Thermomechanical analysis of binary polymer blends

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Thermomechanical analysis by penetration and extension modes, was performed on polyolefin/polystyrene blends (high density polyethylene, low density polyethylene or isotactic polypropylene with atactic polystyrene) and polyolefin/polyolefin mixtures (high density polyethylene or low density polyethylene with isotactic polypropylene). All the measurements were performed on cylindrical specimens obtained directly by extrusion on which extensive mechanical and morphological studies were previously made. It was found that the addition of small quantities of a polymer to a different polymeric matrix tend to modify the thermomechanical behaviour of the whole system. Furthermore the results showed that such an analysis seems to be a suitable tool to get useful information on the thermal and morphological transitions as well as on the interactions between the components in the blends.

Keywords Analysis, thermomechanical behaviour; polymer blends; penetration; extension; polyolefin; polystyrene; morphological transitions

INTRODUCTION

Polymer blends are of the utmost interest because of the possibility of obtaining new materials with improved properties. A systematic study was initiated to elucidate the correlation between processing conditions, morphology and properties on several systems.

The blends made of a glassy component at room temperature (atactic polystyrene) and of a semicrystalline one (low density polyethylene, isotactic polypropylene, high density polyethylene, isotactic polybutene-1, poly-4-methylpentene-1) have been studied extensively[1-3]. Another system consisting of two different polyolefins (high density polyethylene and isotactic polypropylene) has also been investigated[4-6].

Here we report the results of an investigation of the thermomechanical behaviour of some of the binary systems mentioned above.

The thermomechanical analysis seems to be a useful tool to get more information on the thermal transitions and also on the degree of compatibility between the two components of a blend.

EXPERIMENTAL

Homopolymer characterization

The materials used in the present work were atactic polystyrene (PS), from BDH Chemicals; high density polyethylene (HDPE), isotactic polypropylene (PP), and low density polyethylene (LDPE) all provided by RAPRA. The principal molecular properties (number average molecular weight $\bar{M}_n$, weight average molecular weight $\bar{M}_w$, index of polydispersity $\bar{M}_w/\bar{M}_n$ and melt flow index (*MFI*) of such polymers are summarized in *Table 1*. In the case of PS a complete molecular weight distribution curve is reported in *Figure 1*. In addition, in *Table 2* their linear thermal expansion coefficients (α_L) at 20°C are reported[7-8], compared with those of other different materials.

It is possible to note that for rubbery polymers α_L is considerably higher than for glassy polymers, whereas for semicrystalline polymers the higher the crystallinity the lower the thermal expansion coefficient. The values of the linear thermal expansion coefficients, as a function of the temperature for the polymers examined, are reported in *Table 3*[7-9]. All the materials were used as received without further purification.

Blend and specimen preparation

HDPE/PS; LDPE/PS; PP/PS; HDPE/PP and LDPE/PP binary blends were prepared by melt mixing the pelletized components in a laboratory extruder (CSI, max mixing extruder manufactured by Custom Scientific Instruments). For the polyolefin/polystyrene blends the extrusion temperature was 220°C whereas polyolefin/polyolefin blends were processed at 180°C. In such a way cylindrical specimens were obtained. The

Table 1 Characteristics of the polymers used

Polymer code	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n	*MFI* g/10 min
HDPE	8	92	11.6	3.7
LDPE	24.6	215	8.7	0.2
PP	15.6	307	20	3.9
PS	–	100	–	–

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details of the processing conditions and of the apparatus are described in previous papers[1-4]. The blend compositions used in the present work are reported in *Table 4*.

Techniques

A thermomechanical analysis[10-13] by penetration and extension modes, was carried out on specimens having a diameter of 1.5 ± 0.1 mm using a Perkin–Elmer apparatus model TMS-1. The penetration test was performed perpendicular to the axis of the cylindrical specimens, using a wedge-shaped probe selected in order to increase the sensitivity of the method and hence the sharpness of the observed transitions. The probe was loaded with a constant weight (3 g) and the material was heated at a linear rate of 4°C min^{-1}. As the sample expanded the case of a linear variable differential transformer (LVDT) attached to the probe was displaced with respect to its shell. This provided a signal proportional to the probe displacements (expansion, contraction or penetration into the material) monitored as a function of the temperature on a common recording system.

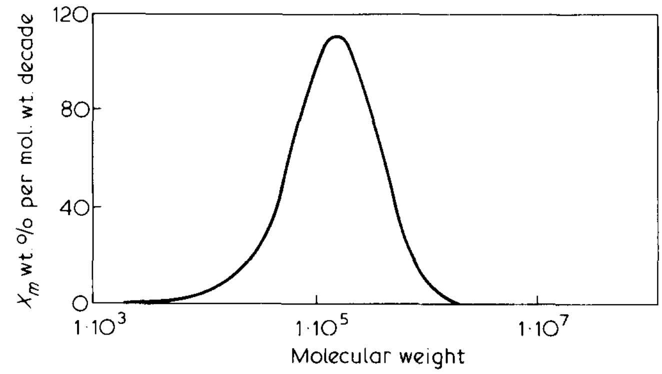

Figure 1 Molecular weight distribution curve for atactic PS used in this work, as provided by BDH Chemical Ltd

Table 2 Coefficients of linear thermal expansion at 20°C*

Material	$\alpha_L \times 10^5$ (°C)
Atactic polystyrene	7
High-density-polyethylene	11–13
Low-density-polyethylene	20–23.7
Isotactic polypropylene	11
Nylon-6,6	9
Nylon-6,6 + 30% glass fibre	3–7 (dependent on orientation)
Polyisoprene unvulcanized	67
Polyisoprene vulcanized	66
Polyisoprene vulcanized + 33% carbon black	53
Neoprene	60

* From refs. 7 and 8

The extension test was performed along the filament axis, using specimens of 1 cm in length, fixed into suitable clamps and subjected to a load of 2 g. The upper clamp remained stationary while the lower clamp was attached to the case of the LVDT. As the specimen was heated, it underwent contractions and/or extensions, causing a displacement of the LVDT and its relative signal was recorded as in a previous penetration test.

The degree of orientation relative to the crystalline regions in the extrudate filaments was qualitatively appraised by X-ray diffraction patterns in the wide angle region (WAXS). The X-ray patterns were recorded photographically by means of a flat camera using a CuKα Ni-filtered radiation.

Birefringence measurements were also performed on the same samples using a polarizing microscope equipped with a Berek compensator in order to estimate eventual structural anisotropy of such materials.

RESULTS AND DISCUSSION

Polyolefin/polystyrene blends

HDPE/PS. The thermomechanical behaviour of samples of HDPE/PS blends, as obtained by extrusion, is

Table 3 Coefficient of linear thermal expansion of the polymers used in the temperature range –53° to 110°C*

Temperature (°C)	HDPE $\alpha_L \times 10^5$ (°C)	LDPE $\alpha_L \times 10^5$ (°C)	PP $\alpha_L \times 10^5$ (°C)	PS $\alpha_L \times 10^5$ (°C)
–53	9.0	–	6.0	–
–35	9.5	10	6.5	–
–20	9.8	13.7	7.0	–
0	10.5	18.3	8.8	–
20	11	23.7	10.5	–
25	12	24.8	12.5	–
40	12.8	29	14	–
60	14.2	37.7	–	7
80	15	40.3	–	–
100	15.8	46.6	–	–
110	–	51.0	–	18

* From refs. 7 and 9

Table 4 Blend compositions

% HDPE	% PS	% LDPE	% PS	% PP	% PS	% LDPE	% PP	% HDPE	% PP
100	–	100	–	100	–	100	–	100	–
95	5	95	5	95	5	90	10	80	20
92.5	7.5	92.5	7.5	90	10	80	20	70	30
90	10	90	10	80	20	70	30	50	50
80	20	80	20	70	30	60	40	40	60
70	30	50	50	60	40	50	50	30	70
60	40	30	70	50	50	40	60	20	80
50	50	20	80	40	60	30	70	–	100
40	60	–	100	30	70	20	80		
30	70			20	80	10	90		
20	80			–	100	–	100		
10	90								
–	100								
(a) HDPE/PS		(b) LDPE/PS		(c) PP/PS		(d) LDPE/PP		(e) HDPE/PP	

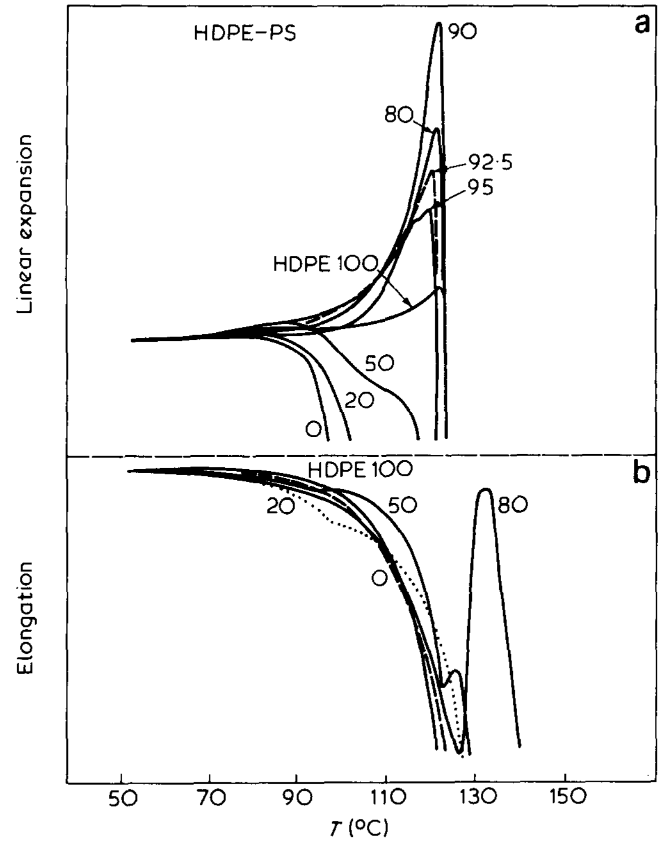

Figure 2 Typical penetration and extension curves of HDPE/PS blends at different compositions. The figures reported on each plot refer to HDPE weight percentage

shown in *Figure 2* where expansion and/or penetration (*Figure 2a*), and elongation and/or contraction (*Figure 2b*) of the specimens are reported as a function of the scanned temperature. The curves of pure PS show a trend almost horizontal at temperatures below its glass transition, T_g, after which a sudden drop, due to the penetration and extension processes, takes place. For blends with high PS content and for specimens containing almost equal proportions of two polymers, the curves (*Figures 2a* and *b*) show, for temperatures lower than the PS T_g, a slight expansion effect due to more rubbery polyolefin contribution (see *Table 2*). Then, for temperatures around the T_g of PS, a shoulder is observed followed by a catastrophic penetration/elongation, due to the melting of the polyethylene. For HDPE, the slope of the curve (*Figure 2a*) increases gradually with rising temperature up to the initial fusion of the polyolefin. A small maximum is reached about ten degrees later, followed by the penetration of the probe. This effect is due to the expansion of first melted regions initially occluded into the overall specimen. The curves of HDPE-rich blends show very high peaks probably due to the strong influence of the PS dispersed particles in the HDPE matrix. In fact at $\sim$90°–100°C the PS occluded domains undergo a sudden volumetric jump due to their T_g, submitting the surrounding material to a high hydrostatic dilation, detected by the LVDT of the apparatus. Such an effect is dependent on composition as shown in *Figure 3* in which the height of the expansion peaks, in arbitrary units, is plotted against the PS percentage. A pronounced maximum is obtained for a composition around 10% of PS. Successively at higher concentrations, the value of the maximum in the expansion curve drops rapidly reaching values close to the pure polyolefin ones. Such a decrease could be due to the fact that with an increase in PS content, the PS domains tend to coalesce, enhancing their size. This yields a higher probability of PS interconnection throughout the material ending on the surface of the specimens. In this way the thermal jump expansion of the PS dispersed particles can be released externally to the sample, which undergoes more easily and slightly earlier to the penetration of the probe.

After melting the HDPE shows only a dilation followed by a creep or flowing of the melt where as the HDPE-righ blends show, in a short temperature range, a sudden shrinkage effect, observable[10] in *Figure 2b*. Since according to X-ray scattering and birefringence measurements all the specimens result to be almost completely isotropic both in the crystalline and amorphous regions, no orientation effect seems to be present in the materials.

Therefore this phenomenon must be tentatively attributed to the influence of the flowing conditions on the morphology of the PS dispersed particles. In fact the PS domains are elongated (as shown in *Figure 4*) along the extrusion direction[3]. Therefore after melting, the released surface tension tends to render them again sphericals, giving a marked contribution to the contraction of the whole sample.

LDPE/PS. Typical thermomechanical curves for LDPE/PS blends are reported in *Figure 5*. For the blends at high PS content (*Figure 5a*) the slopes of the curves show only a slight increase at the beginning with enhancing the temperature and then they drop suddenly. In the corresponding curves of *Figure 5b* the T_g of PS is detected by a sharp change in the slopes before the final elongation.

For LDPE-rich blends the initial slopes are highly enhanced in comparison to that of pure LDPE. This effect, almost absent for HDPE/PS mixtures, can be tentatively attributed to the different molecular structure of LDPE. During the melt extrusion process the low molecular weight fractions of LDPE can be dispersed and partially dissolved in the PS domains, due to the high shear forces and high temperatures acting in the mixing zones of the extruder. At the die outlet the material is quenched in air and rapid crystallization and vetrification

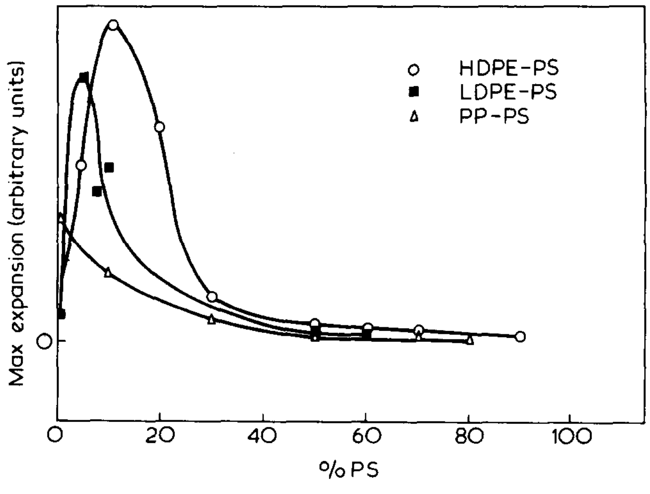

Figure 3 Max. expansion height in arbitrary units as a function of PS percentage for HDPE/PS. LDPE/PS and PP/PS blends

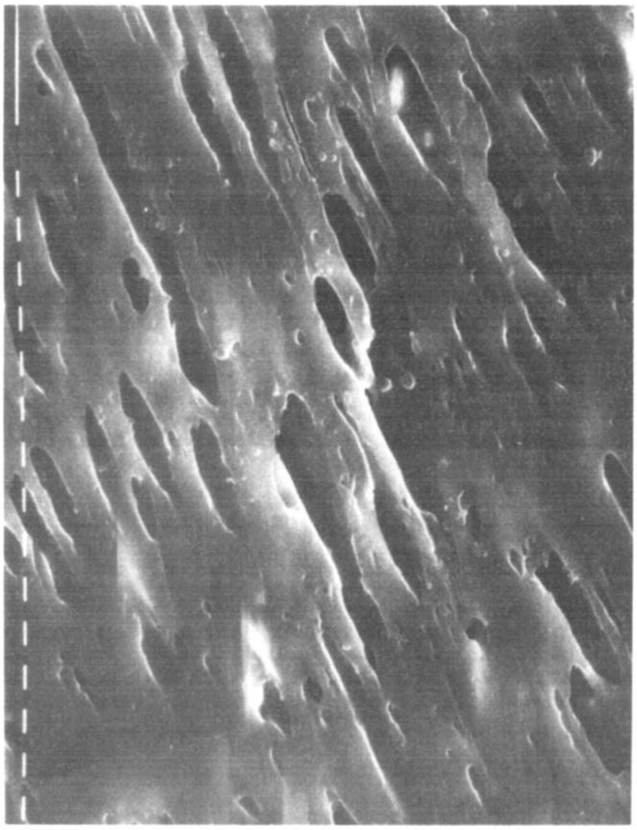

Figure 4 Scanning electron micrograph of a longitudinal section of the HDPE/PS (80/20) blend etched by toluene (magnification = 320X)

will occur. The LDPE fractions trapped in the PS domains lower the T_g of PS. Hence the glass–rubber transition of PS domains is revealed earlier on the temperature scale giving curves with higher slopes than that of the pure LDPE. Such an effect is composition dependent and yields successively beyond T_g and close to the T_m of the polyolefin, a series of maxima, whose height are plotted in *Figure 3*, as a function of PS content. A peak is observed at about 5% of PS, whose interpretation is analogous to that already given in the previous HDPE/PS case.

With respect to the elongation mode the curve for pure LDPE in *Figure 5b*, after an elongation of the specimen due to its thermal expansion and creep, show after melting a sharp shrinkage phenomenon of the whole sample. This can be tentatively attributed to the releasing effect of some forces stored during the filament processing and successively frozen in it. Due to the flow conditions at the die outlet, the end-to-end distances of the polymer chains can increase with regard to their equilibrium melt configuration. Such a situation is frozen in by the successive crystallization of the sample, which creates (together with branching of LDPE) a complex pseudo-crosslinked material.

After melting such entropic elastic forces, mainly oriented along the extrusion direction, will act toward a shrinkage of the specimens. Furthermore for LDPE a slight crystallite orientation was detected by WAXS reinforcing the above mentioned effect.

For LDPE-rich blends a similar behaviour is observed (*Figure 5b*) and here a further contraction effect, due to the morphological transition of the PS domains, elongated along the extrusion direction, can be invoked. Such a phenomenon has been already extensively explained in the case of HDPE/PS mixtures, for which the other two effects are possibly not so effective. Therefore the contraction feature is much more marked for LDPE/PS blends, to the point that the temperature corresponding to the successive catastrophic extension of the sample, easily observable for HDPE/PS mixtures, is here out of scale (note that this temperature is for a LDPE/PP material 150°C, as shown in *Figure 7b*).

But such an effect is not dependent only on weaker or stronger contraction forces but also on the creeping tendency of the material due to its viscosity. The viscosity for branched chains like LDPE ones is higher than for linear macromolecules such as HDPE, PP or PS ones at comparable molecular masses.

This fact provides a further argument explaining the longer delay on the temperature scale of the catastrophic elongation after melting of LDPE with respect to other polymers.

PP/PS. The curves of a thermomechanical analysis for PP/PS blends are drawn in *Figure 6*. Some interesting observations can be made comparing such curves with those of the HDPE/PS and LDPE/PS blends. The samples at high PP content show a more gradual increase in expansion with increasing the temperature. No abrupt change at the T_g of PS and no sharp peak close to the melting point are observed in this case (*Figure 6a*). Similar trend but much more pronounced is also observed for pure PP. As shown in *Figure 3* a plot of the maximum expansion height against composition show for this blend a monotonic decrease.

This different thermomechanical behaviour, can be attributed to some structural differences of the polyolefins.

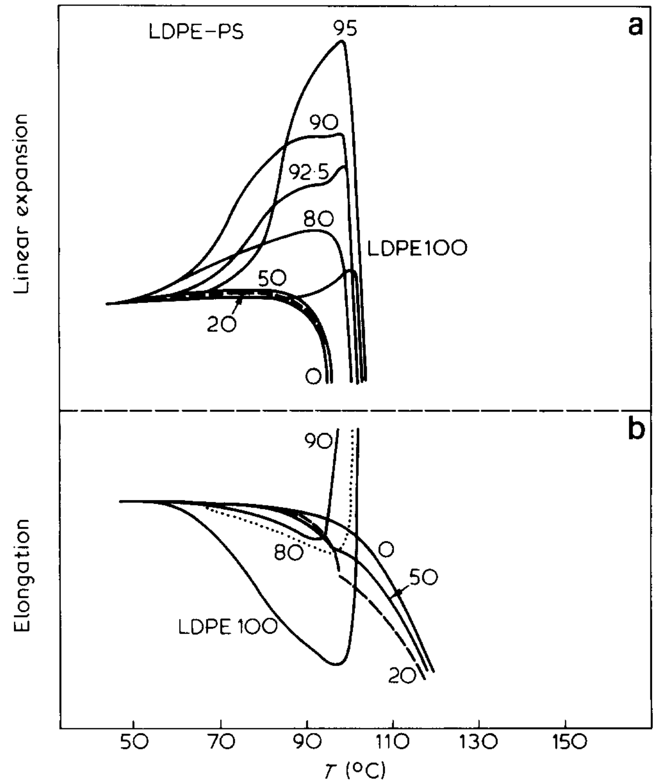

Figure 5 Typical penetration and extension curves of LDPE/PS blends at different compositions. The figures reported on each plot refer to LDPE weight percentage

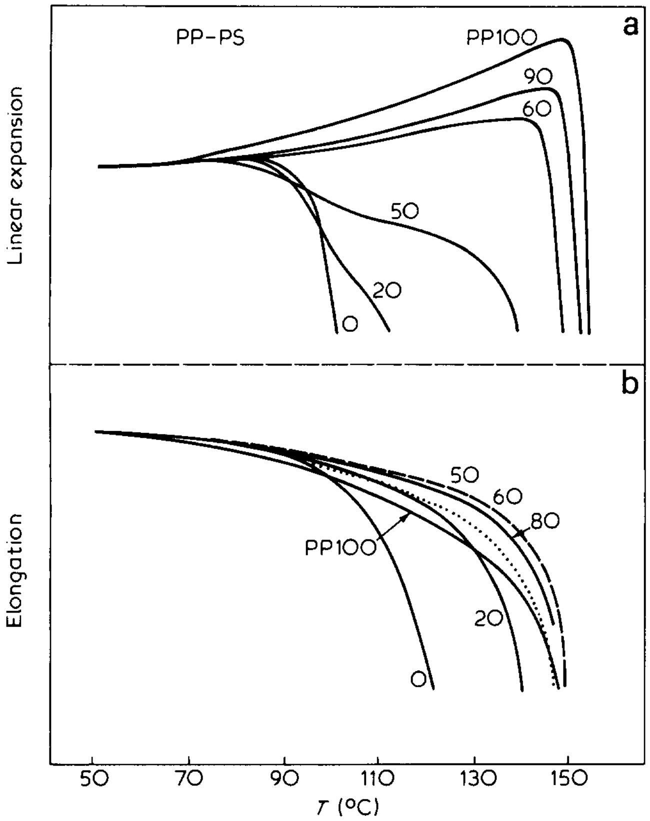

Figure 6 Typical penetration and extension curves of PP/PS blends at different compositions. The figures reported on each plot refer to PP weight percentage

In fact, considering the crystalline polymers as crosslinked materials, the HDPE and LDPE would have a degree of crosslinking higher than PP. The former as a consequence of its higher crystallinity and the latter of the combined effect of crystallinity and branching. Therefore, in the light of these considerations, the samples having PP as matrix are more able to relax the internal stresses caused by the expansion of the PS occluded domains, and consequently no sharp change is present at PS T_g.

Another important observation is the absence in all PP/PS specimens of shrinkage effects during the melting process (*Figure 6b*).

As in the case of HDPE/PS blends no anisotropy behaviour is observed by WAXS and birefringence measurements, therefore no orientation effects are present. Furthermore the PP-rich blends have low melt viscosity and hence the entropic elastic response of the sample after melting is not able to overcome the applied load. As a consequence creep phenomena will prevail over shrinking processes.

Polyolefin/polyolefin blends

Thermomechanical data for LDPE/PP and HDPE/PP blends are reported in *Figures 7* and *8*.

The overall behaviour in penetration mode for the two blends (*Figures 7a* and *8b*) is quite similar. In fact all the samples with polyethylene (LDPE or HDPE) as matrix and PP as dispersed phase expand more than the pure LDPE or HDPE. This feature can be accounted for by a partial mixibility of low molecular weight fractions of PP in the polyethylene matrix, which tend to increase the free volume and hence the linear expansion coefficient of the blends. It can be noted that the PP has a higher polydispersity (see *Table 1*) and a lower 'crosslinking density' than HDPE and LDPE, being less crystalline than HDPE and having no different branching from LDPE. Therefore, large amounts of low molecular weight fractions can be available for such a feature. It is possible to see the above-mentioned expansion effect before the polyethylene melting points occur earlier in the temperature range for LDPE/PP than for HDPE/PP blends, probably because of the higher mixibility of PP in the matrix due to the less regular and less crystalline LDPE.

At temperatures beyond the polyethylene melting points the PP-rich blends exhibit analogous greater expansion effects than the pure PP. This can be due to the melted occluded polyethylene domains, which tend to increase their volume more than the surrounding PP matrix, giving a contribution to the overall dilation of the specimens which is the major effect. Some dissolution of the LDPE or HDPE low molecular weight fractions in the PP matrix can also occur but in this case this may represent only a minor effect.

All these features can be shown more clearly in *Figure 9* where the maximum expansion height is reported as a function of the PP content. Two maxima can be observed at the PP composition where one of the components is a matrix of the system. Lower heights are displayed, instead, by the two homopolymers or by intermediate composition blends (around 50% in PP).

With regard to the elongation mode (*Figures 7b* and *8b*) there is not much difference in the thermomechanical behaviour between LDPE/PP and HDPE/PP mixtures for the PP-rich blends. In fact in both cases only slight inflexions of the curves are observed around the

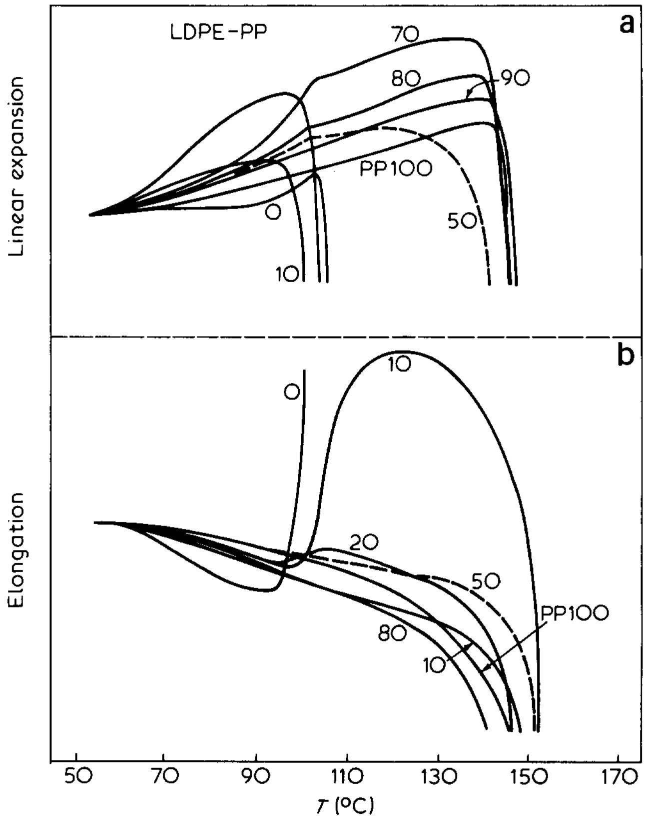

Figure 7 Typical penetration and extension curves of LDPE/PP blends at different compositions. The figures reported on each plot refer to PP weight percentage

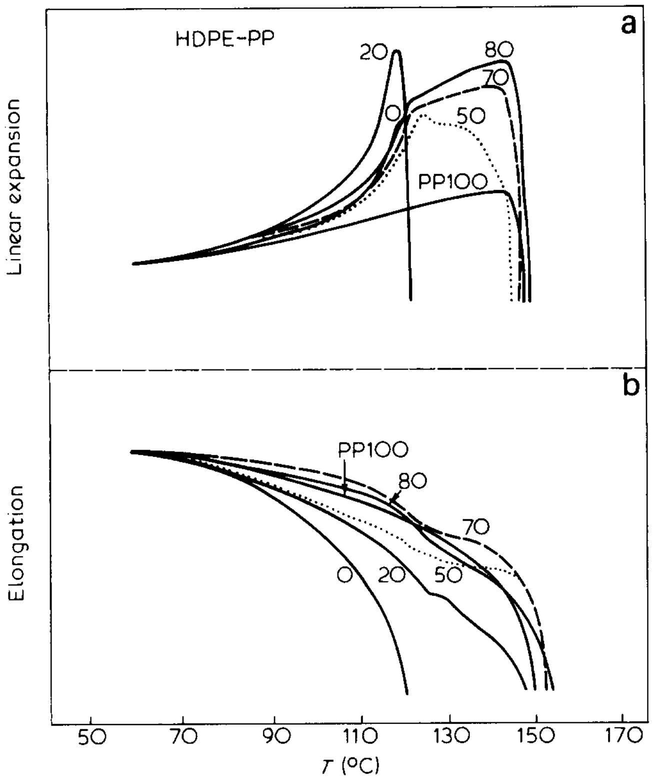

Figure 8 Typical penetration and extension curves of HDPE/PP blends at different compositions as indicated

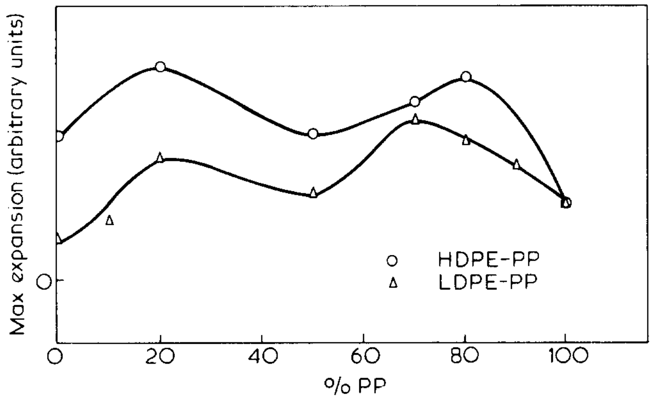

Figure 9 Maximum expansion height in arbitrary units as a function of PP percentage for LDPE/PP and HDPE/PP blends

polyethylene melting temperatures. For low PP content blends, instead, very different features are observed if either LDPE or HDPE is chosen as the component of the mixture. A strong contraction effect, after melting is shown in the former case (*Figure 7b*), which is totally absent in the latter (*Figure 8b*), where only a slight inflexion of the curves corresponds to the HDPE transition. The explanation of such behaviour of LDPE/PP blends, has already been tentatively given in previous similar cases concerning LDPE/PS blends (see *Figure 5b*) and HDPE/PS mixtures (see *Figure 2b*). It should be noted, however, that in HDPE-rich blends containing a PS dispersed phase a small contraction effect is also present whereas in the corresponding blends including PP dispersed particles such a phenomenon is not detectable. This result is related to the diverse overall morphology encountered in the case of the latter blends[14] (see *Figure 10*). As can be seen in the optical micrograph of the longitudinal section of cylindrical filaments of such blends, the PP phase consists of microfibrils, which at higher magnification are shown to be constituted by aligned spherulites. Therefore no influence of the surface tension after melting is active as in the case of elongated PS domains in HDPE/PS blends.

CONCLUSION

In this work two different classes of blends have been examined by thermomechanical analysis. The first class consists of a glassy component at room temperature (PS) and of a semicrystalline one having melting points ranging from 115°C (LDPE) up to 160°C (PP). The linear expansion coefficient (α_L) of the pure polyolefin is enhanced by the addition of small quantities of PS in the case of the polyethylenes, whereas it is lowered in the case of PP.

The second class of blends examined comprises two polyolefins with different melting points. The addition of small quantities of one component to the other tends to increase α_L.

The above mentioned results refer to the temperature scale before the complete melting of the blend after which the melt behaviour can be analysed. From such behaviour, indirect morphological information can be inferred, also being confirmed by direct optical and electron microscopy observations.

For low melting polyolefins (HDPE or LDPE) the addition of PS or PP generates always an increase of α_L, irrespective of the different molecular nature of the two components. But what is more interesting is the possibility of obtaining only high melting polyolefin (PP) materials with enhanced α_L (adding small quantities of a

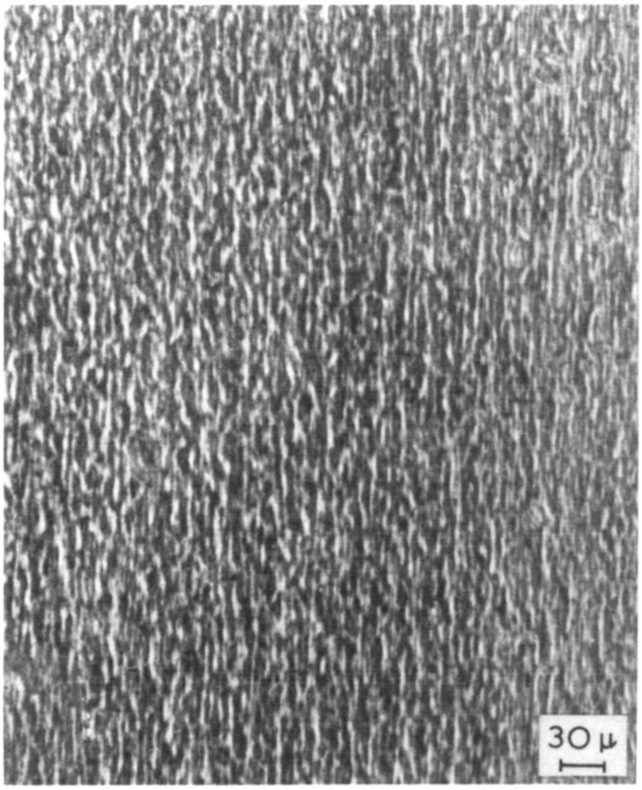

Figure 10 Optical micrograph of a longitudinal section of the extruded filament of the blend HDPE/PP (75/25)

low melting polyolefin) or with lowered α_L (adding PS as dispersed phase). Therefore by choosing suitably the two components one can design proper materials for specific technological end-uses.

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