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PEROXIDE GRAFTING OF POWDERED POLYPROPYLENE BY BUTYL ACRYLATE

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ABSTRACT

The efficiency of the grafting of powdered polypropylene (PP) by butyl acrylate (BA) initiated by tert.-butylperoxy-2-ethylhex-

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as a ratio of the grafted and polymerized monomer was relatively high during the whole course of the reaction and it does not decrease under 0.5. The relatively high polymerization rate and also grafting efficiency at the beginning of the reaction is refered to the gel effect - the monomer is absorbed in the amorphous part of the powdered PP. With increasing the content of monomer in the reaction feed, the content of unsoluble cross-linked polymer increased as the consequence of the radical cross-linking of polybutylacrylate chains. The mechanism of grafting of powdered PP by BA is discussed.

INTRODUCTION

Polymer grafting by polymerizable monomers has long been studied for its possibility of influencing the properties of polymer materials. Our selection of butyl acrylate was based on the possible combination of thermoplastic properties of polypropylene with elastomer properties of the polymerized grafting monomer similarly as it had been done elsewhere [1].

General ideas on the mechanism of peroxide grafting are known but detailed knowledge about the relative significance of competition reactions under various experimental conditions for particular modification procedures is lacking. The interaction of the low-molecular-weight peroxide compounds with polypropylene and polybutyl acrylate chains proceeds by several consecutive reactions, like fragmentation but also branching and crosslinking of macromolecules [2-8]. In addition to these complex reactions that cause changes in molecular weight, there also occur structural transformations on the polypropylene chain where the length and the shape of macromolecules do not change. It is the formation of the double bonds in a macromolecule [9] or the hydrogen substitution on the chain for larger groups originating from the radicals of peroxide compound.

The properties of the final product depend strongly on the degree of homogeneity of butyl acrylate-grafted polypropylene and on the adhesion at the interphase of unequal polymers and macromolecular chains. Both physical factors determining the resulting properties will again be strongly affected by the selected conditions of the chemical modification of polymer like temperature, distribution of grafting monomer and peroxide in polymer particles at the start of radical reaction. Also, the ratio between the rate of polymerization and ß-scission of PP chains – both are dependent on the diffusion rates of reactants. The solubility of butyl acrylate, its diffusion rate and also grafting efficiency increase with temperature. So in a certain temperature region a better homogeneity and also phase stability of the system can be expected. On the other hand, at higher temperature, the rate of homopolymerization also increases, and it is able to compete with the rate of the transport of the monomer to polypropylene and thus to raise the inhomogeneity of the final product. A complete scheme of the process of PP grafting with BA has not been published till now due to the complex nature of the process in the solid phase. Our present study should be a contribution for better understanding of this process.

We have chosen the measurement of grafting efficiency and the melt flow index of the modified polymer as a method for evaluating the influence of the variable parameters on grafting and the resulting properties.

EXPERIMENTAL

Materials

Polypropylene powder as an unstabilized product of Borealis AG, Austria (Daplen-B) was used. Polymer was kept in a container in a nitrogen atmosphere. MFI = 0.28 g/10 min.

Tert. butylperoxy-2-ethylhexanoate (TBPEH) was used as a commercial product of Peroxidchemie.

The inhibitor of polymerization was removed from butyl acrylate (commercial product of Chemapol) and from divinylbenzene (commercial product of Merck) before use by washing with a sodium hydroxide water solution (5 wt%) and after separation, monomers were distilled *in vacuo*.

Procedures

Peroxide solution in the monomer was homogeneously impregnated into powdered polypropylene by intense mixing in a glass reactor in a nitrogen atmosphere (2 hours). The grafting was done in sealed glass ampoules (7 ml) in an inert atmosphere. After the selected time of annealing, the ampoule with a sample was cooled, opened and washed with hydroquinone-containing ethanol. Then, the polymer was dried and conversion of the polymerized butyl acrylate was determined from weight differences. To determine the amount of grafted monomer, the dried sample was dissolved in hot xylene, the inhomogeneous solution (with a low content of insoluble gel) was then allowed to cool to 20ºC, grafted and non-grafted polypropylene precipitated and butyl acrylate homopolymer remained in the solution. A solution of homopolymer was filtered off and the insoluble part of polymer was washed several times with xylene at laboratory temperature and dried in a vacuum drier to constant weight.

The crosslinked portion was determined by extraction of the pressed sample in boiling xylene.

The amount of grafted monomer, **m**, in wt% onto polypropylene was determined from the weight increase after grafting according to the equation

$$\mathbf{m\% = \frac{a - b}{c} \;.\; 100}$$

a - amount of the polymerized monomer

b - amount of the extracted homopolymer

c - the whole amount of the grafted polypropylene after extraction of polybutyl acrylate

Grafting efficiency was calculated as a ratio between the grafted monomer and the polymerized monomer.

Melt flow index (MFI) of the stabilized modified polypropylene was determined by a standard method with non-automatic apparatus at 230ºC, 2.16 kp.

The composition of the crosslinked part of the grafted PP with both monomers (BA and DVB) was calculated from the results of elemental analysis of the non-soluble rest of the samples after extraction with boiling xylene.

RESULTS AND DISCUSSION

Time Dependence of Grafting Efficiency

The conversion of butyl acrylate and the data on grafting efficiency (Table 1, Figure 1) show inconsistencies. Looking for instance at the determined grafting efficiencies in Table 1, in addition to the scatter of the results, certain tendencies are identifiable. Relative grafting efficiency is already reached at low BA conversion.

The mentioned observation can be explained by a rapid polymerization of butyl acrylate in swollen polypropylene. The acceleration of the polymerization as well as grafting in swollen polymer is conditioned by higher viscosity in the place of reaction [10, 11] but also the ratio of propylene units to butyl acrylate higher than in the capillary system of polypropylene particles with pure monomer. A new rise in grafting efficiency at almost complete monomer con-

TABLE 1. Time Dependence of the Conversion of the Polymerization of Butyl Acrylate and the Efficiency of its Grafting in a Matrix of Powdered Polypropylene and at Initiation with Tert.Butylperoxy-2-Ethylhexanoate (37 mmol/kg feed) and the initial monomer concentration of 20 wt% at 98°C.

Reaction Time [min]	Formed PBA [wt%]	Conversion of Monomer [wt%]	Grafted PBA [wt%]	Efficiency of Grafting
2	6.6	33	5.0	0.76
3	5.7	29	4.6	0.81
4	6.7	34	6.2	0.93
5	7.1	36	5.7	0.80
6	12.3	62	7.8	0.63
7	14.5	73	9.4	0.65
9	17.1	86	11.1	0.65
11	17.3	87	8.7	0.50
15	17.6	88	12.4	0.71
45	17.9	90	13.3	0.74
75	18.6	93	14.4	0.77
105	18.5	93	14.8	0.80
135	18.3	92	14.4	0.79
165	18.3	92	14.3	0.78
195	18.4	92	14.7	0.80
210	18.4	93	15.5	0.84

version of about 10% can be explained by additional crosslinking of homopolymer polybutyl acrylate macromolecules. The calculated value of the grafting efficiency is partially influenced by the insoluble crosslinked polybutylacrylate, which does not need to be bound to the PP chains. The results of grafting at lower temperature (Table 2) and of the block polymerization of butyl acrylate, where formation of insoluble gel was also detected, are also in accord with the idea of additional crosslinking after polymerization of the present polymer. With the increasing content of the crosslinked polymer, the melting flow index of the modified polymer decreases as expected.

The Influence of the Initial Monomer Concentration and the Temperature

Generally, the increase of the efficiency with the increasing conversion of the polymerized monomer in homogeneous systems, where additional

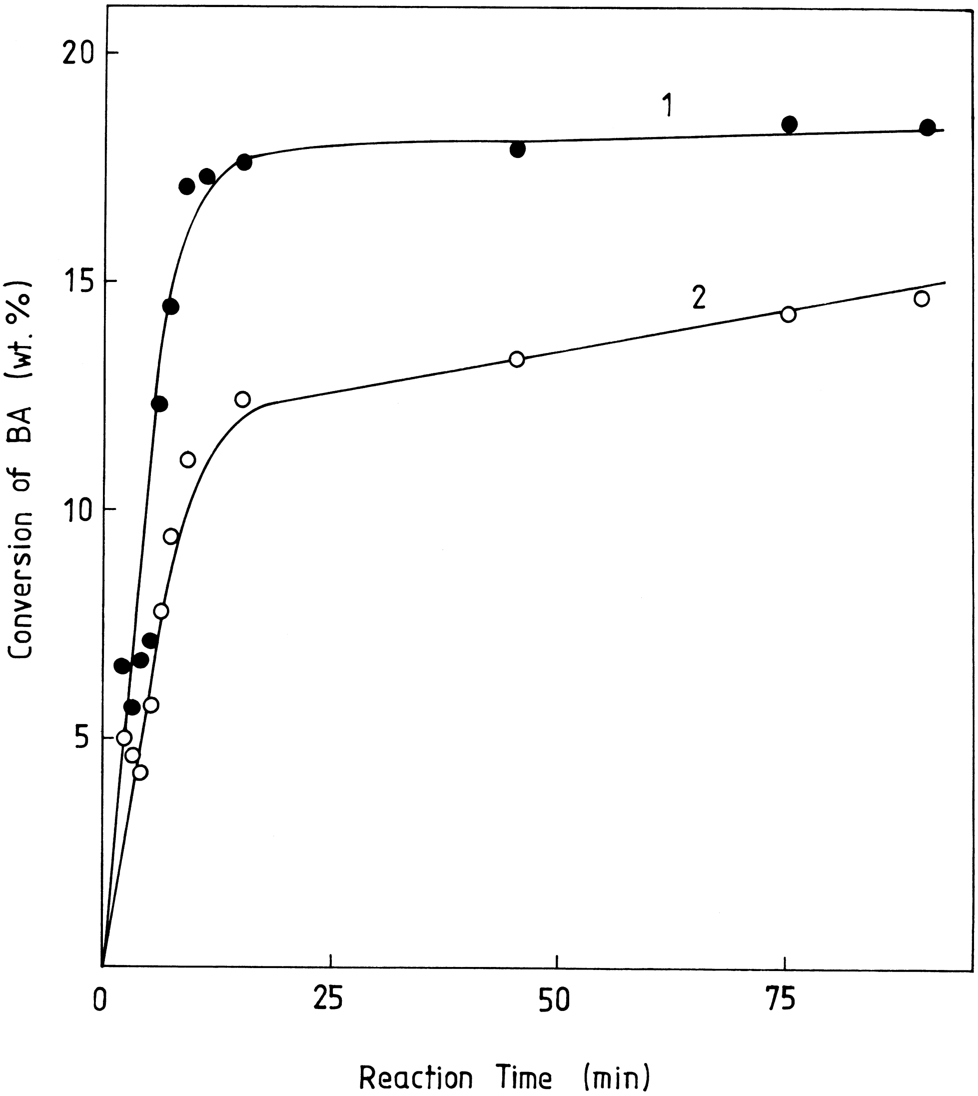

Figure 1. Time dependence of wt% of all polybutyl acrylate formed (1) in polypropylene powder and wt% of grafted polybutyl acrylate (2) branches at 20 wt% of the initial monomer concentration tert.butylperoxy-2-ethylhexanoate was used as initiator, the concentration of 37 mmol/kg of reaction mixture for butyl acrylate (98°C).

TABLE 2. The Values of the Monomer Conversion to Polybutyl Acrylate (Grafted and Homopolymer PBA), of the Content of Insoluble Part and MFI During Grafting with Butyl Acrylate ([BA] = 20 Wt%) Initiated with Tert.Butylperoxy-2-ethylhexanoate (37 mmol/kg feed) at 90°C.

Time [min]	FORMED PBA [wt%]	Conversion of PBA [wt%]	Grafted PBA [wt%]	Efficiency of grafting	Insoluble part [wt%]	MFI[a] [g/10 min]
5	7.8	39.0	6.5	0.83	4.2	11.5
10	14.2	71.0	9.8	0.69	6.9	2.5
15	17.2	86.0	11.3	0.66	4.4	0.5
20	17.8	89.0	13.3	0.75	6.5	0.4
30	17.9	89.5	9.6	0.54	3.1	0.4
60	18.1	90.5	11.2	0.62	8.6	0.4
120	18.3	91.5	12.0	0.66	11.7	0.3
420	18.2	91.0	13.1	0.72	11.9	0.3

[a] MFI of non-grafted iPP = 0.28 g/10 min.

crosslinking does not take place, follows from the gradual increase in the ratio of the monomer units of polymer and the grafting monomer. The increase in this ratio of concentrations should be accompanied by an increase in the portion of radical reactions of the initiator with polypropylene in comparison with butyl acrylate; the result should be the rise in the initiation rate of grafting to the detriment of the homopolymerization of the present monomer.

If the results of grafting are compared with different initial concentration of butyl acrylate in polypropylene powder (Table 3) we see an increase in grafting efficiency with the increasing concentration of butyl acrylate in the reaction feed. These results confirm the hypothesis already mentioned concerning the additional crosslinking, particularly of polybutyl acrylate chains. The increase of the gel content in the modified polymer is substantially greater than the increase in butyl acrylate concentration in the reaction system. Higher gel content may be interpreted by the mutual recombination of polybutyl acrylate macroradicals and by the transformation of unstable tertiary alkyl (poly-propylene) radicals (in an addition reaction with butyl acrylate monomer) into secondary macroradicals which are less reactive to fragmentation.

TABLE 3. The Effect of Butyl Acrylate (BA) Concentration on Grafting Efficiency, The Amount of Crosslinked Polymer (Gel) Formed, and Melt Flow Index (MFI), Using Tert.butylperoxy-2-ethylhexanoate (TBPEH) (37 Mmol/Kg Feed) as Initiator

BA [wt. %]	**Reaction temperature** [°C]	**Reaction time** [hours]	**Formed BA** [wt. %]	**Grafted BA** [wt. %]	**Efficiency of grafting**	**Gel** [a] [wt. %]	**MFI** [b] [g/10 min]
10	**70**	70	9.2	5.3	0.53	0	0.20
	80	21	9.2	6.0	0.60	0	0.20
	90	7	9.3	6.8	0.73	0.7	0.08
	98	3.5	9.3	6.5	0.70	0.8	0.08
20	**70**	70	18.9	15.0	0.79	0.05	0.13
	80	21	18.7	15.3	0.82	0.1	0.13
	90	7	18.9	16.8	0.89	9.9	0.08
	98	3.5	18.3	16.1	0.88	8.9	0.09
30	**70**	70	22.9	18.0	0.79	19.8	0.14
	80	21	28.2	23.5	0.83	17.3	0.12
	90	7	27.9	26.0	0.93	38.0	0.09
	98	3.5	27.4	26.7	0.98	82.0	0.08

a) After extraction in boiling xylene for 14 hours.
b) MFI of non-grafted iPP = 0.28 g/10 min.

The grafted products show lower MFI values than the starting material which is in line with the crosslinking of the modified polymer and with the stabilization mechanism for polypropylene (reaction of unstable polypropylene macroradicals with butyl acrylate) during the grafting, initiated by decomposition of peroxide. This suggestion would also account for the fact that at 30 wt% of butyl acrylate, the gel content is higher than the amount of polymerized monomer (Table 3); this means that polypropylene grafted chains joined the network structure.

The effect of temperature on the grafting efficiency is unambiguous. With the increasing temperature the grafting efficiency increases also in cases where the crosslinking as a side reaction can be neglected.

TABLE 4. The Effect of Divinylbenzene (DVB) Concentration on Crosslinking During Grafting of 20 Wt% of Butyl Acrylate (BA) on Powdered Polypropylene in a Sealed Ampoule. Grafting was Initiated with Tert.butylperoxy-2-ethylhexanoate (37 Mmol/Kg Mixture) for 7 Hours at 90°C.

DVB [wt%]	**Grafted BA** [wt%]	**Insoluble Part** [a] [wt%]
0	14.8	11.9
0.05	16.8	19.9
0.06	16.7	16.7
0.07	16.6	16.6
0.08	16.7	17.4
0.09	17.0	17.1
0.10	17.1	17.9

[a] After extraction in boiling xylene for 14 hours.

Crosslinking by Multifunctional Comonomer

Already in the presence of 0.05 wt% divinylbenzene all polymerized butyl acrylate is crosslinked in grafting feed (Table 4). Polypropylene chains enter the crosslinking structure only in a small measure as it is seen from the average value (0.8%) of the difference, which we obtain by subtracting % of polymerized butyl acrylate from % of insoluble product. We can also expect from the tendency of the effect of the rising concentration of divinylbenzene on the amount of bound polypropylene that the crosslinking comonomer does not increase the grafting efficiency. It is even probable that under the effect of the crosslinking agent butyl acrylate gel is formed in the crosslinked structure of polybutyl acrylate in the capillary system of the polypropylene powder grains already in the first phases of polymerization. Multifunctional monomer can thus accelerate the polymerization of butyl acrylate by the mechanism of the gel effect before additional swelling into the polypropylene matrix at increased temperature; this will result in lower grafting efficiency in comparison with the grafting without divinylbenzene.

One of the evident effects of the growing divinylbenzene concentration is the decrease in melt flow index of modified polymer. The melt flow index of the sample of butyl acrylate-grafted polypropylene without crosslinking agent is 0.076 g/10 min, at 0.05 wt% of divinylbenzene it is 0.02 g/10 min, and at 0.06

wt% only 0.01 g/10 min. It means that as the crosslink density in polybutyl acrylate increases, the melt flow index of the modified polymer decreases, which appears to be logical.

By evaluating the crosslinking structure of modified polymer a question is raised which type of crosslinks will prevail in the insoluble gel. In principle, it could be crosslinks between the chains of the same or chemically different polymer chains.

In the case of an admixture of multifunctional monomer, under the conditions similar to our experiment, it seems that the dominant crosslinked bridges will be formed by divinylbenzene between butyl acrylate units.

In the absence of multifunctional monomer in the polymerization feed, the situation is little more complicated with respect to smaller differences in the reactivity of the precursor of crosslinked bonds. Polypropylene chains can be crosslinked as it is known in peroxide crosslinking but, more efficiently, through acrylate segments as it follows from the study of the preparation of an IPN system of similar structure [4] and from the results of the block polymerization of pure butyl acrylate. In our experiment, during initiation with tert.butylperoxy-2-ethylhexanoate (185 mmol/kg) and at 90°C in a sealed ampoule under nitrogen, polybutyl acrylate block will be formed with the content of 30 wt% of crosslinked product. After 7-hour annealing, which is the majority of the time of peroxide decomposition in the polymer already formed, as much as 71% of polymer from the original weight of butyl acrylate is crosslinked. Next to the crosslinks between acrylate monomer units there are also crosslinks of chemically unequal segments since grafting and probably also recombination of unequal macroradicals proceeds there. Moreover, the difference in the reactivity of the precursors of crosslinking is balanced by concentration ratios of particular reactants under the conditions of grafting applied, which will support the formation of crosslinks between unequal polymer chains.

Composition of the Crosslinked Proportion

The concept of the formation of crosslinked product at grafting of PP is leant on the chemical analysis of the not soluble proportion of the grafted PP (Table 5). For determining the crosslinking mechanism of BA/DVB system model experiments with considerably higher DVB-content were carried out. From the data on the carbon and hydrogen content of the elemental analysis of the samples, the number of butyl acrylate units in the network structure was calculated.

TABLE 5. The Influence of Crosslinker Concentration (Divinylbenzene - DVB) I in the Mixture with Butyl Acrylate (BA) (30 Wt%) Onto Crosslinking of Grafted Polypropylene and the Content of BA in Non-Soluble Gel (NG) Using Tert. butylperoxy-2-ethylhexanoate (TBPEH) (37 mmol/kg feed) at 90°C (reaction time 7 hours).

DVB in Feed [wt%]	Amount of Grafted Monomers [wt%]	Amount Of NG [wt%]	Amount of BA in NG [wt%]
0.5	27.2	22.7	82.9
1.0	27.5	22.5	73.4
1.5	27.6	26.2	69.5
2.5	27.9	28.2	66.8

The increase of divinylbenzene from 0.5 to 2.5 wt% as a crosslinker leads to the increase of PP chains in the crosslinked grafted product from 17 to 33%. The explanation is based on the presence of the higher concentration of divinylbenzene in PP phase, which takes place also during the crosslinking of PP. The solubility of nonpolar bifunctional monomer in PP prevents the fragmentation of alkyl macroradicals and incorporates PP into the network structure of the modified product.

The Effect of Polar Comonomer

The additional functionalization of polybutyl acrylate chains through copolymerized carboxyl groups can be of various types. It is useful to know well in advance how the process of the grafting of butyl acrylate itself will be affected by an admixture of polar monomer.

From the realized experiments (Table 6), a smaller effect of the monomer concentration on grafting efficiency can be derived, which appears to be, probably by mistake, higher than in the absence of acrylic acid (Tables 2 and 3); most probably it is due to the worse copolymer solubility in cold xylene. The entry of the polar monomer into the non-polar matrix should be slower and to a lesser degree and, therefore, it should support the formation of heterogeneous regions in the modified polymer and thus lower the grafting efficiency.

TABLE 6. Characteristics of Grafting of Polypropylene with Butyl Acrylate in the Presence of Acrylic Acid (Always 5 Wt% in All Experiments) Initiated with Tert.-butylperoxy-2-ethyl-hexanoate (37 mmol/kg reaction mixture)

Reaction temper. [°C] / **Reaction time** [min]	**BA** [wt.%]	**Copolymer**		**Efficiency of grafting**	**MFI** [a] [g/10 min]
		Total [wt. %]	**Grafted** [wt. %]		
90 / **420**	**10**	9.1	7.7	0.85	0.03
	20	19.3	17.2	0.89	0.01
	30	22.0	19.5	0.89	0.02
98 / **210**	**10**	10.5	9.5	0.91	0.02
	20	13.9	11.2	0.81	0.03
	30	28.8	27.0	0.94	0.13

a) Values for non-extracted samples of modified polypropylene
MFI of non/grafted iPP = 0.28 g/10 min.

From among the results listed in Table 6, the low conversion of the polymerized monomer (only about 70% instead of above 90%) that is difficult to explain, should be commented. The difference will be caused by partial solubility of the more polar copolymer in ethanol at which unreacted monomers should have been removed from the reaction mixture. The expected solubility of a part of non-grafted copolymer can then elucidate the higher calculated efficiency of grafting as compared with the results from the grafting of pure butyl acrylate, since it is the ratio between % of grafted polymer and the overall conversion that is at issue. On the other hand Table 6 shows that the ratio of BA/AA has practically no influence on the grafting efficiency.

The presence of copolymerized acrylic acid in modified polymer lowers generally the melt flow index (c. f. the data in Table 6 and Tables 2-3); this is apparently associated with greater intermolecular forces, particularly with the possibility of the formation of hydrogen bonds between carboxyl groups.

CONCLUSION

The efficiency of butyl acrylate grafting onto powdered polypropylene changes with the conversion level of monomer due to a competition between the monomer diffusion and the rate of polymerization under the gel effect.

The observed unexpected increase of grafting efficiency with the increased feed concentration of BA results from additional crosslinking of polybutyl acrylate chains.The presence of divinylbenzene as a nonpolar crosslinker in grafting feed increases the amount of PP segments in the network of the modified product.

Copolymerization of acrylic acid with butyl acrylate substantially lowers the melt flow index of grafted PP.

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