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Properties of polyethylene–polypropylene blends

Part 2 *Thermal, swelling and mechanical characterization of strained samples with fibrous morphology*

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Differential scanning calorimetry, wide-angle X-ray scattering, swelling in n-hexane and mechanical tensile tests have been performed on cylindrical specimens with a fibrous morphology of high-density polyethylene–isotactic polypropylene blends. Such specimens were obtained by cold-drawing unoriented samples (obtained directly by extrusion, whose properties were studied in a previous paper) in an Instron machine at 60° C. The resulting behaviours of fibrous specimens have been compared with those of the initial isotropic samples having a spherulitic morphology. The mechanical properties of unoriented samples have also been compared with the data of other works found in the literature. Such a comparison suggests that, especially for blends of two semicrystalline polymers, not only must the molecular characteristics be accurately specified but also other parameters such as crystallinity, melting points and morphological features, in order to clearly explain the different types of behaviour observed.

1. Introduction

It is well known that for a semicrystalline polymer Young's modulus is defined by a tensile stress–strain curve at vanishing deformation. Here the behaviour is linear and the deformations are perfectly reversible since the material remains, structurally speaking, in a state of quasi-equilibrium during the tests. At higher elongation values the trend becomes less than linear and some permanent deformation begins to occur after unloading the specimen. Such a feature is evidence that some permanent morphological changes start to occur in the original structure of the polymer [1]. At the yield point (defined as $d\sigma/d\epsilon = 0$, where σ and ϵ are the stress and strain) a neck appears, generally along the specimen, and beyond this region a definite fibrous morphology develops in the necked portion of the samples [1]. This is very clearly seen from wide-angle X-ray diffraction (WAXD) patterns. Therefore, in a very idealized and schematic way, this region of the stress–strain curve can be thought of as the separation point between two very differently structured materials: (1) the initial spherulitic unoriented specimens; (2) the final oriented samples with fibrous morphology. Of course the two structure species, even though of the same chemical nature, exhibit quite different properties.

In the first paper of this series [2], thermal, swelling and mechanical properties of the initial isotropic species, obtained directly by extrusion, have been examined in a preliminary way. In this second paper the same properties, relative to the final oriented material species, have been analysed and the resulting data compared with those of the initial extruded isotropic specimens. Furthermore, at the beginning of the present work the initial mechanical stress–strain features such as the Young's modulus and the yield point values have been compared with the data of other authors,

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obtained on samples of the same chemical nature. The main purpose of the present work is to analyse the mutual influence of the two components during fibre formation by studying the dependence of several properties on the composition and morphology of the blends.

2. Experimental procedures

2.1. Materials

The following polymers were used in the present work: high-density polyethylene (PE) ($\bar{M}_w = 166\,000$; $\bar{M}_n = 10\,200$; $\bar{M}_w/\bar{M}_n = 16$; MFI* $= 3.7$ g $(10\,\text{min}^{-1})$; $\rho = 0.96\,\text{g cm}^{-3}$), isotactic polypropylene (PP) ($\bar{M}_w = 307\,000$; $\bar{M}_n = 15\,600$; $\bar{M}_w/\bar{M}_n = 20$; MFI $= 3.9$ g $(10\,\text{min})^{-1}$; $\rho = 0.906\,\text{g cm}^{-3}$) and RAPRA† standards HDPE$_1$ and PP$_1$ respectively. The polymers did not contain any additives.

2.2. Blend preparation

Polymeric blends were obtained by melt mixing pelletized components at 180° C (typically $10\,\text{mm}^3$ pellet) in a laboratory extruder (CSI max mixing-extruder, model CS-194, manufactured by Instron Scientific Instruments Inc.). The standard procedure is described in a previous paper [1]. The composition range of the PE–PP blends used is given below in wt%:

PE	0	10	30	50	70	90	100
PP	100	90	70	50	30	10	0 .

2.3. Fibre preparation

The cylindrical specimens obtained by extrusion were successively cold-drawn at 60° C using a tensile Instron machine at a constant cross-head speed of $5\,\text{mm min}^{-1}$, up to an elongation ratio of about 10.

All the samples showed classical neck formation characteristic of ductile behaviour in semicrystalline polymers. It is to be noted however that, with the test conditions used initially (room temperature and cross-head speed of $5\,\text{mm min}^{-1}$), only the pure PE and PP unoriented extruded samples extended so readily on cold-drawing to give fibre samples long enough to be clamped (in order to be redrawn in the Instron machine). In contrast, the blend samples exhibited a very low elongation-at-break and therefore the cold-drawing temperature for all the specimens was increased to 60° C. The necked portions of the samples so obtained were then cut to obtain cylindrical fibres on which subsequent measurements were performed.

2.4. Methods

The following techniques, as previously carried out on extruded unoriented samples [2], were also used on the fibrous samples, i.e. differential scanning calorimetry (DSC) wide-angle X-ray scattering (WAXS), gravimetric and axial swelling, picnometry and stress–strain measurements. In order to perform tensile mechanical tests the oriented drawn fibres were wound onto suitable clamps mounted on the Instron machine.

3. Results

3.1. Mechanical properties of extruded unoriented blend specimens

The stress–strain curves for PE–PP blends, obtained by tensile deformation of the cylindrical extruded isotropic specimens have already been discussed in the first paper of this series [2]. However in the opinion of the authors it is very interesting to compare such data with literature results [3, 4], obtained for similar high-density polyethylene–isotactic polypropylene blends. Therefore for a complete comparison, the pure PE and PP characterizations, the material sources and the additives in the blends with appropriate references are reported in Table I. Furthermore, the mixing procedures, the specimen preparations and the final sample geometries are also mentioned in the same table.

The moduli, E, of the isotropic extruded samples are compared in Fig. 1, where Curve C shows lower values compared with Curves A, B and D which are very close in value. Such a result is probably due to the effect of the addition of 1% of an antioxidant to the blend of Curve C, (see Table I). This plasticizes the material and may also alter the crystallinity and morphology of the homopolymers. The yield strength, σ_y, and the elongation at yield, ϵ_y, are reported as a function of content PP in Fig. 2. σ_y is comparable for each blend but the shapes of the curves differ from each other significantly. Curve A, in fact, shows a strong positive synergism at about 80% PP; Curves B and D show a minimum at about 25% PP and Curve C is a straight line connecting the values of the pure components. ϵ_y against percentage PP for Curve A shows also a maximum at almost the same percentage value as

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*MFI is melt flow index.

†RAPRA is the Rubber and Plastics Research Association of Great Britain, Shawbury, Shrewsbury, UK.

TABLE I Comparison of homopolymer properties and specimen blend preparation used by different authors

Code	Reference	Density		MFI		Molecular parameters		Source		Blend additives	Mixing procedure	Specimen preparation	Sample shape
		PE	PP	PE	PP	PE	PP	PE	PP				
A	Greco *et al.* [2] (and present work)	0.960	0.906	2.5	3.9	$\bar{M}_n = 1.66 \times 10^5$ $\bar{M}_w > 1.02 \times 10^4$	$\bar{M}_n = 3.07 \times 10^5$ $\bar{M}_w = 1.56 \times 10^5$	Rapra $HDPE_1$	Rapra PP_1	–	Miniextruder at 180° C	Extrusion	Cylinder
B	Robertson *et al.* [3]	0.964	Standard moulding grade	0.2	414	–	–	DGDA Union Carbide	E_{116} Enjay	–	Brabender plasticorder at 190° C	Dumb-bell from moulded sheet	flat dogbone
C	Deanin *et al.* [4]	0.965	0.902	0.7	4.0	–	–	Dow 70065	Hercules profax 6523	1% Geigy Inorganox 1076 anti-oxide	2 roll differential speed-mill at at unknown temperature	Dumb-bell from moulded sheet	Flat dogbone
D	Greco *et al.* [5]	0.960	0.906	2.5	3.9	$\bar{M}_n = 1.66 \times 10^5$ $\bar{M}_w = 1.02 \times 10^4$	$\bar{M}_n = 3.07 \times 10^5$ $\bar{M}_w = 1.56 \times 10^4$	Rapra $HDPE_1$	Rapra PP_1	–	Brabender plasticorder at 200° C and Miniextruder at 200° C	Extrusion	Cylinder

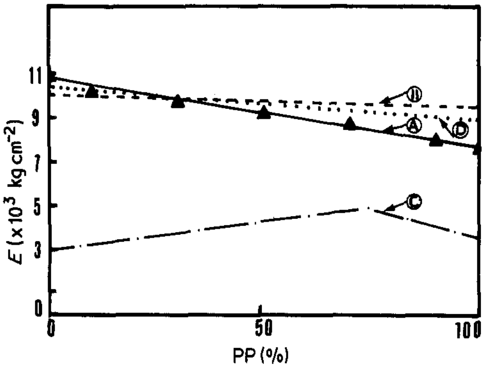

Figure 1 Moduli E as a function of PP content obtained by different authors. The curves are labelled A, B, C and D as indicated in Table I.

the corresponding curve for σ_y, whereas Curves C and D both show negative synergistic effects. A tentative interpretation of the behaviour of Curve A for both σ_y and ϵ_y has been given elsewhere [2], but it cannot be used to generalize for all the other different results, observed in Figs 1 and 2 which will be more thoroughly, even though qualitatively, discussed in the last part of the present paper.

3.2. Fibrous specimen properties

3.2.1. X-ray scattering

The WAXS diffraction patterns of the samples obtained by cold-drawing at room temperature show a high orientation along the fibre axis of the PE and PP crystallites within the blends, characteristic of a fibrous morphology of both the components. Neither co-crystallization phenomena nor shifts in the spacing of the reflections are observed.

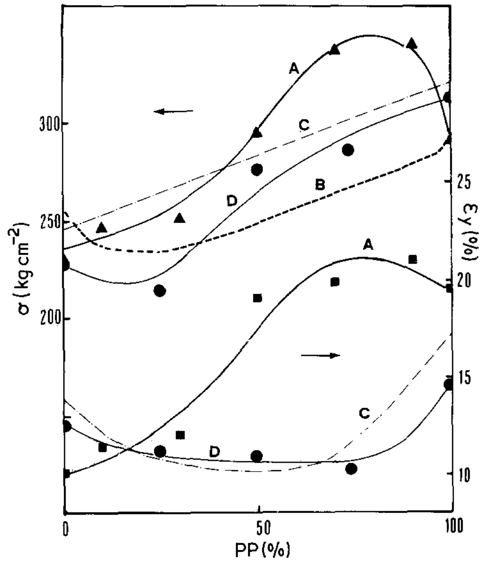

Figure 2 Yield strength σ_y and elongation at yield ϵ_y as a function of PP content, obtained by different authors. The curves are labelled A, C and D as indicated in Table I. (The average errors are respectively ± 20 kg cm^{-2} and ± 1.5% for Curves A. No indication of the errors was given in the literature for the other curves.

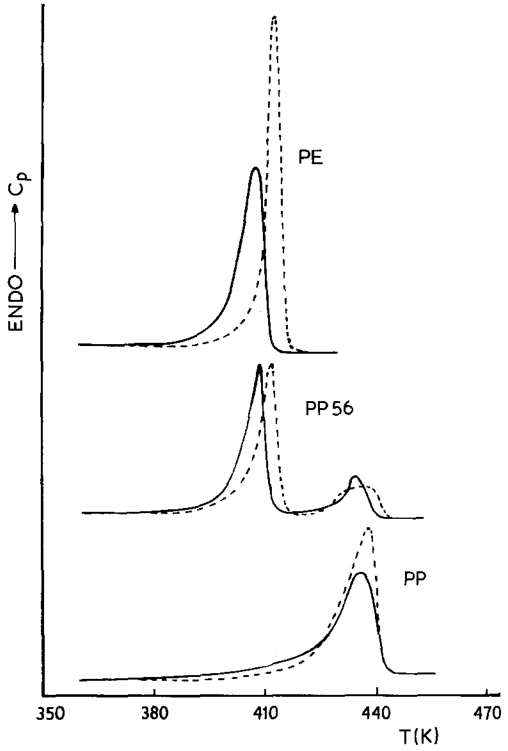

Figure 3 DSC thermograms of fusion for strained fibres (dashed lines): (a) pure PE; (b) 50% PP; (c) pure PP. Solid lines represent the second melting cycle thermograms.

3.2.2. Thermal properties

Typical first and second run DSC thermograms for blends and homopolymers with a starting fibrous morphology are shown in Fig. 3. The endotherms of fusion of the first run homopolymer and of the PE in the blends are sharper than those of the samples which have been recrystallized from the melt (solid lines). Such an effect may be accounted for by a narrower distribution of crystallite sizes in the fibres.

The melting peaks of PP in blends with a fibrous morphology are broader than the corresponding peaks for isotropic blends. This behaviour may be explained by the fact that during fusion, the PE fibrils melt before the PP ones, inducing a certain amount of disorder in the adjacent PP regions.

The melting point (T_m) and the fractional crystallinity (X_c) of PE crystallites in the fibrous

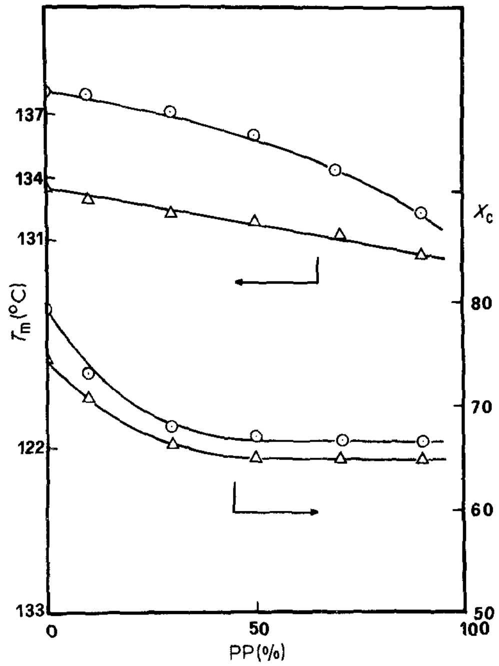

Figure 4 Melting points T_m and fractional crystallinity X_c of PE for strained fibres (circles) as a function of PP content. Triangles represent values corresponding to the initial isotropic extruded samples.

blends as a function of PP content, are reported in Fig. 4 (circles). The melting points of PE fibres are slightly higher than the corresponding values of the isotropic extruded samples (triangles in Fig. 4) especially at low and intermediate PP contents. This result shows the effect of an improvement in crystal perfection and/or of an increase in the dimensions of the PE crystals due to the mechanical treatment of the samples. PE crystallinity is slightly affected by cold-drawing.

A similar plot for T_m and X_c of PP fibres, is shown in Fig. 5; also, in this case the T_m of the fibres is higher than the T_m of isotropic extruded samples. The fractional crystallinity, X_c, of fibres is sharply decreased at low PP contents when a PE matrix is surrounding the isolated PP fibrils. On the contrary at high PP contents, when PP is the matrix of the system, an enhancement in the crystallinity of PP fibres is observed. It is interesting to point out that the crystallinity values calculated from the DSC curves can be slightly affected by mutual interference of the two crystalline phases during the heating up of the blend samples.

3.2.3. Swelling properties

Gravimetric and axial swelling of the fibrous blends were also measured as a function of time.

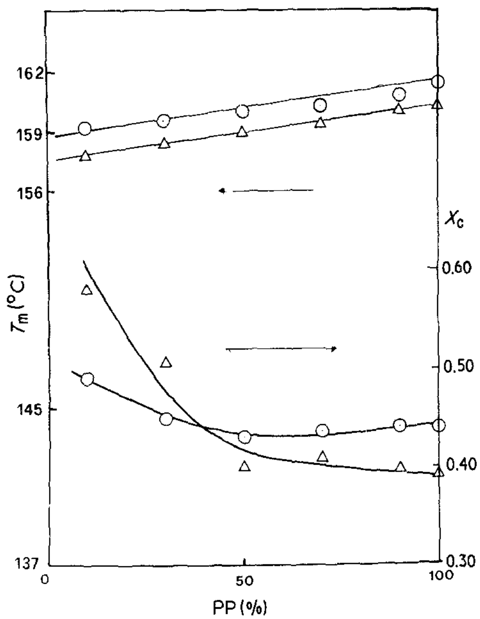

Figure 5 Melting points T_m and fractional crystallinity X_c of PP for strained fibres (circles) as a function of PP content. Triangles represent values corresponding to the initial isotropic extruded samples.

Their equilibrium values (full circles in Fig. 6) are reported as a function of PP content. They show an almost linear trend with absolute values much greater than those corresponding to the isotropic extruded samples (squares in Fig. 6). This may be due mainly to craze formation in the fibres during the mechanical treatment and also to changes in morphology which may alter the absorbing properties of the materials.

The axial swelling decreases linearly with increasing PP content indicating a shrinkage phenomenon of the fibres as a result of swelling. Such behaviour may be due to the solvent, which increases the chain molecule mobility thereby releasing the stresses frozen in the material during mechanical deformation. An analogous, even stronger, stress releasing action may be obtained by thermal effects, i.e. keeping the dry fibres at 70° C for 5 h, as also shown in Fig. 6 (open circles). The extent of fibre shrinkage, which is almost negligible for pure PE specimens, is enhanced with increasing PP content of the fibrous samples. Such an effect can be attributed to the higher plasticity of pure PE with respect to pure PP due to the very different chain mobility in the amorphous regions of the two homopolymers. In fact the frozen stresses can be released in pure PE with almost no additional increase of free volume by solvent or thermal actions, which become more

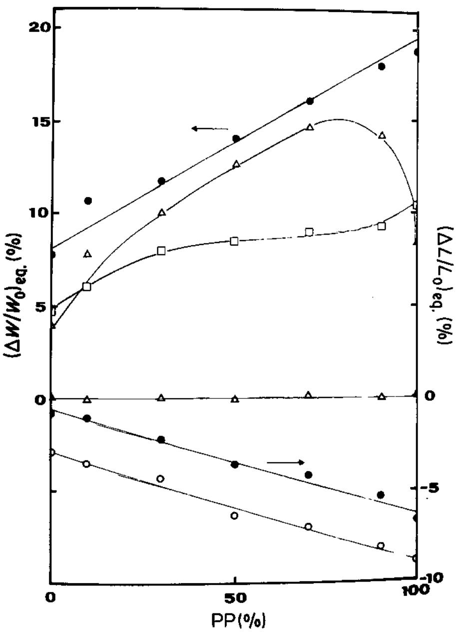

Figure 6 Equilibrium gravimetric and axial swelling as a function of PP content. Extruded samples (squares); first swelling data of fibres (full circles); second swelling data of fibres (open triangles); thermal axial shrinkage at 70° C (open circles).

and more necessary with increasing PP content. On the same plot, data are also reported relative to fibres which had been swollen once, then dried under vacuum and swollen again. The gravimetric swelling data of the pure components are greatly reduced to about the values of the extruded samples. The blend values, instead, except for PP content close to pure PP, seem to reach swelling values only slightly lower than those obtained during the first swelling operation. This hinderance to craze healing for blend fibres may be due to some kind of interaction occurring between the PE and the PP fibrils which makes the crazed structure, formed during the mechanical cold-drawing, more stable and less reversible. Furthermore, no axial swelling in such a case is detectable. Therefore, the swelling occurs only in a radial direction, or better, it may probably be due to the moving of existing crazes into the fibres. Such a hypothesis is also supported by density measurements performed on dry fibres of the pure component, which gave density values much lower than those corresponding to the initial extruded samples (about 0.75 g cm^{-3} for PE and 0.80 g cm^{-3} for PP fibres). Stress whitening was also present along the oriented specimens and disappeared by cold-rolling the fibres.

TABLE II Mechanical behaviour of oriented blend specimens as a function of their composition

Composition (wt%)	E_y ($\times 10^4$ kg cm^{-2})	σ_r ($\times 10^3$ kg cm^{-2})	ϵ_r
PE_{100}	12	3.4	0.20
PP_{10}	5.0	4.0	0.28
PP_{20}	6.5	3.7	0.22
PP_{30}	3.0	3.4	0.31
PP_{40}	6.9	3.9	0.36
PP_{50}	6.1	3.4	0.23
PP_{60}	5.3	3.2	0.35
PP_{70}	5.5	3.8	0.28
PP_{80}	4.4	3.8	0.39
PP_{90}	4.8	3.5	0.17
PP_{100}	4.9	3.4	0.20

3.2.4. Mechanical properties

Stress–strain curves have been obtained for all the oriented blend specimens at room temperature and at a cross-head speed of 5 mm min^{-1}. From these curves average values (calculated on a basis of at least seven tests) of the Young's modulus, E, the tensile strength, σ_r, and the elongation-at-break, ϵ_r, are reported in Table II as a function of blend composition. The Young's modulus of pure PE (12 times greater than that of the corresponding unoriented extruded sample) decreases suddenly as soon as a small amount of PP is added and remains so over the entire composition range, about constant and equal to the pure PP modulus (which is about seven times higher than that of the corresponding extruded unoriented specimen). The strength, σ_r, and the elongation-at-break, ϵ_r, seem to be quite independent of blend composition showing no difference in the mechanical behaviour of the homopolymer and blend fibres with respect to the ultimate properties. No literature data were available of such properties for comparison.

4. Concluding remarks

From the experimental observations the following remarks can be made.

WAXD patterns show no co-crystallization phenomena in the extruded samples as well as in the oriented drawn fibres.

The melting points are slightly higher for fibres than for unoriented samples suggesting an improvement of crystal perfection and/or an increase in the dimensions of the PE and PP crystals subsequent to mechanical treatment.

The second-cycle swelling data show that craze formation (evidenced also by density measurements and by the stress whitening effect visible on the drawn samples) seems to be reversible by solvent action in the case of pure PE and PP, whereas almost a total absence of reversibility is shown by their blends. Such a feature may be due to some kind of interaction existing between PE and PP fibrils in the blends.

With respect to the mechanical stress–strain curves the following considerations can be made.

At very low deformations the Young's moduli of the unoriented extruded specimens show no particular interactions between the diverse phases and their dependence on concentration is attributable mainly to the total amount of crystallinity of the blends [2]. Therefore the different authors' data are very close in value, except for type C, where a third component has been added to the blend.

At the yield point very unsimilar behaviours are observed by the authors mentioned in Table I. The various synergistic or linear trends with varying composition seem to depend in such a case on the molecular characteristics of the two components and on the processing conditions used for making the specimens.

In the plastic zone, after the yield point, propagation for blends in the necking zone is very unstable at room temperature, whereas it becomes very easy at 60° C. This effect is probably due to the enhanced molecular mobility in the amorphous regions of PE and PP in some way interlocked in the necking zone. This effect can be considered as a further indication (already mentioned in the swelling phenomenon and in the yield region) that some kind of interaction could be present between PE and PP regions during cold-drawing of the specimens. At room temperature, easy fibre formation with no flow instability can be obtained by adding a small amount (5 wt%) of an ethylene–propylene random co-polymer to such blends. This acts as a compatibilizer in the amorphous regions of the material and behaves like a lubricant during mechanical cold-drawing of the blends [6].

Finally the mechanical behaviour of the fibrous oriented sample seems to be quite independent of blend concentration. In fact only pure PE shows moduli higher than those of the other blends and pure PP. Furthermore, the ultimate strength and the elongation at break are always equal to those of pure homopolymers over the entire composition range.

It may be concluded from the previous considerations and from comparison with data in the literature that many important factors affect the properties of PE–PP blends observed on varying the blend composition:

(1) The molecular parameters of the two homopolymers (as given for blends A and D and as MFI for blends B and C in Table I).

(2) The mechanical and thermal histories used for making the samples (mixing procedures, specimen preparation, sample shapes).

(3) The morphologies of the extruded samples.

(4) The existing interactions between the two homopolymer phases.

Therefore all such factors must be specified and analysed from case to case to achieve a complete and thorough knowledge of the behaviour of a blend consisting of two semicrystalline polymers.

Work is in progress in our laboratory to analyse the morphology of such blends by means of optical and electron microscopy.

References

1. A. PETERLIN, *Polymer Eng. Sci.* 17 (1977) 183.
2. R. GRECO, G. MUCCIARIELLO, G. RAGOSTA and E. MARTUSCELLI, *J. Mater. Sci.* **15** (1980) 845.
3. R. E. ROBERTSON, D. R. PAUL, *J. Appl. Polymer Sci.* 17 (1979) 2579.
4. R. D. DEANIN, M. F. SANSONE, *Polymer Symposia* 19 (1978) 211.
5. R. GRECO, unpublished work (1980).
6. R. GRECO, G. RAGOSTA and E. MARTUSCELLI, unpublished work (1981).

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