Mechanochemical Grafting of Some Inorganic Supports

INTRODUCTION

The increase in the chemical reactivity of polymers and inorganic crystalline compounds by mechanical dispersion has been reported. Generally, the fresh surfaces obtained by vibratory milling have been used as grafting supports and demonstrated the mechanism of this process[1-5] and a method to make new products with important applications.[6-11]

This note deals with the mechanochemical grafting by vibratory dispersion of some inorganic compounds used as filling materials in the PVC processing to improve some mechanical properties.

EXPERIMENTAL

Grafting was carried out on a vibratory mill of the LS-60 type VEF Kefama Katzutte, Thürnigen, East Germany, fitted with stainless steel grinding bodies. The reaction vessels were equipped with a thermostatic jacket and 9 mm diameter balls used as grinding bodies.

The process parameters were the following: the filling ratio 0.50%; temperature 18 ± 2°C; the inorganic support/monomer ratio 1:1.

Mica, kaolin, and volcanic tuff were used as inorganic supports, which were previously dried at 100 ± 5°C and introduced simultaneously with the monomer into the reaction vessels. The vibratory milling was carried out in inert medium using a technique previously described.[11]

Acrylonitrile (AN), methyl methacrylate (MeM), and vinyl chloride (VCL) were used as monomers. The acrylonitrile and methyl methacrylate freshly purified were volumetrically measured while the liquid vinyl chloride (cooled with liquid nitrogen), measured with a special dosing device, was poured at room temperature into the reaction vessel, where it turned into the gaseous state.

The reaction product was treated with methanol, filtered, and the solid product dried under vacuum in order to remove the methanol and traces of unreacted monomer. The product obtained was successfully used as filling material in the PVC processing. The homopolymers were removed by extraction in a Soxhlet apparatus in solvents such as dimethylformamide (DMF), benzene (B), and cyclohexanone (CH).

The grafting reaction was characterized by estimating the conversion and grafting degrees.

RESULTS AND DISCUSSION

The conversion degree was calculated according to the equation

$$\text{conversion } \% = (A/B) \times 100$$

where A = the amount of the product obtained after milling (g) and B = the initial amount of monomer and inorganic support (g).

The data obtained were used for plotting the conversion degree vs. time. They represent ascending lines which are assigned to the development of the mechanosynthesis reactions, which shows a maximum value followed by a descending line owing to the mechanodegradation process.

In the case of polyacrylonitrile grafted on kaolin, mica, and volcanic tuff (Fig. 1), the conversion degrees are maximum at 72 h. The effectiveness order of the grafting process given by conversion degree is: kaolin > mica > volcanic tuff.

Besides the variation of the conversion, the modification of the grafting degree against the conversion was also followed. The grafting degree was calculated accordingly to the equation

$$\text{grafting degree } \% = (b/a) \times 100$$

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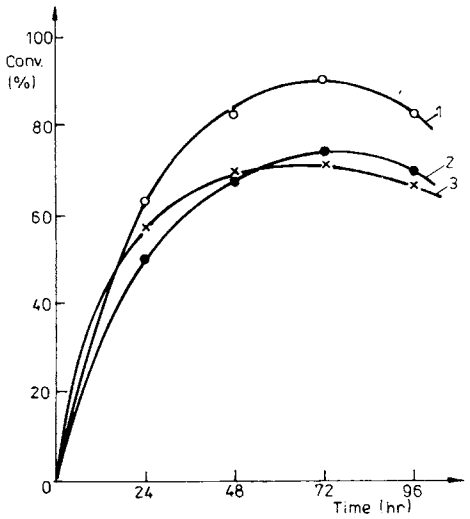

Fig. 1. The conversion degree variation as a function of grinding duration: (1) PAN grafted on kaolin; (2) PAN grafted on mica; (3) PAN grafted on volcanic tuff.

where a = the total quantity of polymer (g) and b = the quantity of grafted polymer after extraction of the homopolymer (g).

The variation in grafting degree vs. time for the inorganic supports grafted with PAN (Fig. 2) is depicted. The maximum values appear as in the case of the conversion degrees at 72 h.

The homopolymer extracted in DMF, for PAN grafted onto one of the three inorganic supports (volcanic tuff) at different grinding durations were reprecipitated in a nonsolvent (methanol) and after drying at 100°C were used for the determination of the molecular weight by the viscosimetric technique.

The Clealand and Stockmayer relation for PAN in DMF at 25°C was used[12]:

$$[\eta] = 2.43 \times 10^{-4} \overline{M}_v^{0.75}$$

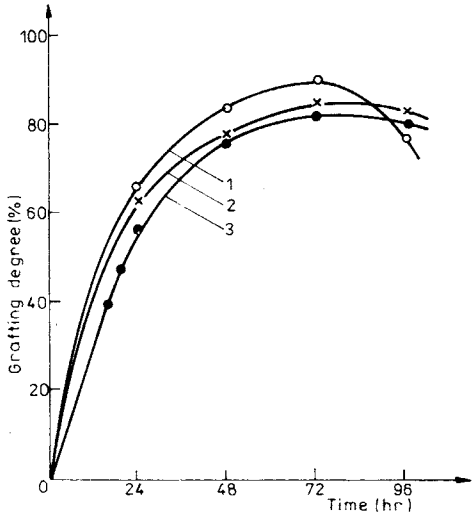

Fig. 2. The grafting degree variation as function of grinding duration: (1) PAN grafted on kaolin; (2) PAN grafted on mica; (3) PAN grafted on volcanic tuff.

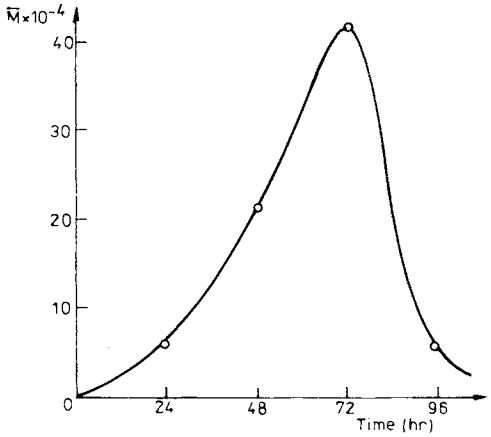

Fig. 3. The molecular weight variation of polyacrylonitrile extracted as a function of reaction duration.

The intrinsic viscosity was obtained by extrapolating the η_{sp}/C plot, at infinite dilution. As a result of these measurements, the molecular weight values of nongrafted PAN were obtained (Fig. 3).

These results are in good agreement with those concerning the reaction duration with conversion variation, supporting the hypothesis that mechanosynthesis processes predominated and in the second descending one the mechanodegradation reaction becomes more intense. The grafted polymers were used as filling materials in order to obtain plates of hard PVC.

The homogenizing of PVC with the fillers and other ingredients was performed on the roller mixer. The mixings were carried out on a roller mixer at 170°C, for 10 min, parameters which ensured a good homogenization of the polymer with the ingredients. The recipe for making a hard material contains 100 g PVC-S, $K_w=67$, 1.5 g lead soap, 1.5 g lead tribasic sulfate, 0.6 g stearine, and 0.5 g. calcium stearate. The films obtained by roller mixing were pressed in

TABLE I
Physicomechanical Characteristics of PVC with and without Filling Materials (Up to10%)

Sample	Tensile strength (kgf/cm²)	Izod impact strength (kgf cm/cm²)	Elongation at break (%)
Standard sample	624	5.39	13.5
PVC + kaolin	531	5.21	10.0
PVC + PAN grafted on kaolin (72 h grindings)	587	9.69	10.4
PVC + PMeM grafted on kaolin (72 h grindings)	610	6.04	8.5
PVC + PVC grafted on kaolin (72 h grindings)	566	8.74	10.4
PVC + volcanic tuff	552	2.48	11.0
PVC + PAN grafted on volcanic tuff (72 h grindings)	570	9.72	12.0
PVC + PMeM grafted on volcanic tuff (72 hrs grindings)	605	5.6	10.5
PVC + PVC grafted on volcanic tuff (72 h grindings)	685	8.86	12.5

a mold (200 × 200 mm) at 170°C and 175 atm for 10 min (preheating) + 10 min (pressing), yielding plates of 0.5 and 1.0 mm thickness.

The samples removed from plates were tested for Izod impact strength, elongation at break, and tensile strength. The experimental data given in Table I present the physical and mechanical characteristics of PVC with and without fillers. The impact strength increases when PAN is grafted on volcanic tuff. The other characteristics such as the elongation at break and the tensile strength have values close to the standard sample, some of them being even higher (in the case of PVC grafted on volcanic tuff).

SUMMARY

This paper presents experimental results concerning the grafting of some monomers on the inorganic supports by vibratory milling.

The conversion and grafting degree depend on the time and the nature of the inorganic support. The products obtained may be successfully used as filling materials in PVC processing, leading to the improvement of some of its properties.

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