

Impact-resistant Polypropylene/Natural Rubber Blends

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It has been demonstrated previously that blends of polypropylene with natural rubber having high impact strength at low temperatures may be prepared by blending in the presence of m-phenylenebismaleimide. The potential for a cheaper additive system, phenolformaldehyde resin with zinc oxide, to replace the m-phenylenebismaleimide has been investigated. The resin and zinc oxide are at least as effective as m-phenylenebismaleimide in increasing both the notched Izod and falling weight impact strength of the blends at low temperatures. Other properties are also generally affected in a similar manner. The effect of the level of resin and zinc oxide on impact strength is considered in terms of the mechanisms leading to increased impact strength, and appropriate levels of resin and zinc oxide are identified. There is a considerable cost advantage in the use of resin and zinc oxide.

The blending of rubbers with polypropylene (PP) to provide improvements in impact strength has been studied widely¹⁻⁷, and blends of PP with ethylene/propylene or ethylene/propylene/diene (EPDM) rubbers are produced commercially as impact-resistant PP. Other rubbers have been investigated in this role, including synthetic polyisoprene, though this did not prove to be suitable⁷. There are arguments which suggest that blends of PP and polyisoprene suffer from a lack of interfacial adhesion, which is detrimental to the impact properties of the blend³. However, the preparation of blends of PP with natural rubber (NR) possessing good impact strength at low temperatures through blending in the presence of m-phenylenebismaleimide (HVA-2) has been reported⁸.

HVA-2 has the potential to combine with both PP and NR radicals produced during mastication to form copolymers capable of promoting good interfacial adhesion between the two phases, and it also crosslinks the NR phase to a low degree. It is known that both of these actions can increase impact strength in rubber-toughened thermoplastics⁹. The relative contribution of the two mechanisms

to the improvement in the impact properties of blends of PP and NR given by the use of additives such as HVA-2 has been considered more recently^{10,11}, and it has been suggested that the two are complementary though the latter makes the greater contribution provided that the former is also present.

HVA-2 is technically suitable as an additive to promote good impact properties in blends of PP and NR, but the high cost of this material may cause it to be used at a level below the technical optimum. Other potentially suitable additives have been identified¹⁰, including phenolformaldehyde resin with a catalyst to promote crosslinking of the NR phase. The catalyst considered previously was stannous chloride dihydrate, but this compound has some drawbacks, and this communication reports more recent work which has shown that phenolformaldehyde resin activated with zinc oxide is a suitable alternative additive system to HVA-2.

MATERIALS AND METHODS

A viscosity-stabilised grade of NR, SMR CV, was used. Two grades of PP have been con-

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sidered, one a homopolymer grade (Propathene GWM 22, ICI) and the other a copolymer grade with a flexural modulus of 1400 MPa (Propathene GWM 101, ICI). Both grades of PP have a melt flow index (MFI) of 4 g per 10 min under *Condition L* of ASTM D1238. The HDPE used in ternary blends is a homopolymer with a MFI of 0.75 under *Condition P* of ASTM D1238 (Unifos DMS 5140). Zinc oxide, HVA-2 (DuPont), phenolformaldehyde resin (SP1045, Schenectady-Midland), and the antioxidants (Permanax WSO, Vulnax Int., and Irganox PS800, Ciba-Geigy) were used as supplied.

Blends were prepared in a BR Banbury mixing on a 1 kg scale at a rotor speed of 116 r.p.m. and with steam heating at 0.28 MPa. NR, polyolefin(s) and zinc oxide, when used, were charged into the Banbury and HVA-2 or SP1045 were added after 2 min, following the melting of the PP at 1.5 min. Antioxidants (0.2 p.p.h.p. each of WSO and PS800) were added after 4.5 min, and the batch was dumped after 5 min at a temperature in the range 175°C–185°C. The blends were sheeted on a mill prior to granulation.

MFI were measured at 190°C under a load of 5 kg (ASTM D1238, *Condition P*). Die swell was measured on the cold extrudate from the MFI test. Izod impact testing was performed on injection-moulded, BS-notched test-pieces in the temperature range –50°C to 23°C. Instrumented falling weight impact testing was performed over the same temperature range on injection-moulded discs 60 mm in diameter and 1.5 mm in thickness using a support diameter of 50 mm and a hemispherical-nosed dart with a diameter of 12.5 mm. The drop height was 50 cm, and the energy available to rupture the test-piece was 65 J. The impact force/time curve was collected, and allowance was made for the slowing of the dart during impact in the calculation of energy absorbed by the test-piece. The falling weight impact strength is given by the energy absorbed to failure of the test-piece. The tensile properties of the blends were measured on dumbbell test-pieces with a gauge length of 12.5 mm cut from the injection-moulded discs. The measurements were made

at 23°C using an Instron tensometer operating at a crosshead speed of 50 mm per minute.

RESULTS

Two series of blends containing 15% NR have been considered, binary blends of a homopolymer grade of PP with NR and ternary blends comprising a copolymer grade of PP, NR and HDPE. Each series includes a blend prepared in the absence of additives and a blend prepared in the presence of HVA-2 in addition to the blends prepared with various levels of phenolformaldehyde resin and zinc oxide (Tables 1 and 2). In accord with previous reports^{8,10,11} the use of these additives in the preparation of the blends caused a marked reduction in the MFI of the blend (Tables 1 and 2). Die swell during the MFI test tended to be reduced by the additives, a reflection of crosslinking of the NR phase^{10,11}.

The notched Izod impact strength of the binary and ternary blends are presented as functions of temperature in Figures 1 and 2 respectively. The addition of HVA-2 to either of these types of blend gave the expected increase in impact strength. The phenolformaldehyde resin/zinc oxide system was at least as effective in increasing notched Izod impact strength. In the binary blends, the resin and zinc oxide are more effective and impact strength is higher at the higher level of resin. The effect of level of zinc oxide on impact strength is not marked. In the ternary blends, there is no consistent difference between the efficacy of the two additive systems over most of the temperature range in which failure occurred, and neither the level of the resin nor the level of the zinc oxide exerts a consistent effect within the limits considered here.

The falling weight impact strength of the ternary blend at low temperatures is increased by the addition of HVA-2 (Table 3), as reported previously^{10,11}. The phenolformaldehyde resin with zinc oxide is also effective in increasing falling weight impact strength, despite the presence of the particulate zinc oxide. As with notched Izod impact strength, there is little consistent difference between the abilities of the additive systems to increase falling weight

TABLE 1. PROPERTIES OF 15 : 85 NR: HOMOPOLYMER PP BLENDS

Item	Blend No.					
	1	2	3	4	5	6
Additives (p.p.h.p.)						
HVA-2	—	0.5	—	—	—	—
SP1045	—	—	1.0	1.0	2.0	2.0
ZnO	—	—	0.5	1.0	0.5	1.0
Properties						
MFI (g/10 min)	8.7	0.67	0.49	0.30	0.66	0.42
Die swell (%)	70	70	38	38	31	28
Yield stress (MPa)	24	25	23.8	24.5	24.2	24.2
Yield strain (%)	16	13.5	16	13.5	12.5	14.5
Tensile strength (MPa)	28.2	29.1	33.9	34	35.1	34.5

TABLE 2. PROPERTIES OF 15 : 75 : 10 NR: COPOLYMER PP : HDPE BLENDS

Item	Blend No.					
	7	8	9	10	11	12
Additives (p.p.h.p.)						
HVA-2	—	0.5	—	—	—	—
SP1045	—	—	1.0	1.0	2.0	2.0
ZnO	—	—	0.5	1.0	0.5	1.0
Properties						
MFI (g/10 min)	8.6	1.2	0.71	0.41	0.16	0.17
Die swell (%)	63	47	66	47	23	17
Yield stress (MPa)	18.4	19.8	19.6	19.3	19.6	19.8
Yield strain (%)	20.5	15.5	17	17	16.5	16.5
Tensile strength (MPa)	25.4	29.7	30.4	30.2	31	30.9

impact strength at these low temperatures, although the blend containing the highest level of resin and zinc oxide generally has the highest impact strength.

Only HVA-2 gave a significant increase in the yield stress of the binary blend based on a homopolymer grade of PP, which was evident in earlier work on binary blends based on the copolymer grade of PP⁸ (Table 1). Yield strain is reduced by both types of additive, and tensile strength is increased markedly, in accord

with previous experience. The ternary blends based on the copolymer grade of PP do show an increase in yield stress due to both types of additive, in addition to the reduced yield strain and higher tensile strength (Table 2).

DISCUSSION

A reduction in MFI of a blend due to the presence of additives during the preparation has been associated with one mechanism of increasing impact strength, increased interfacial

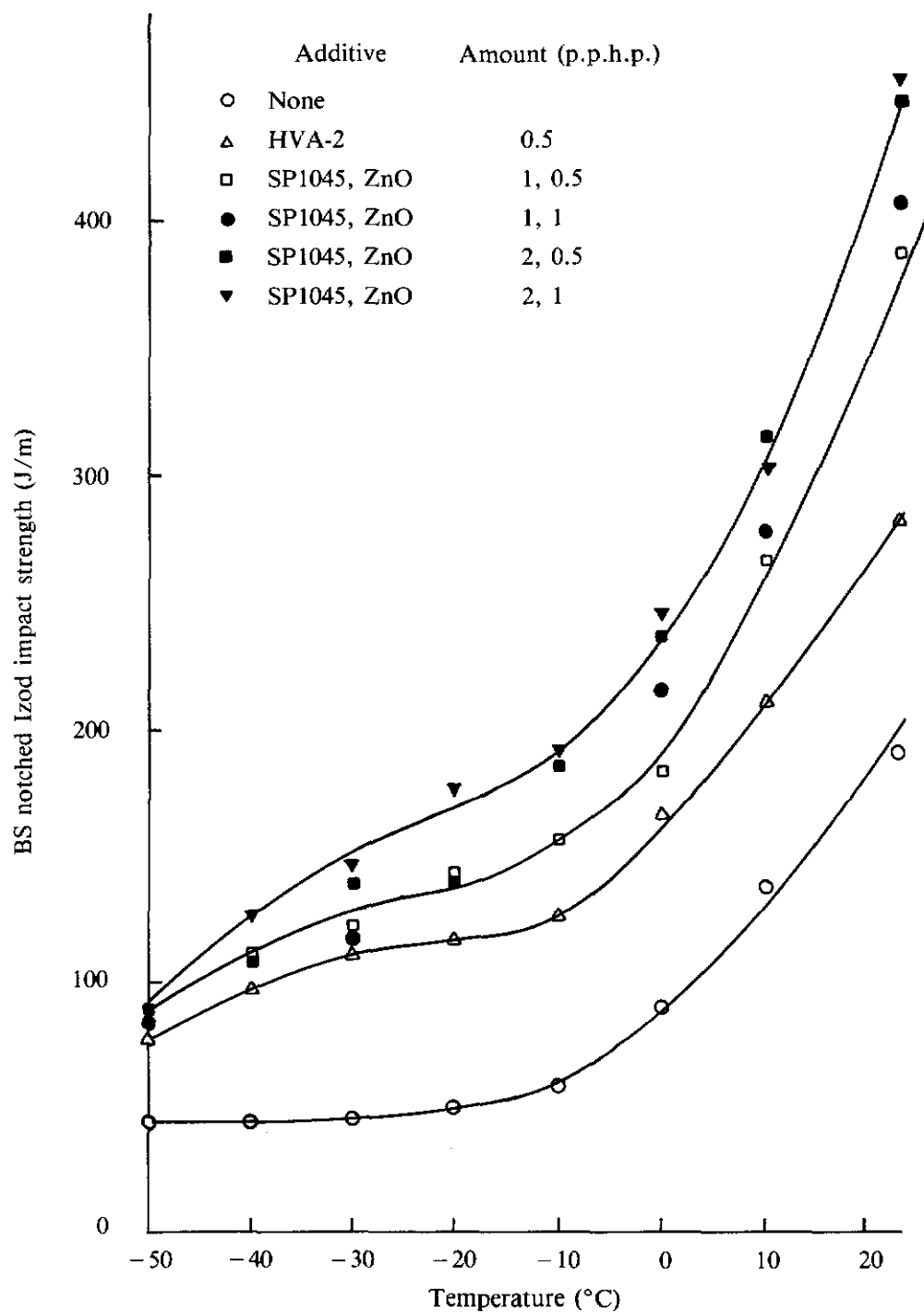


Figure 1. BS notched Izod impact strength of 15:85 NR: homopolymer PP blends as a function of test temperature, showing the effect of HVA-2 and resin/zinc oxide.

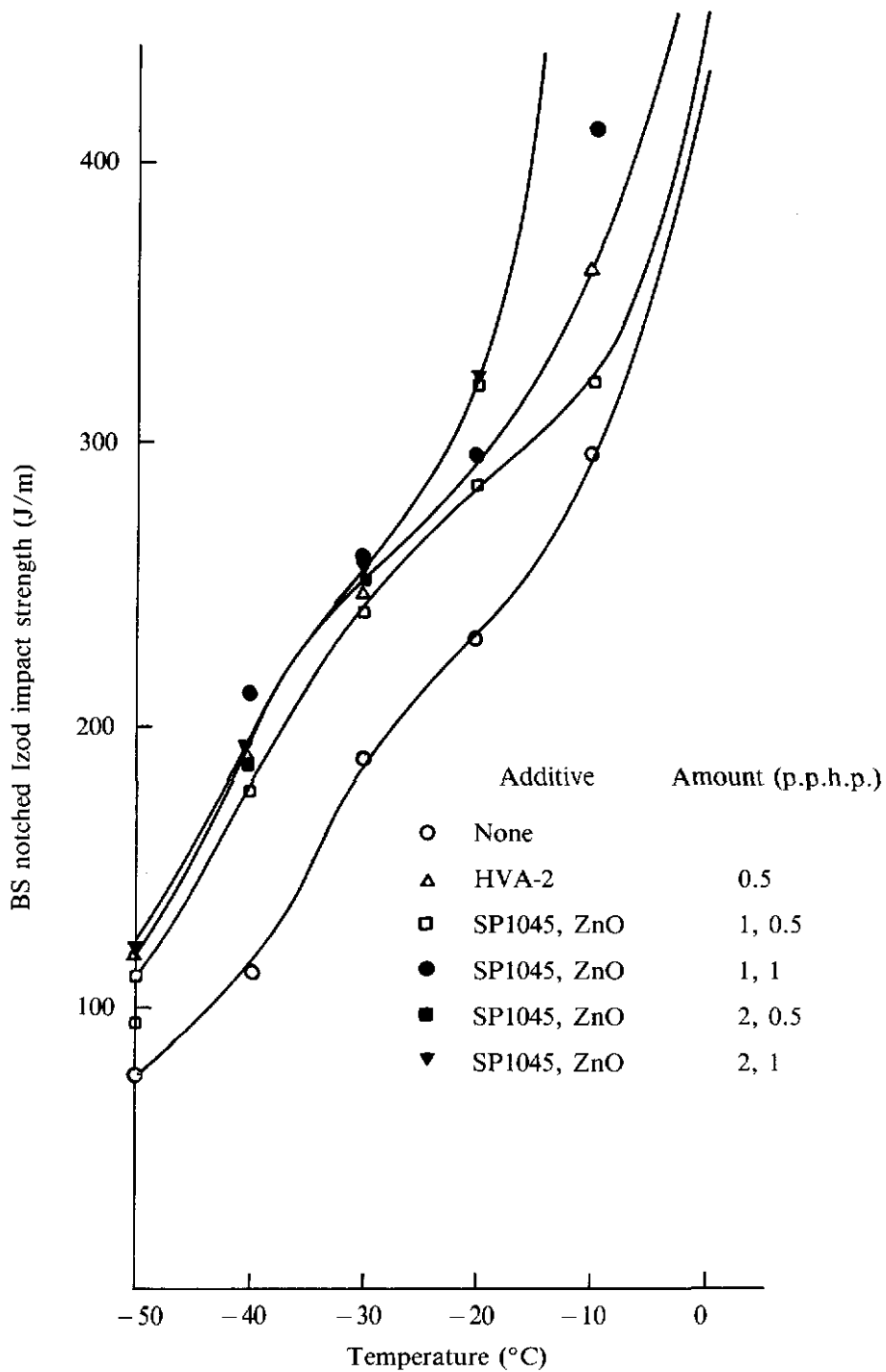


Figure 2. BS notched Izod impact strength of 15:75:10 NR: copolymer PP: HDPE blends as a function of test temperature, showing the effect of HVA-2 and resin/zinc oxide.

TABLE 3. FALLING WEIGHT IMPACT STRENGTH OF 15 : 75 : 10 NR : COPOLYMER PP : HDPE BLENDS

Blend No.	Falling weight impact strength (J)		
	-20°C	-35°C	-50°C
7	11.7	12.8	8.6
8	11.8	14.3	13.3
9	12.1	12.1	13.3
10	12.8	14.2	13.7
11	12.5	14.3	13.1
12	12.8	15.0	14.2

adhesion. A reduction in die swell is associated with another mechanism, crosslinking of the NR phase. The maximum benefit in terms of impact strength is realised when both mechanisms are operating.

Some care must be exercised in relating impact strength and die swell, since there are competing effects. Additives which increase interfacial adhesion without crosslinking the NR phase cause an increase in die swell^{10,11}. The die swell of a blend prepared in the presence of an additive which increases interfacial adhesion and causes crosslinking of the NR is therefore affected by both of these processes, and it is not a simple reflection of the degree of crosslinking. However, the Izod impact strength of the binary blends does correlate with the die swell of the blends, which increases with increasing level of resin and is greater for the blends containing the resin than the blend containing HVA-2.

Such discrimination between the two additive systems and the effect of crosslink density, as indicated by die swell, is not readily evident in the Izod impact strength of the ternary blends. However, it has been demonstrated that the effect of crosslinking the NR phase on the Izod impact strength of a blend is most marked at temperatures above about -30°C to -20°C^{10,11}, and this is also apparent for the binary blends considered here. The high impact strength of the ternary blends curtailed the temperature range over which it was measured, and for the majority of that range

there is little consistent difference between the blends. Nonetheless, the limited data available above -20°C are in accord with a higher impact strength at a higher level of crosslinking, as indicated by a lower die swell.

It has been shown that, in common with other rubber-modified thermoplastics¹², there is an optimum degree of crosslinking of the NR in blends with PP above which impact strength decreases^{10,11}. Given that the difference between the Izod impact strengths of the blends containing 1 p.p.h.p. and 2 p.p.h.p. resin is not large, the optimum level of crosslinking is probably achieved with a resin level close to 2 p.p.h.p.

It is not unusual for two such different measures of impact strength as notched Izod and falling weight to give different relative assessments of a number of materials. However, in this instance the falling weight impact strengths of the ternary blends present a similar assessment of the effect of the additives as notched Izod impact strength. Both additive systems increase the falling weight impact strength of the blend at low temperatures, and there is little consistent difference in the increase provided by the two additives or by the two levels of resin. The additives not only increase the falling weight impact strength of the blend, the ductile-brittle transition temperature is also reduced. The latter parameter is defined as the highest temperature at which the energy absorbed to failure is coincident with the energy absorbed to peak load during impact. The ductile-brittle transition temperature of the blend without additives⁷ is close to -50°C, since the energy absorbed to peak load is 8.45 J. The falling weight impact strengths at -50°C of the blends prepared in the presence of additives are well in excess of the energies absorbed to peak load, which all lie between 9.16 J and 9.23 J, and the ductile-brittle transition temperatures for these blends are therefore below -50°C.

From a practical viewpoint, the marked reduction in the MFI of a blend caused by the additives may seem disadvantageous, since it suggests a substantial reduction in processability.

However, it has been shown that the MFI of a blend prepared in the presence of HVA-2 is not a reliable indicator of processability — the viscosity of the blend is only slightly increased by the additive at the high shear rates prevailing in processing by injection moulding⁸.

CONCLUSIONS

Phenolformaldehyde resin with zinc oxide is effective in increasing the impact strength of NR/PP blends at low temperatures, when added during the preparation of the blends. Both notched Izod impact strength and falling weight impact strength are increased, and the ductile-brittle transition temperature in the latter test is reduced. In the practically more interesting ternary blends, the resin and zinc oxide increase yield stress and tensile strength. The resin with zinc oxide could replace the more expensive HVA-2 as an additive and, given the relatively small differences observed between the two levels considered here, 1 p.p.h.p. of resin with 0.5 p.p.h.p. zinc oxide is adequate. At current prices, this represents a reduction in the cost of the additive of about 75%.

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