

Preparation and Properties of Graft Copolymers of Vinyl Chloride on Atactic Polypropylene

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Synopsis

The possible uses of atactic polypropylene as the basis of grafting for the preparation of graft polymers of vinyl chloride are studied. Graft parameters and glass transition temperatures of the graft products obtained are specified at different compositions of the graft products. After blending the graft products with pure poly(vinyl chloride) or ABS/poly(vinyl chloride) blends, some application-related properties are discussed with respect to the grafting degree and the amount of graft product contained.

INTRODUCTION

At present, a state has been reached in the development of new catalyst systems for the stereospecific polymerization of propylene making unnecessary the isolation of the atactic component included in isotactic polypropylene.¹⁻³ Meanwhile, this atactic polypropylene has attained such a wide and varied field of application that manufacture of specialties in local production facilities seems to be appropriate.^{4,5}

Apart from the known application of atactic polypropylene in unmodified form, e.g., for paper lamination and coating, roof and sealing webs, bituminous mass, insulation material, backing of weighty carpet tiles, adhesive and sealing material, and as lubricant additives,⁶⁻⁸ new possibilities of application are emerging such as a substitute for plasticizer in expanded PVC pastes,⁹ for partial substitution of rubber included in impact-resistant polystyrenes,¹⁰ as a substitute for rubber, as filler and plasticizer for cable sheathings,^{11,12} and as an additive for polymer compounds.¹³

Atactic polypropylene may be modified by thermal degradation in the presence of organic peroxides into plasticizers to be used for rubber compounds,¹⁴ by chlorination into plasticizers for PVC,¹⁵ by ozonization,¹⁶ or by specific functionalization,^{17,18} among others.

With regard to the preparation of polymer blends, modification of propylene through graft copolymerization is prosperous.^{19,20} In this connection, the graft polymers of styrene, acrylates, and vinyl acetates on atactic polypropylene have been subjected to a more detailed investigation.²¹⁻²⁴ Graft products of vinyl chloride and vinyl acetate onto the above polyolefin are of industrial importance and the preparation and selected properties of them are outlined in the following.

EXPERIMENTAL

Base of Grafting

The atactic polypropylene used as base for grafting is a technical product from Kombinat Salushi (Most ĀSSR). The density has been determined to be 0.870 g/cm³ (298 K) and the number-average molecular weight of the atactic polypropylene component soluble in toluene up to 298 K (80.4 wt %) has been measured by use of vapor-pressure osmometry to be 5550 g/mol. The component insoluble in *n*-heptane at 371.6 K was 8.7 wt %.

Procedure

The polymerizations have been carried out in aqueous medium in an autoclave equipped with baffle. To prepare the polypropylene/vinyl chloride graft products, the following recipes have been used:

Mass ratio between polypropylene and vinyl chloride: 1:0.1–1:5.66

Mass ratio between organic phase and water: 1:2

Initiator: 0.8 wt % dilauroyl peroxide (based on vinyl chloride)

Dispersant: 0.2 wt % polyvinyl alcohol (based on organic phase, K value according to Fikentscher, 65 and residual acetate content, 15%)

Polymerization temperature: 333 K

Polymerization time: 6 h

Preswelling period at room temperature: 1 h

Analysis and Properties of Graft Products

The degree and yield of grafting of polypropylene/vinyl chloride graft products have been determined by extraction with dimethyl formamide and corrected with respect to the amount of atactic polypropylene (4.1 wt %) soluble in dimethyl formamide.

$$\text{grafting degree (GD)} = \frac{\text{grafted monomer mass}}{\text{grafted base mass}}$$

$$\text{grafting yield (GY)} = \frac{\text{grafted monomer mass}}{\text{mass of monomer finally converted}}$$

The glass transition temperatures have been determined by means of the Perkin-Elmer DSC-2 device and argon (heating rate 10 K/min).

Preparation of Blends from Graft Products

The graft polymers have been blended with suspension PVC (K value 60), suspension PVC (K value 58), and ABS (emulsion polymer containing 18.5 wt % of polybutadiene as graft base) in a Buss-Ko kneader at processing temperatures of 175 and 160°C, respectively.

The specimens have been prepared and tested on notch impact resistance, tensile strength, elongation, bending strength, and melt flow index in accor-

dance with TGL 25496, TGL 28727, TGL 14068, TGL 14070, TGL 14067, and TGL 25244.

RESULTS AND DISCUSSION

The graft polymerization of vinyl chloride on atactic polypropylene has been studied in aqueous medium over the wide range of the mass ratio between polypropylene and vinyl chloride of 10–0.177 within the starting mixture. These experiments revealed that under the given experimental conditions, the polymerization started only at lower mass ratios between polypropylene and vinyl chloride (e.g., 0.177) with forming a homogeneous, non-stick and fine-grained suspension polymer. This is obviously due to the relatively low viscosity of the organic phase at start of reaction, which has been reached only at this point, and the softening temperature of the products towards the end of reaction, which was above polymerization temperature.

Figure 1 shows the dependence of conversion and degree and yield of grafting on mass ratio between vinyl chloride and atactic polypropylene within the starting mixture at constant initiator concentration with respect to the monomer. As can be seen from this graph, the conversion increases with growing amount of monomer in the starting mixture, indicating the retarding effect of polypropylene during graft polymerization reaction. With the mass ratio between polypropylene and vinyl chloride amounting to 10, a polymerization conversion has not been measurable under the prevailing conditions.

Also, with increasing amount of vinyl chloride in the starting mixture, the grafting degree increases while the grafting yield decreases because of less probability of an existing polypropylene chain in the vicinity of the growing particle. The proper grafting reaction takes place mainly at the CH group of the atactic polypropylene and only to some extent at the methylene and

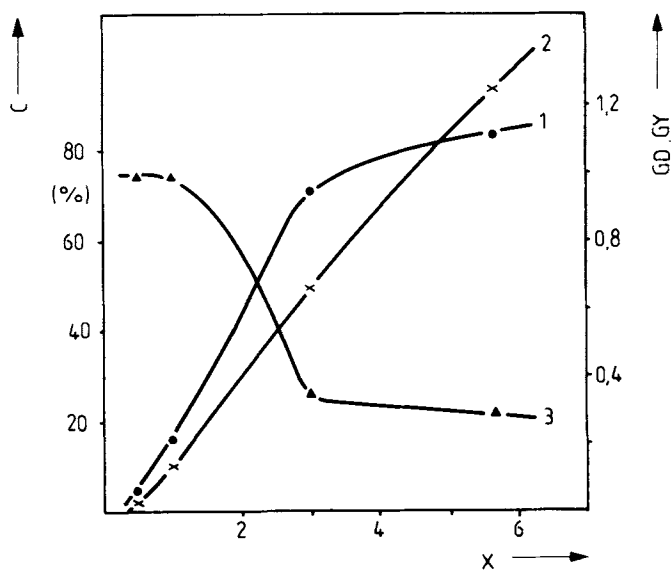


Fig. 1. Dependence of conversion (C, 1), grafting degree (GD, 2), and grafting yield (GY, 3) on the mass ratio between vinyl chloride and atactic polypropylene in the starting mixture (X).

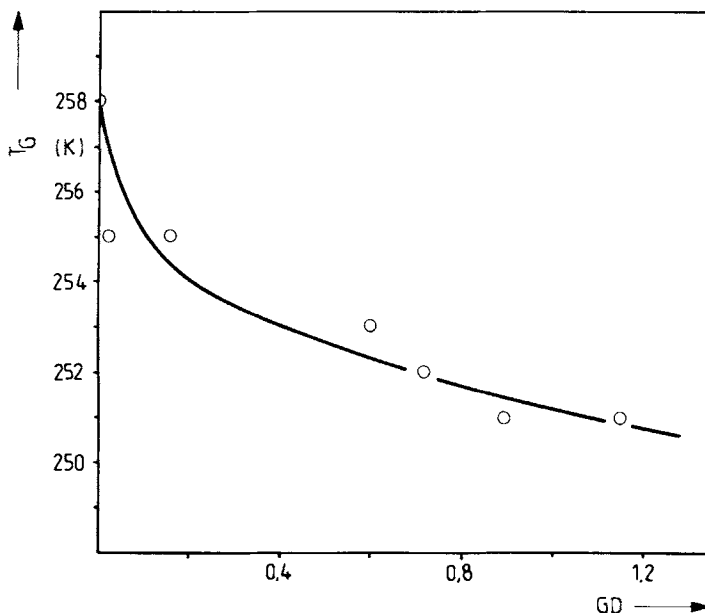


Fig. 2. Dependence of the glass transition temperature of atactic polypropylene (T_g) on grafting degree (GD).

methyl group as can be concluded from the respective data of transfer constants resulting from investigations on model substances.²⁵

The different conditions of graft polymerization and, accordingly, the different quantities of homopolymer formed cause variations in the thermal transition points, in particular near the transition temperature of atactic polypropylene. Figure 2 shows the dependence of glass transition temperature of atactic polypropylene, measured by means of the DSC, on the grafting degree of polypropylene-vinyl chloride graft products unextracted. It indicates that in contrast to atactic polypropylene-vinyl chloride graft polymer freed from homopolymer and obtained by radiation grafting,²⁶ the glass transition temperature decreases with rising grafting degree of vinyl chloride to temperatures lower than that of pure atactic polypropylene of 258 K.

The reason for this behavior, which is also observed with a number of impact-resistant polymer combinations such as for example ABS,²⁷ is the different temperature dependence of the expansion coefficients of the two polymers and the incorporation of polypropylene particles in the poly(vinyl chloride) matrix by vinyl chloride grafted. The decrease of glass transition temperature is found with both rising grafting degree and decreasing rubber content. This gives evidence of the fact that, for example, products with grafting degrees of 0.022 and 0.16 reassume the glass transition temperature of 258 K if remeasured after extracting the poly(vinyl chloride) component with dimethyl formamide.

The properties of graft product blends of VC on atactic polypropylene with other polymers, with emphasis on poly(vinyl chloride) and ABS are of particular interest.

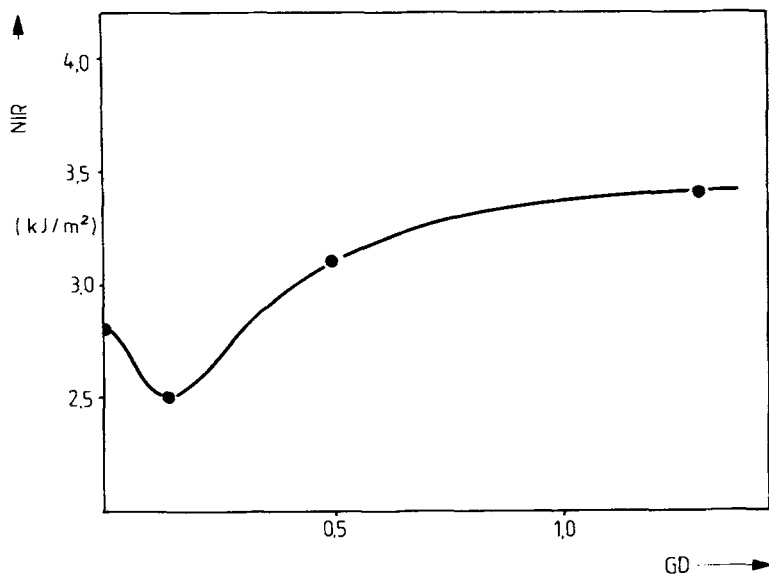


Fig. 3. Correlation between notch impact resistance (NIR) and grafting degree (GD) of the blends of polyvinyl chloride with polypropylene-vinyl chloride graft products.

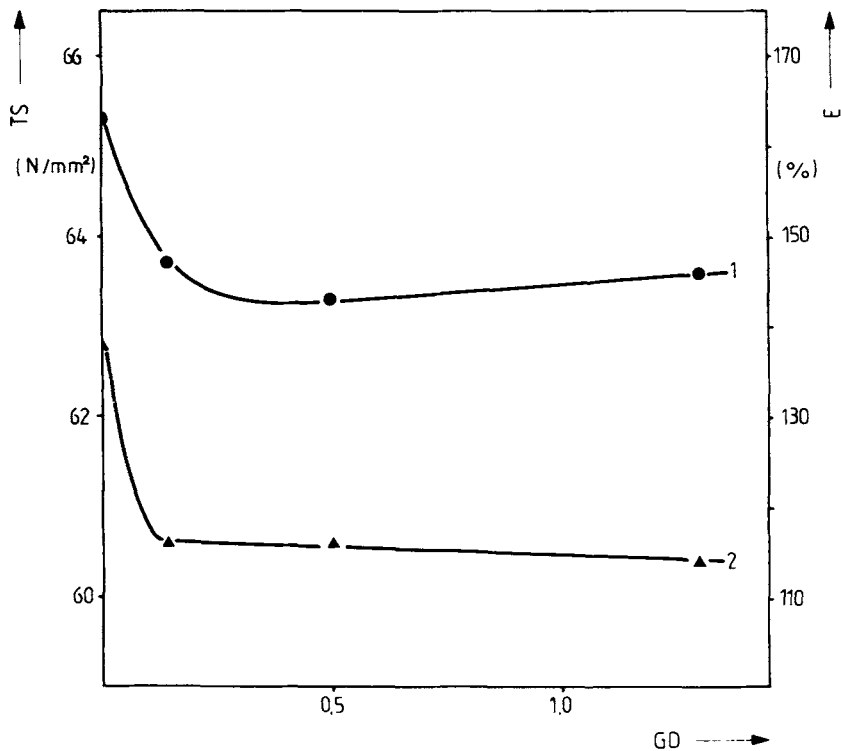


Fig. 4. Dependence of tensile strength (TS, 1) and elongation (E_1 , 2) on the grafting degree (GD) of polypropylene-vinyl chloride graft products in blends with polyvinyl chloride.

For graft product blends including normal suspension poly(vinyl chloride) of the Fikentscher K value of 60, the dependence of notch impact resistance on the grafting degree of the graft polymer at 296 K and at constant atactic polypropylene content of 1 wt % found in the blend is shown in Figure 3. The slight drop of notch impact resistance at low grafting degree compared to pure poly(vinyl chloride) is attributed to the linkage of the polypropylene phase to poly(vinyl chloride) being still inadequate. After this slight drop, the notch impact resistance increases with rising grafting degree. This increase along with the grafting degree is typical of numerous impact-resistant polymer systems such as impact-resistant polystyrene.²⁸ As compared with pure poly(vinyl chloride) (vide ordinate), the decrease in tensile strength and elongation is only low and, with rising grafting degree, the two items remain relatively constant (see Fig. 4). The melt flow index (463 K, 212 N) drops from 8.0 to 6.0 g/10 min at a grafting degree of 1.3, indicating the increased melt viscosity. A decrease in tensile strength and an increase in melt viscosity have also been observed with vinyl chloride graft products obtained through peroxidized atactic polypropylene and blends of poly(vinyl chloride) with chlorinated atactic polypropylene.^{15,29,30} The use of graft polymers of

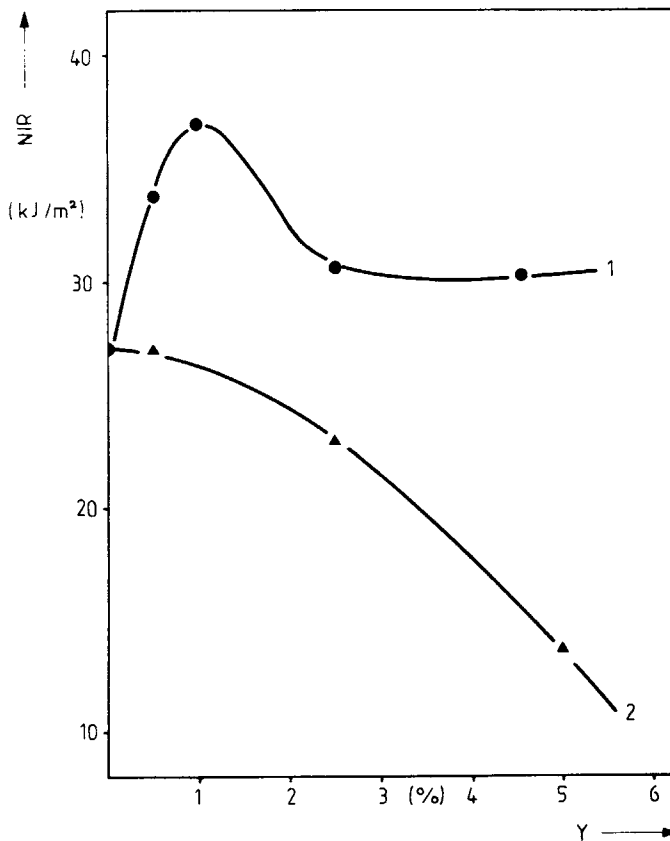


Fig. 5. Correlation between notch impact resistance (NIR) and content (Y) of polypropylene-vinyl chloride graft product (1) and atactic polypropylene (2) in blends composed of polyvinyl chloride and ABS.

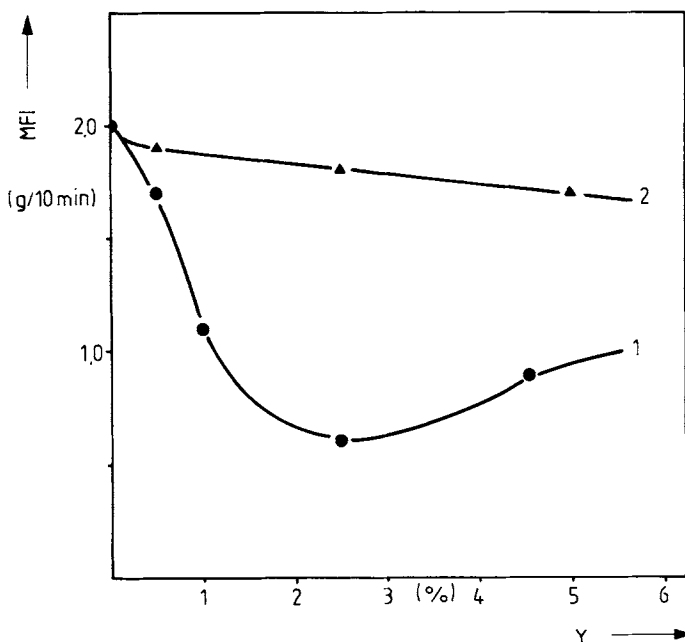


Fig. 6. Dependence of melt flow indices (473 K, 49.05 N, MFI) on the content (Y) of polypropylene-vinyl chloride graft product (1) and atactic polypropylene (2) in blends composed of polyvinyl chloride and ABS.

vinyl chloride on atactic polypropylene blended with polyvinyl chloride and ABS, enables the preparation of homogeneous products with increased thermal stability and notch impact resistance.³¹

For the blends consisting of 60 wt % ABS and 40 wt % poly(vinyl chloride), Figure 5 indicates the dependence of notch impact resistance on the amount of added polypropylene-vinyl chloride graft product at 293 K while the poly(vinyl chloride) content is reduced in comparison with the addition of pure atactic polypropylene. The graft product used had a content of 82.5 wt % of vinyl chloride and an average grafting degree of 1.15. It can be seen that in comparison with a pure poly(vinyl chloride)/ABS blend (vide ordinate) the maximum notch impact resistance is reached at nearly 1 wt % of graft product added whereas, with the addition of pure polypropylene, the notch impact resistance decreases immediately. This may be due to the linkage of polypropylene to poly(vinyl chloride) through grafting.

The dependence of melt flow indices (473 K, 49.05 N) on the added amount of atactic polypropylene or graft product, shown in Figure 6, indicates only a negligible effect on the flowability of the ABS/poly(vinyl chloride) melt in case of pure polypropylene while, with the addition of graft polymers, the melt flow index becomes substantially lower, showing an increased melt viscosity similar to the above blending with only poly(vinyl chloride).

Bending strength and tensile strength are less effected by addition of atactic polypropylene or graft product (see Fig. 7). Especially, in case of a higher amount of atactic polypropylene, both items decrease extremely in

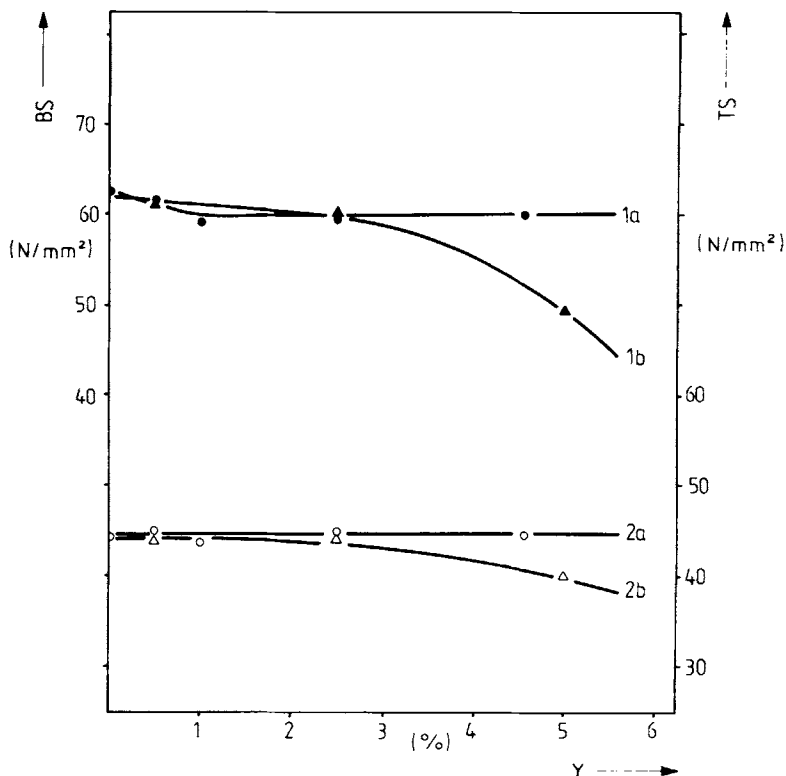


Fig. 7. Correlation between bending strength (BS, 1), and tensile strength (TS, 2) and content (Y) of polypropylene-vinyl chloride graft product (a) and atactic polypropylene (b) in blends composed of polyvinyl chloride and ABS.

contrast to that of the graft polymer blends, which may account for a relatively higher polypropylene amount, among others.

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