxide or a vulcanisation system based on sulphur (Table I). Dicumyl peroxide (DCP) was supplied by Hercules Inc., Wilmington, DE, USA. Compounds based on the homopolymers but containing DCP (NR/DCP and PE/DCP) were prepared to compare the effect of DCP on the individual components of the blends. The stabilizers selected for investigation were:

(a) IPPD: Isopropyl paraphenylene diamine, an anti-degradant for rubber, supplied by Polyolefin (India) Ltd., Mumbai.

(b) IRG: Irganox 1010 (Ciba Specialty Chemicals), a high molecular weight phenolic anti-oxidant (1178 g mol^{-1}) recommended for use as a thermal (processing) stabilizer.

(c) TIN: Tinuvin 783 (Ciba Specialty Chemicals), a blend of two high molecular weight hindered amine stabilizers (Chimassorb 944, 2000–3100 g mol^{-1} and Tinuvin 622, 3100–4000 g mol^{-1}) recommended for use both as a thermal stabilizer and a light stabilizer.

The blends were prepared in a Brabender Plasticorder by melt mixing the plastic and the rubber at 150°C at 60 rpm using a cam type rotor for about 5–6 minutes. The polyethylene component was melted first and the rubber was then added and blended. The stabilizer was mixed at this stage. The curative (DCP) was added at a level of 1 phr as required and the mixing continued until the torque increased by 3–4 units. The compounds based on the homopolymers but containing DCP (NR/DCP and LDPE/DCP) were also prepared. The hot mass was pressed into a sheet of 3 mm thickness from which test slabs of 2 mm thickness were prepared by compression molding in a hydraulic press at a temperature of 150°C for 3 min. at 5 MPa pressure. The slabs were subsequently cooled under pressure.

2.2. Ageing
Accelerated thermal and thermo-oxidative ageing tests were followed in the present investigation. The air ageing was conducted in an air oven (model FC 712, Blue M Electrical Co.) at various times and temperatures (65°C, 80°C and 95°C). Selection of times and temperatures was done after prolonged trials so that meaningful measurements could be carried out. It is well known that natural rubber without any stabilizer degrades even to a liquid form at higher temperature or longer ageing times. The thermal ageing experiment was performed in a closed oven using the same temperatures and times. The aged samples were allowed to rest at room temperature for 16 h and the physical properties were then measured. The percentage change in physical properties due to ageing was reported.

Rectangular sample sheets of dimensions 120×75 mm were used for ultraviolet radiation (UV) ageing studies. The samples were kept in a Q.U.V. Accelerated Weathering Tester, (Q-Panel Company, Cleveland, USA), according to ASTM G53 procedure, where one side of the samples was exposed to UV. The exposure cycle used was 8 hours UV at 50°C followed by 4 hours water condensation. After exposure and condensation, dumbbell specimens were punched out from the sheets with ASTM die C and tensile properties were evaluated as per ASTM D412. Averages of three such tests are reported here.

For sunlight ageing studies, dumbbell shaped samples (punched out from the sheets with ASTM die C) were exposed to sunlight in a Perspex container for 10, 20, 30 and 40 days respectively. Temperature and humidity conditions during the studies were as follows:

Maximum humidity:	83%
Minimum humidity:	33%
Maximum temperature:	25°C
Minimum temperature:	15°C

After the exposure for a stipulated time period, the tensile properties of the samples were evaluated and the results were compared with the unaged (control) samples. An average of three such tests is reported here.

2.3. X-ray analysis
X-ray diffraction studies were made of the aged samples to follow changes in morphology caused by the elevated temperature treatment. Diffractometer traces were obtained using a Philips X-ray diffractometer (Type PW1710) and contained the prominent (110) and (200) peaks of polyethylene both in the polyethylene homopolymer and in the blends. Crystallinity was

TABLE I Formulation of the mixes

Sample no.	Composition
70NR30PE	NR/LDPE: 70 : 30
60NR40PE	NR/LDPE: 60 : 40
70NR30PE*	NR/LDPE: 70 : 30 + 1 phr DCP
70NR30PE S*	NR/LDPE: 70 : 30 + ZnO, 2.5 phr; Stearic acid, 1 phr, Sulfur, 1 phr; MBT, 0.75 phr; TMTD, 0.1 phr;
70NR30PE/IPPD	NR/LDPE: 70 : 30 + 1 phr IPPD
70NR30PE/IPPD*	NR/LDPE: 70 : 30 + 1 phr IPPD + 1 phr DCP
70NR30PE/IRG	NR/LDPE: 70 : 30 + 1 phr IRGANOX
70NR30PE/IRG*	NR/LDPE: 70 : 30 + 1 phr IRGANOX + 1 phr DCP
70NR30PE/TIN	NR/LDPE: 70 : 30 + 1 phr TINUVIN
70N30PE/TIN*	NR/LDPE: 70 : 30 + 1 phr TINUVIN + 1 phr DCP
70NR30PE/IRG/TIN	NR/LDPE: 70 : 30 + 0.5 phr IRGANOX + 0.5 phr TINUVIN
NR*	NR + 1 phr DCP
PE*	LDPE + 1 phr DCP

NR: Natural Rubber; LDPE: Low Density Polyethylene; DCP: Dicumyl peroxide; IRGANOX 1010 : Antioxidant for PE; IPPD: Antioxidant for NR; TINUVIN 783: UV stabilizer for PE.
*These samples are crosslinked.

estimated by deconvoluting the crystal peaks using ORIGIN^{TM} software and comparing the sum of the areas under the crystal peaks to the total area above the background.

2.4. Mechanical testing

Tensile tests were performed on the unaged and aged samples according to ASTM D412-80 test method using dumb-bell shaped test pieces which were punched out from the molded sheets with BS-E type die. The tests were carried out in a Zwick Universal Testing Machine model 1445 at $25 \pm 2°$C and a crosshead speed of 500 mm/min. The results reported here are averages of three samples. The spread in repeated measurements was $\leq \pm 10\%$.

2.5. Dynamic mechanical analysis

Dynamic mechanical analysis of the blends and the individual polymers were performed on a Rheometrics Scientific MK-II model DMTA in the dual cantilever bending mode. The experiments were carried out at a frequency of 10 Hz at a heating rate of $2°$C/min. and a double displacement amplitude of 64 μm over a temperature range of -100 to $+150°$C. The storage modulus, E', loss modulus, E'', and loss tangent, $\tan \delta$, were measured for each sample in this temperature range.

2.6. Surface morphology of the degraded samples

Surface morphology of the degraded samples was characterized using a Leitz Mettalux-3 Optical Microscope. A scanning electron microscope (SEM) (JEOL JSM5890) was also used for this purpose. The degraded surfaces were sputter coated with gold and SEM photographs were taken within 48 hours of completing the ageing treatment.

3. Results and discussion
3.1. X-ray diffraction

The results of X-ray diffraction and the crystallinity measurement are given in Fig. 1 and Table II. Polyethylene has 41% crystallinity, while natural rubber is amor-
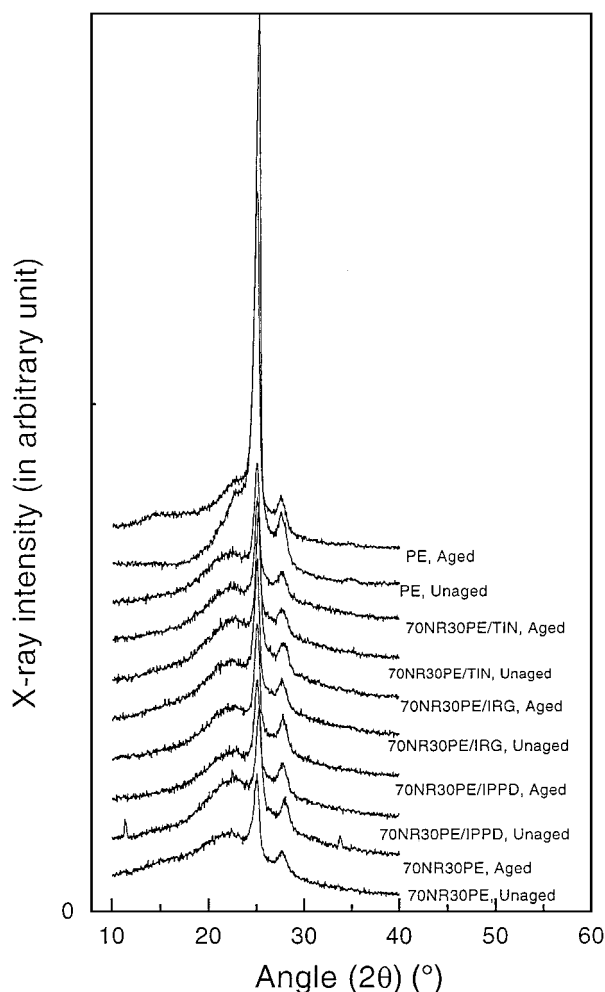

Figure 1 X-ray diffraction patterns of unaged and aged samples.

phous. On ageing of polyethylene, the crystallinity decreased to 34% presumably due to thermal degradation. On incorporating natural rubber into polyethylene, the crystallinity dropped to 11% which equals the value calculated from the PE proportion in a 70NR/30PE blend if the PE component retains the same crystallinity as observed in the homopolymer. The value is marginally increased on incorporation of the additives like IPPD, Tinuvin or Irganox. During ageing, however, the crystallinity of the blend samples changed by no more than $\pm 1\%$, in contrast with the homopolymer, indicating that the crystalline fraction was not affected by ageing in presence of the additives.

3.2. Tensile properties

The effects of ageing on mechanical properties of various thermoplastic elastomers are given in Table III. 70NR30PE thermoplastic elastomer showed a tensile strength of 3.45 MPa and 100%, 200% and 300% modulus of 1.95, 2.45 and 3.00 MPa respectively. On ageing at 65, 80 and 95°C, there was a gradual decrease of tensile strength with increase of temperature, possibly due to degradation of the polymers, which also led to reductions in the 100%, 200% and 300% modulus. After 48 hours ageing at 80°C, a 44% drop in tensile strength and a 25% drop in 200% modulus were observed. Replacement of natural rubber by polyethylene, as in 60NR40PE, resulted in improved thermo-oxidative stability of the blend and loss of properties

TABLE II X-ray data of thermoplastic elastomers before and after air ageing

Sample no. (Miller Indices)	2θ Crystalline peak center, (deg)		Crystallinity, %
	Low (110)	High (200)	
70NR30PE*	24.98	27.74	10
	(25.24)	(28.03)	(11)
70NR30PE/IPPD*	25.04	27.80	13
	(25.05)	(27.84)	(14)
70NR30PE/IRG*	25.00	27.73	12
	(25.13)	(27.89)	(13)
70NR30PE/TIN*	25.00	27.78	13
	(24.96)	(27.71)	(14)
PE*	24.97	27.68	41
	(24.85)	(27.56)	(34)

*All samples were crosslinked with 1 phr DCP. Ageing was carried at 80°C for 48 hours.
The values in the parentheses indicate the results after ageing.

TABLE III Effects of ageing in air on mechanical properties of various thermoplastic elastomers and their individual components

Samples	Temp. (°C)	Time (h)	TS (MPa)	Mod. at 100% (MPa)	Mod. at 200% (MPa)	Mod. at 300% (MPa)	EB%
70NR30PE		0	3.45	1.95	2.45	3.00	380
	80	48	1.95	1.55	1.85	–	207
	95	16	1.90	1.25	1.55	1.75	362
	65	16	3.15	1.35	1.70	2.22	477
60NR40PE		0	5.30	3.40	4.10	4.80	365
	80	48	3.70	3.15	3.50	–	277
	95	16	3.20	2.85	2.85	3.25	321
	65	16	4.90	2.45	2.90	3.50	488
70NR30PE*		0	3.90	2.45	3.75	–	215
	80	48	2.35	1.30	1.85	2.35	301
	95	16	3.25	1.25	1.80	2.35	334
	65	16	4.20	1.90	2.90	4.05	316
70NR30PE/S*		0	16.30	2.20	3.40	4.80	739
	80	48	22.90	3.05	4.40	6.20	770
	95	16	21.30	2.80	4.25	6.00	755
	65	16	22.50	2.55	3.85	5.55	795
70NR30PE/IPPD		0	4.00	1.70	2.30	2.90	444
	80	48	3.85	2.15	2.70	3.15	409
	95	16	3.80	1.50	1.90	2.30	598
	65	16	3.90	1.35	2.50	3.65	505
70NR30PE/IPPD*		0	5.75	2.15	3.35	4.45	393
	80	48	4.15	2.15	2.85	3.65	345
	95	16	5.05	1.90	2.60	3.50	474
	65	16	6.55	2.25	3.35	4.50	486
70NR30PE/IRG		0	3.10	1.70	2.20	2.60	394
	80	16	2.70	1.70	2.10	2.50	368
	80	24	2.70	1.70	2.00	2.40	357
	80	48	2.75	1.75	2.15	2.60	362
	95	16	2.90	1.60	2.00	2.25	436
	65	16	3.50	2.55	2.15	2.60	431
70NR30PE/IRG*		0	4.90	2.25	3.25	4.45	351
	80	16	5.50	2.00	3.00	4.10	421
	80	24	4.85	2.45	3.37	4.75	305
	80	48	5.20	2.15	3.20	4.40	380
	95	16	5.10	2.05	3.05	4.10	382
	65	16	6.00	2.00	3.10	4.20	414
70NR30PE/TIN		0	2.65	1.60	2.00	2.50	344
	80	16	2.50	1.60	1.90	2.10	438
	80	24	1.75	1.25	1.55	–	275
	80	48	2.00	1.25	1.55	1.85	376
	95	16	1.95	1.35	1.65	–	284
	65	16	3.60	1.85	2.35	3.00	401
70NR30PE/TIN*		0	4.40	2.20	3.40	4.35	295
	80	16	3.70	1.90	2.80	3.70	306
	80	24	2.15	1.75	–	–	166
	80	48	3.40	1.90	2.70	–	289
	95	16	3.90	2.20	3.80	–	257
	65	16	4.90	2.70	2.11	–	266
70NR30PE/IRG/TIN		0	2.45	1.50	2.05	2.30	344
	80	16	2.80	1.40	1.70	2.00	561
	80	24	2.05	1.20	1.55	–	358
	80	48	2.40	1.40	1.60	1.90	470
	95	16	1.85	1.35	1.65	–	251
	65	16	3.45	2.00	2.50	–	388
NR*		0	0.65	0.30	0.40	0.50	472
	80	16	1.80	0.20	0.30	0.40	1003
	80	24	0.45	0.10	0.20	0.30	633
	80	48	1.50	0.15	0.25	0.35	1041
	95	16	0.95	0.20	0.30	0.40	820
	65	16	1.90	0.20	0.30	0.40	1073
PE*		0	7.70	7.50	–	–	98
	80	16	11.00	10.60	–	–	167
	80	24	11.15	–	–	–	100
	80	48	11.10	11.30	–	–	111
	95	16	12.05	5.87	–	–	101
	65	16	11.05	11.00	–	–	78

*These samples are crosslinked (please see Table I).

in this compound due to ageing was reduced. The tensile strength fell by about 30% at 80°C for 48 h ageing. When the thermoplastic elastomer was prepared by dynamic vulcanisation with dicumyl peroxide, the strength of the sample was improved due to crosslinking. On ageing at 65°C, there was an increase of tensile strength by 8% over the original value, although the modulus values continuously decreased. Dynamic vulcanization by sulfur and accelerator resulted in significant enhancement of strength and modulus. On ageing, both the tensile strength and modulus increased initially before a final drop. The elongation at break followed a similar trend. The initial increase is due to post-vulcanization reaction during ageing.

When IPPD, an antioxidant for rubber, or Irganox, a stabilizer for polyethylene, was added, thermooxidative stability was increased. During ageing, the fall in properties of these samples was minimal. For example, for the system with IPPD (70NR30PE/IPPD), there was approximately 4% drop in tensile strength on 48 h ageing at 80°C. The modulus increased and

the elongation at break decreased under these conditions. These values are much higher than those of the control samples after ageing. With Irganox, a similar trend was observed, although the initial values were slightly lower and the resistance to degradation was marginally poorer. For example, the tensile strength drop in this case was 11%, as compared to 4% in the case of 70NR30PE/IPPD. The trend in properties of two representative samples and the controls with ageing time is shown in Fig. 2. With a Tinuvin UV stabilizer, the tensile strength and the modulus values fell during 48 h ageing at 80°C. At 65°C ageing for 16 h, slight improvement in properties was observed, possibly due to gelling. With a combination of Irganox and Tinuvin, the tensile strength dropped to 25% at 95°C ageing for 16 h, while the 70NR30PE/IPPD sample displayed about 5% decrease under the same conditions. It is apparent that natural rubber degraded faster and anti-oxidant for natural rubber is required for better thermo-oxidative stability of the thermoplastic elastomers (although natural rubber particles are embedded in and surrounded
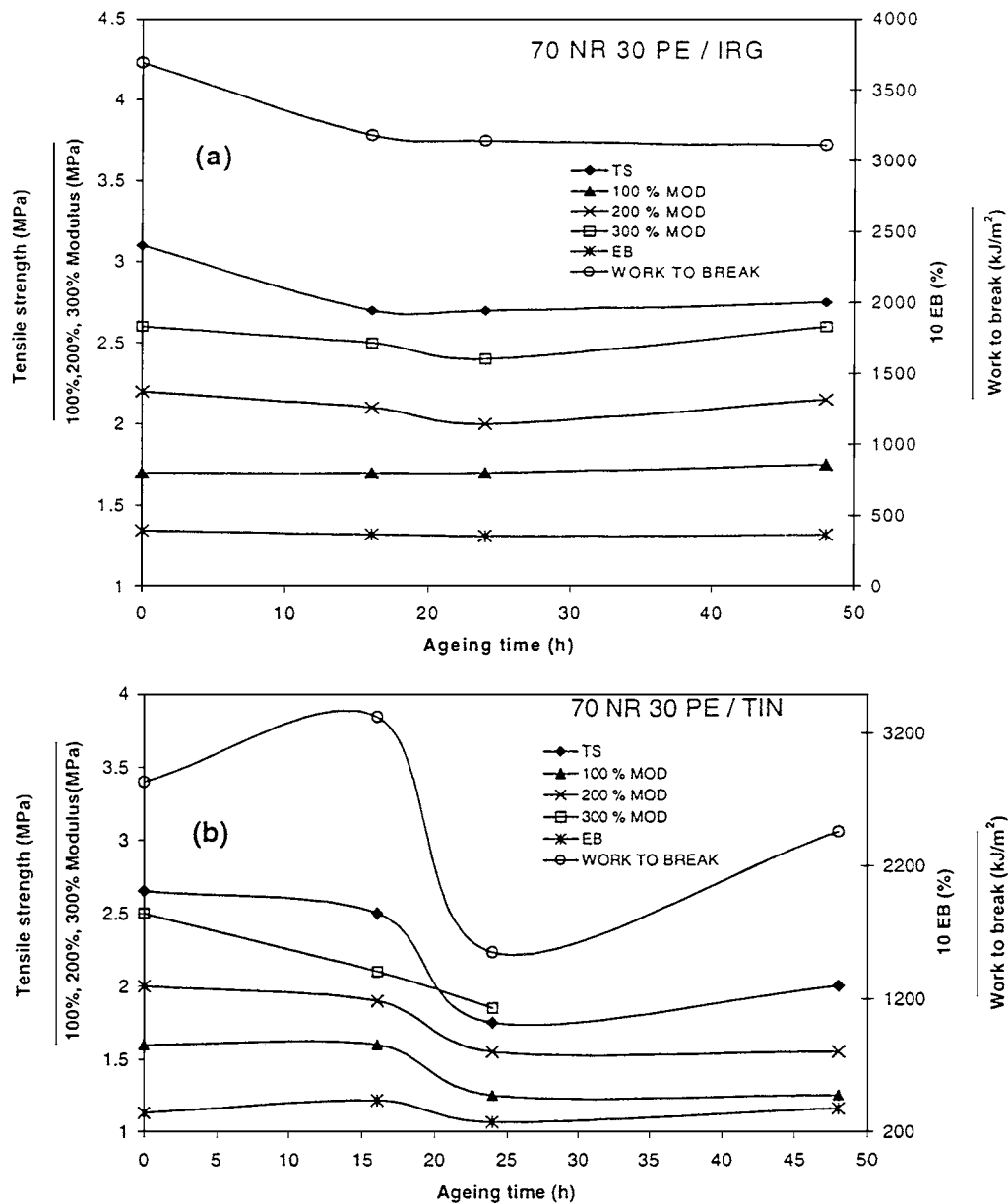

Figure 2 Change in tensile properties with ageing time at 80°C for (a) 70NR30PE/IRG, (b) 70NR30PE/TIN, (c) NR*, (d) PE*. (Continued.)
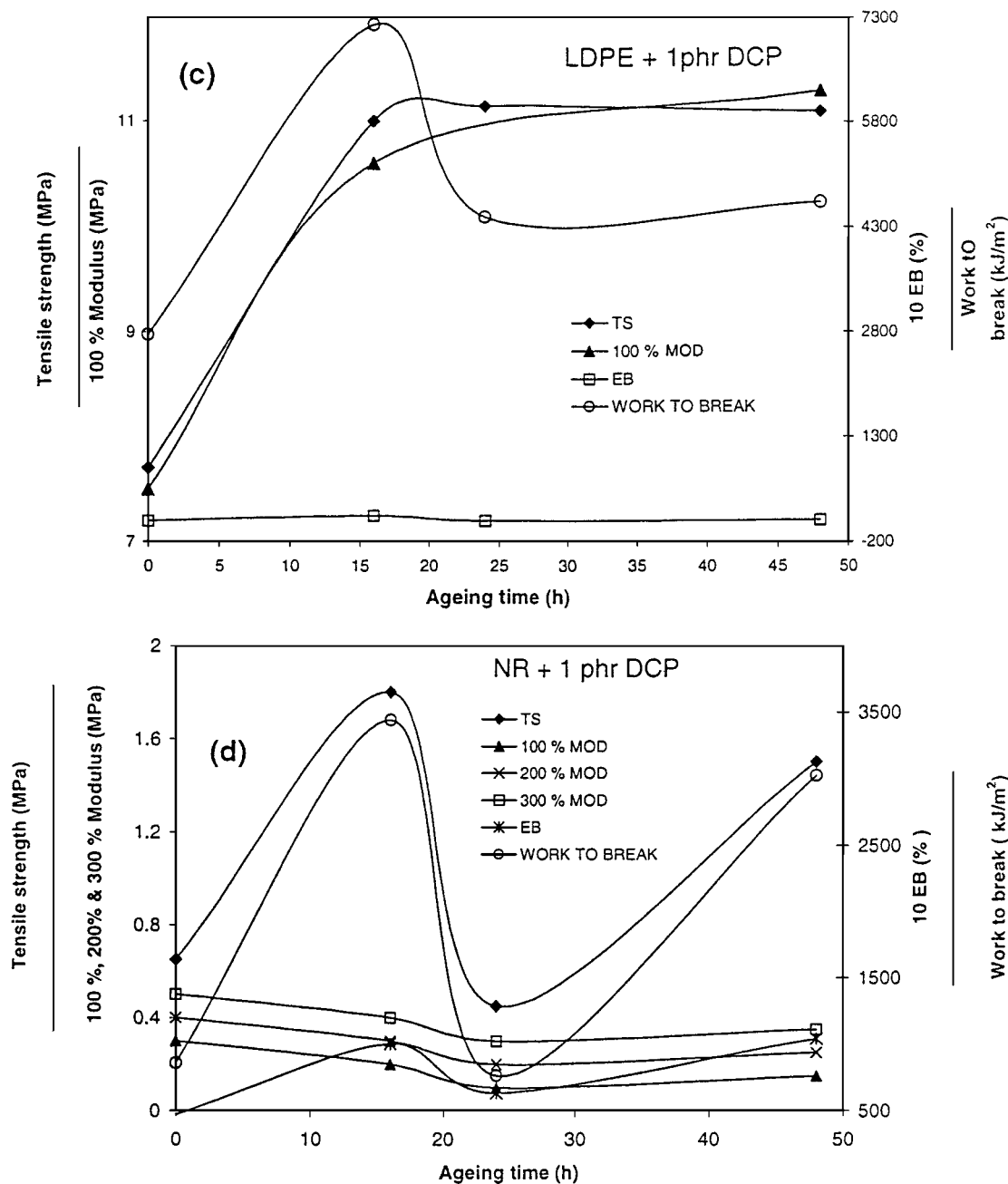
Figure 2 (continued.)

by a continuous matrix of polyethylene). In order to understand these effects more clearly, the individual polymers, i.e., natural rubber and polyethylene were subjected to ageing (Fig. 2 and Table III). It was interesting to note that all the properties of polyethylene improved after 80°C ageing. At 65°C and 95°C ageing also, the tensile strength of PE increased. For natural rubber, there was no systematic variation of tensile strength, although the modulus decreased, which is probably an effect of chain scission due to oxidative degradation.

In order to separate out the effect of oxidation from the thermal ageing, a few samples were thermally aged at different temperatures and times in a sealed oven allowing no air circulation. The results are reported in Table IV. It was observed that thermal ageing was less severe than the oxidative ageing. For example, 70NR30PE sample aged at 95°C for 16 h registered

a drop of 27% in tensile strength under heat ageing, while the drop was 45% under oxidative ageing. The 200% modulus decreased by about 6% under heat ageing and 37% under air ageing. The influence of IPPD on dynamic vulcanization has a similar effect, as described under thermo-oxidative ageing. The presence of oxygen in thermo-oxidative degradation clearly accelerates the degradation, as the temperature gradients, additive evaporation and other factors remain the same.

It has been noted that the samples containing IPPD had higher tensile strength. This phenomenon was not reported earlier for this system. During mixing in the Brabender, natural rubber undergoes degradation lowering its molecular weight. IPPD presumably reduces the breakdown of natural rubber. Higher molecular weight in rubber leads to higher strength.

An explanation for the above results on ageing can be sought using a combination of (i) degradation of

TABLE IV Mechanical properties of the samples during heat ageing

Sample	Temp. (°C)	Ageing time (h)	TS (MPa)	EB (%)	100% modulus (MPa)	200% modulus (MPa)	300% modulus (MPa)
70NR30PE		0	3.45	380	1.95	2.45	3.00
	80	8	3.30	360	2.10	2.60	3.00
	80	16	3.00	368	1.90	2.30	2.80
	80	24	3.10	334	1.95	2.40	2.85
	65	16	3.50	447	1.60	2.00	2.50
	95	16	2.50	274	1.90	2.30	–
60NR40PE		0	5.30	365	3.40	4.10	4.80
	80	8	4.70	359	3.20	3.90	4.40
	80	16	4.80	400	3.10	3.60	4.20
	80	24	4.20	289	3.10	3.65	4.10
	65	16	5.10	475	2.70	3.30	4.00
	95	16	4.00	339	2.80	3.30	3.80
70NR30PE*		0	3.90	215	2.45	3.75	–
	80	8	4.40	280	2.20	3.40	–
	80	16	3.60	276	1.80	2.80	–
	80	24	4.00	216	2.50	3.80	–
	65	16	3.80	308	2.20	3.50	–
	95	16	2.70	229	1.70	2.50	–
70NR30PE/S*		0	16.30	739	2.20	3.40	4.80
	80	8	22.00	785	2.50	3.90	5.50
	80	16	25.20	831	2.90	4.20	5.90
	80	24	22.10	770	2.90	4.20	6.00
	65	16	22.50	767	2.90	4.40	6.30
	95	16	23.50	771	3.00	4.60	6.50
70NR30PE/IPPD		0	4.00	444	1.70	2.30	2.90
	80	8	5.10	568	2.00	2.50	3.10
	80	16	4.40	514	1.70	2.30	2.90
	80	24	4.30	470	1.90	2.40	2.90
	65	16	4.60	542	1.80	2.30	2.90
	95	16	3.60	395	1.90	2.50	3.00
70NR30PE/IPPD*		0	5.75	393	2.15	3.35	4.45
	80	8	5.70	449	2.00	3.00	4.10
	80	16	4.80	426	2.00	3.00	4.10
	80	24	3.90	268	2.30	3.30	–
	65	16	5.30	394	2.10	3.10	4.20
	95	16	5.10	370	2.40	3.40	4.40

*Crosslinked sample (see Table I).

TABLE V E' and tan δ values of various samples

		At T_g		At 25°C	
Sample no.	T_g of rubber	tan δ	Log E'	tan δ	Log E'
70NR30PE	−41°C	0.761	8.804	0.177	7.603
70NR30PE/IRG	−42°C	0.741	8.918	0.169	7.774
70NR30PE/IPPD	−42°C	0.904	9.119	0.179	7.730
70NR30PE, ageing at 80°C for 48 hours	−40°C	0.874	9.011	0.205	7.717
70NR30PE/IRG, ageing at 80°C for 48 hours	−40°C	0.856	9.116	0.169	7.783
70NR30PE/IPPD, ageing at 80°C for 48 hours	−41°C	0.861	9.112	0.180	7.820
70NR30PE, ageing at 80°C for 36 hours	−39°C	0.876	8.977	0.217	7.706
70NR30PE, ageing at 80°C for 72 hours	−40°C	0.884	8.941	0.178	7.700

the rubber and plastics components (and the effect of any additives—a topic which will be explored more fully elsewhere [9]); (ii) chemical and morphological changes during ageing; and (iii) changes in crystallinity in the PE component. From the results given above (Section 3.1) it was apparent that the crystallinity of the PE component in the blends did not change markedly on ageing and explanation (iii) can be disregarded.

Hence, it may be concluded that the observed changes in mechanical properties must be due to either or both of the first two factors ((i) and (ii)) listed above.

3.3. Dynamic mechanical properties

The dynamic mechanical properties of various rubber-plastic compositions with and without additives are shown in Fig. 3 and Table V. The 70NR30PE blend displayed two main transitions in the temperature range −60 to +120°C—one at −41°C and another at 87°C. The first one is due to the glass transition of NR and the second one is due to the α-transition of polyethylene. The β-transition normally observed for pure polyethylene around −50°C is probably merged with the glass transition peak of the natural rubber. The glass transition occurred at a higher temperature than that observed
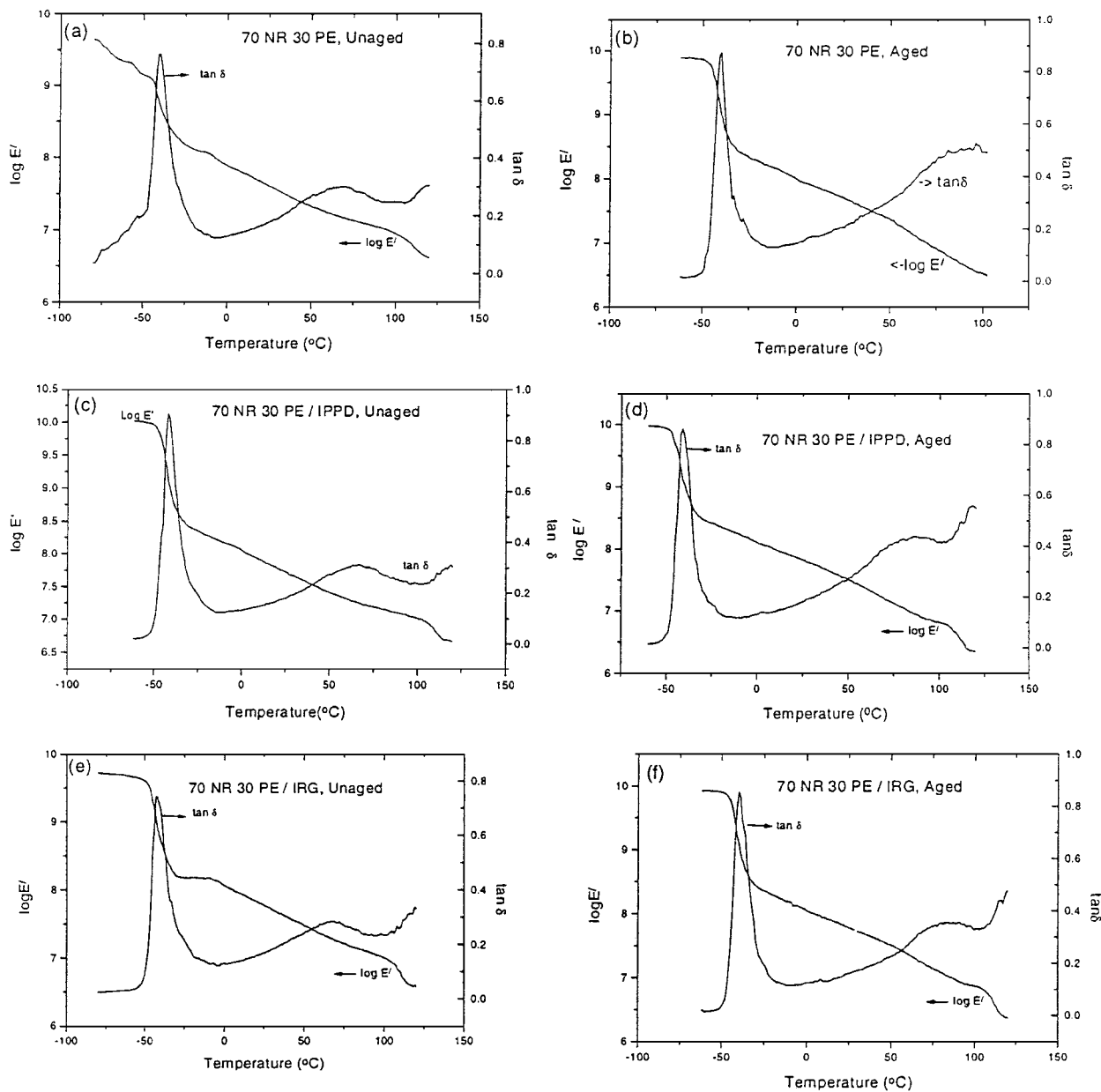
Figure 3 DMTA spectra of unaged and aged blends (a) 70NR30PE unaged, (b) 70NR30PE aged, (c) 70NR30PE/IPPD unaged, (d) 70NR30PE/IPPD aged, (e) 70NR30PE/IRG unaged, (f) 70NR30PE/IRG aged.

for unblended NR. This probably arises from morphological constraints in the system having natural rubber dispersed in the continuous matrix of polyethylene. When the sample was air aged for different times at 80°C, the glass transition temperature of NR, and E' and tan δ at T_g, and E' and tan δ at 25°C were all altered, Table V. For example, after 48 h ageing, tan δ values as well as E' increased. The glass transition temperature increased by 1°C. After still longer ageing times, E' and tan δ at 25°C decreased. As discussed earlier, ageing is accompanied by two processes simultaneously—chain scission and crosslinking induced by joining of the free radicals. In the initial stage of ageing, E' increased due to increase in molecular weight of the system by crosslinking, which is also apparent from the increase in the glass transition temperature. However, simultaneous chain scission releasing small molecules caused an increase in the tan δ value.

When IPPD or Irganox was added to the system, the main transitions were still observed (Fig. 3). The glass

transition temperature of NR for both IPPD and Irganox systems (unaged) were located at -42°C, Table V. While with IPPD, log E' (Pa) at T_g increased from 8.804 to 9.119, the increase was not as much with the blend containing Irganox. The tan δ value also increased for 70NR30PE/IPPD. The results of tan δ at 25°C are comparable, although E' increased with the presence of the additives. On ageing at 80°C for 48 h, the two peaks due to the glass transition of NR and the α-transition of PE were still observed in all the samples. The glass transition temperature was slightly higher due to crosslinking for 70NR30PE/IPPD, similar to that of the control sample. Log E' at T_g did not change, although there was a decrease of tan δ, as compared to the unaged IPPD system. The values of E' and tan δ at 25°C were marginally higher. 70NR30PE/IRG showed higher values of tan δ at T_g, while the values at 25°C were found to be comparable. The results clearly indicate that there is an interplay between chain scission and crosslinking. Compared to the system without

TABLE VI Percent decrease in tensile properties of 70NR30PE* blend with and without IPPD exposed to UV radiation

Duration of exposure (days)	Decrease in tensile strength (%)	Decrease in elongation at break (%)	Decrease in modulus at 300% elongation (%)
10	22.22	0.31	14.30
	(23.60)	(14.40)	(10.72)
20	26.40	2.03	16.81
	(34.83)	(25.72)	(11.00)
30	29.20	7.66	16.52
	(43.82)	(27.30)	(19.30)
40	41.70	21.41	16.81
	(44.94)	(24.15)	(20.64)

Values in the parentheses indicate the results of the sample without IPPD.
*Crosslinked sample (in Table I).

TABLE VII Change in tensile properties of 70NR30PE blend with and without IPPD exposed to sunlight

Duration of exposure (days)	Change in tensile strength (%)	Change in elongation at break (%)	Change in modulus at 300% elongation (%)
10	−6.74	−10.44	+5.63
	(−8.33)	(−5.78)	(+1.74)
20	−24.72	−29.63	+14.74
	(−40.28)	(−20.00)	(−19.13)
30	−26.97	−20.50	−4.55
	(−31.94)	(−18.28)	(−10.14)
40	−30.34	−21.15	−7.77
	(−47.22)	(−31.72)	(−18.26)

Values in the parentheses indicate the results of the sample without IPPD.

additives, the changes in the system with additives are smaller.

3.4. UV and sunlight ageing

The effects of UV ageing in a commercial artificial weathering unit and natural sunlight ageing up to 40 days on the mechanical properties of unprotected and IPPD-protected samples are shown in Table VI. The samples containing IPPD were chosen, as this imparted the best properties to the thermoplastic elastomer under all conditions. It is observed that the tensile strength decreased gradually with time of ageing. The modulus and the elongation at break followed the same trend. After 40 days of UV ageing, there was approximately 45% decrease in tensile strength, while 25% decrease in elongation at break was observed. With IPPD, this reduction in property was much lower. For example, after 30 days ageing the tensile strength and the elon-gation at break decreased by 29% and 8% respectively compared to 44% and 27% respectively for 70NR30PE. The modulus value also was lowered by 17% in the case of the IPPD protected samples. The reason for lowering of the properties is the degradation of the rubber phase, which is less when protected with IPPD.

The sunlight aged samples also show deterioration in properties with time (Table VII). Although the decrease was lower in the first 10 days exposure, the changes in properties were as severe as the UV aged samples at longer ageing time.

3.5. Surface morphology

SEM photographs of the unaged 70NR30PE and 70NR30PE/IPPD are shown in Fig. 4a and b. The natural rubber phase was etched out with toluene. Hence, the dark regions in the photographs correspond to the natural rubber. Finer domains were observed in the samples
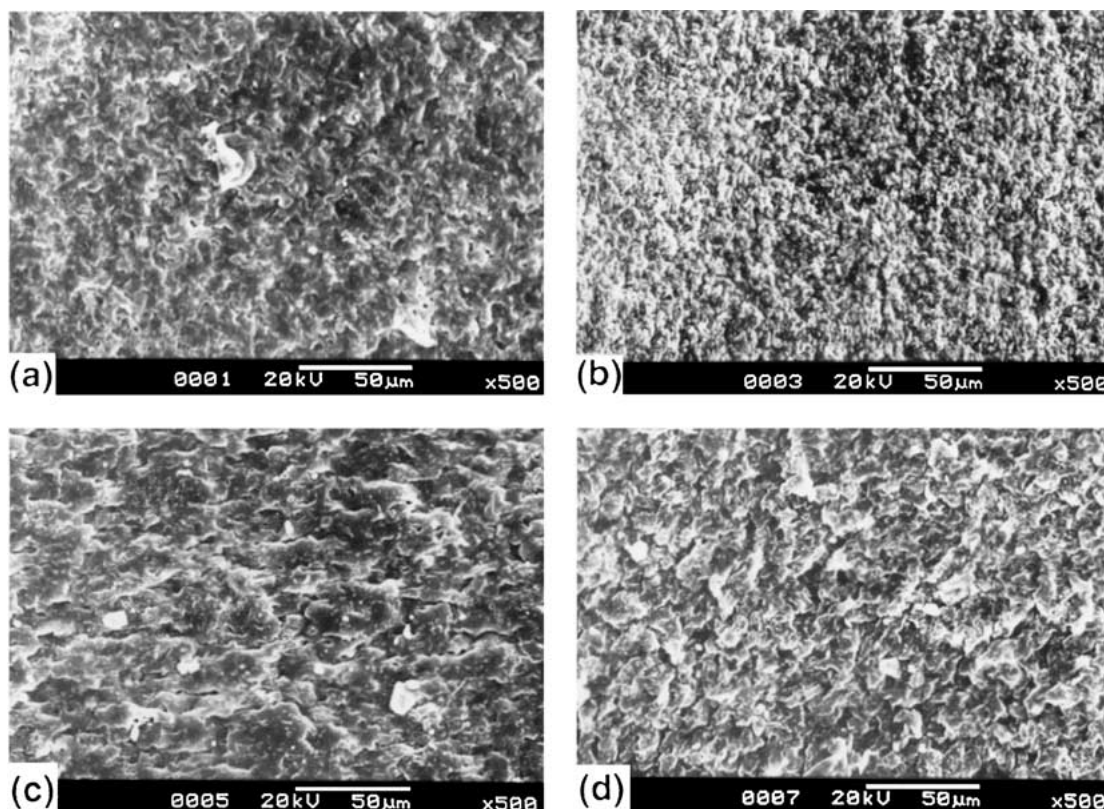

Figure 4 SEM photomicrographs of (a) 70NR30PE unaged, (b) 70NR30PE/IPPD unaged, (c) 70NR30PE oven aged at 80°C for 48 hours, (d) 70NR30PE/IPPD oven aged at 80°C for 48 hours.
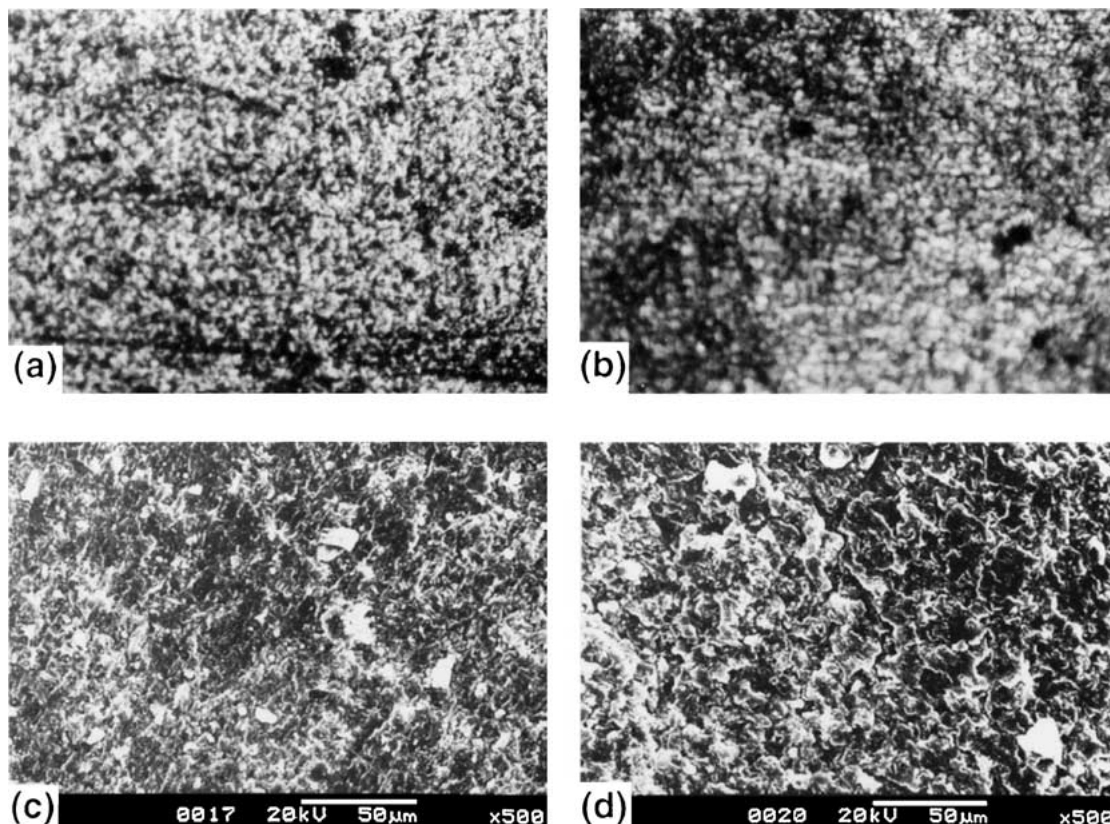
Figure 5 SEM and optical photographs of (a) 70NR30PE UV aged for 40 days and examined under an optical microscope at 20% stretching, (b) 70NR30PE/IPPD UV aged for 40 days and examined at 25% stretching under an optical microscope, (c) 70NR30PE/IPPD UV aged for 20 days, (d) 70NR30PE sunlight aged for 20 days.

containing IPPD. On ageing at 80°C for 48 h in an air oven, the surface morphology changed (Fig. 4c and d). It is apparent that natural rubber domains become larger. A few holes joined transversely were also visible in 70NR30PE, especially at higher ageing time and at high magnification.

Optical micrographs of both the UV aged samples with and without IPPD do not register any cracking, Fig. 5a and b. For example, when 40 days aged 70NR30PE and 70NR30PE/IPPD samples were stretched to 20% or 25% extension, no cracking appeared. Even at high magnification, no cracks were visible (Fig. 5c). It may be noted however, when these samples were photodegraded using fluorescent tube type UVA 340 (Q-Panel Company), severe cracks appeared on extending the test pieces [9]. This simply indicates that the severity of damage is not as high as that when using UVA 340 exposure. The sunlight aged samples did not display an specific feature, as shown in Fig. 5d even under prolonged periods of sunlight ageing and an extension of the test pieces.

4. Conclusions

Thermal, UV- and sunlight ageing behaviour of thermoplastic elastomeric natural rubber–polyethylene blends was investigated. The effects of antioxidant/stabilizer and dynamic vulcanization were also studied.

1. X-ray diffraction measurement indicated marginal change of crystallinity of the blends, although there was 7% drop in crystallinity of polyethylene under similar conditions.

2. On thermal ageing at 65°, 80° and 95°C, there was a decrease of tensile strength and modulus especially after longer times. The tensile strength and modulus of dynamically vulcanized blend increased initially before a final drop. The stabilizers IPPD, Irganox or Tinuvin improved the ageing properties. Thermal oxidation of the same blends was less severe than the thermo-oxidative ageing.

3. Dynamic mechanical properties indicated two main transitions of rubber-plastic blends. When the samples were air aged, the glass transition temperature of NR, E' and tan δ at T_g and at 25°C were altered in most cases. For example, for 70NR30PE/IPPD system, the glass transition temperature of NR was slightly higher and tan δ at T_g was lower.

4. UV- and sunlight ageing caused the properties to deteriorate in both protected and unprotected samples drastically especially after long ageing times.

5. SEM and optical micrographs revealed finer domains in the samples containing IPPD. The surface morphology did not change significantly, as no cracking appeared while the samples subjected to the longest times/highest temperatures of ageing were examined at different extensions under the microscope.

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