CHLORINATED POLYPROPYLENES

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Abstract

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As was noted by Natta and co-workers ([1]), when chlorine reacts with crystalline polypropylene, white brittle substances are formed (the degree of brittleness depends on the chlorine content), which slowly split off chlorine at 80–100°. At a considerable chlorine content, complete disruption of the regular structure occurs.

The conditions of synthesis and the properties of the products as a function of the chlorine content in the polymer have not been described.

In this connection, it was of interest to investigate in more detail the process of chlorination of polypropylene obtained on the catalytic system $Al(C_2H_5)_3$ and $TiCl_4$ (I) (33% amorphous fraction and 45% isotactic fraction), and of the polymer obtained on the catalytic system $Al(C_2H_5)_3$ and $TiCl_3$ (II) (7% amorphous fraction and 85% isotactic fraction).

Chlorination was carried out in chlorobenzene medium in the presence of initiators (radical donors) or without them.

For 1 liter of chlorobenzene, 45–50 g of polypropylene were taken, and at 45° gaseous chlorine was introduced through a bubbler at a rate of 40–45 g/hour. After this, the temperature in the reactor was raised to 75–80° and maintained at this level throughout the entire process. If the reaction was carried out in the presence of initiators, then during the whole reaction 0.28 g of azobisisobutyronitrile or another compound readily generating radicals at the experimental temperature was added every hour.

The polymer was isolated from the solution by precipitation with alcohol (for example, methanol) or by distilling off the solvent with steam.

Figure 1 gives the kinetics of chlorination of polypropylene (I) and (II) in the presence of initiators (curves 2 and 1, respectively) and of (I) without an initiator (curve 3). The use of an initiator increases the rate of the process, especially for polypropylene with a higher content of the isotactic fraction. We did not succeed in reaching the elemental composition $(C_3H_3Cl_3)_n$ under these conditions even with prolonged chlorination in the presence of an initiator.

When chlorine is introduced into the polymer, sharp changes occur: the material obtained first cakes together (10–15.0% Cl), then passes through a stage of fibrous material, corresponding to a polymer of the structure $(C_3H_5Cl)_n$ (40–50% Cl), and finally, with further treatment, a noncombustible powdery material

is obtained. In accordance with the increase in chlorine content in polypropylene, the solubility of the material increases, the viscosity decreases (especially in the presence of an initiator, Fig. 2), and the density increases (Figs. 3, 2). All the samples obtained proved to be amorphous under electronographic examination.

The decrease in the intrinsic viscosity of polypropylenes (I) and (II) indicates rupture of the polymer chain at the C–C bond (chain destruction). The increase in the density of the chlorinated polypropylenes permits the assumption that after introduction of 30-35% chlorine both polymers acquire the same or mutually similar structure, whereas the general structure of the initial···

of the polymers differed substantially in their content of amorphous and isotactic fractions, which affected the density of the initial samples (density (I) was 0.89 ± 0.005, and density (II) 0.92 ± 0.005).

Interesting results were obtained from measuring the softening temperature of chlorinated polypropylenes as a function of chlorine content. At low chlorine content in the polymer, the softening temperature

[Figure 1 and Figure 2]

Fig. 1. Kinetics of chlorination of polypropylenes: 1–(II), 2–(I) in the presence of dinitrile of azoisobutyric acid, 3–(I) without initiator

Fig. 2. Change in polymer viscosity as a function of chlorine content: 1–(I), 2 –(II))

of the samples decreased, after which, with further introduction of chlorine into the polymer molecule, it began to increase and, at a chlorine content in the polymer of 65-66%, rose to 200° and higher (Fig. 3, 1). The polymer containing 15-20% chlorine had the lowest melting temperature, i.e., the polymer in which the side CH_3 groups contain less than one chlorine atom.

[Figure 3]

Fig. 3. Change in melting temperature (1) and density of samples (2) as a function of chlorine content

If it is assumed that all chlorine atoms replace hydrogen only in the side CH_3 groups, then, obviously, the decrease in temperature is due to disruption of the highly regular structure of the polymer, owing to the interaction of weakly positive CH_3 groups with negative CH_2Cl groups. When the number of CH_2Cl groups exceeds 1/3–1/2 of all side CH_3 groups present, the polymer molecule apparently can again become more regular, evidently because of mutual repulsion of similarly charged CH_2Cl groups, which begins to lead to an increase in the melting temperature of the polymer. When only CH_2Cl groups are present in the polymer, the polymer acquires the melting temperature of the isotactic product (165-175°). Upon introduction of two chlorine atoms into the CH_3 groups, polypropylene acquires a distinct melting temperature of about 200°.

Fig. 4. Thermomechanical curves of chlorinated polypropylene

Figure 1: Fig. 4. Thermomechanical curves of chlorinated polypropylene

Further introduction of chlorine proceeds extremely slowly; moreover, the softening temperature of the polymer increases still more, and the polymer itself becomes increasingly brittle.

The analogous phenomena observed in the chlorination of both isotactic and atactic polymers can also be explained by the possibility of replacement of hydrogen by chlorine at a tertiary carbon atom, which causes disruption of the regular spatial orientation of the substituents in the macromolecule and destruction of the crystalline structure.

Similar results are also obtained in the study of thermomechanical properties on Kargin' s balance (Fig. 4). The thermomechanical test data show a fairly distinct melting temperature of the samples.

Chlorinated polypropylenes with a chlorine content in the polymer chain of more than 45% have no highly elastic region, and from the glassy state pass immediately into the viscous-flow state.

Fig. 4. Thermomechanical curves of chlorinated polypropylene (penetration of a punch 3 mm in diameter; load 740 g/cm^2, $\tau = 10$ sec. 1 –original, 2 –23.0% Cl, 3 –36.5% Cl, 4 –49.2% Cl, 5 –56.5% Cl, 6 –59.0% Cl, 7 –61% Cl, 8 –64.0% Cl, 9 –65.4% Cl)

Like all chlorine-containing polymers, samples of chlorinated polypropylene (I) and (II) are prone to easy evolution of gaseous HCl. Thus, the samples studied, with an average chlorine content of about 60% (polymer of the structure $(C_3H_4Cl_2)_n$), readily split off HCl already at 108-123° (according to Congo red). The usual stabilizers used for stabilizing polyvinyl chloride sharply raised the decomposition temperature of the chlorinated polypropylenes.

Thus, the addition of 4% calcium stearate raised the decomposition temperature to 171-173°, soybean-oil epoxide to 174°, and lead silicate to 188°.

It should be noted that the stabilized and then reprecipitated samples again had a low decomposition temperature (on the order of 118-130°).

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CITED LITERATURE

1. G. Natta, P. Pino, G. Mazzanti, *Chim. e Ind.*, **37**, No. 12, 1934 (1955).

Note: Figure translations are in progress. See original paper for figures.