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BRIEF COMMUNICATIONS

Melting of Polyolefins in Presence of Liquids

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Abstract—The existence of a section with a constant melting point in the curve of melting polyolefins in presence of a liquid was confirmed experimentally by the method of differential scanning calorimetry.

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Earlier [1, 2] the examination of special features of the processes of melting and formation of polymer crystallites allowed us to substantiate the viewpoint, according to which in the phase diagram of unrestrictedly mixing systems amorphous-crystalline polymer–liquid (see the figure) there is a section inside which the melting point T_m of the polymer is independent of the high-molecular component content ω_2. In other words, if the initial heterogeneous mixtures contains ω_b or more mass fractions of a liquid, the polymer becomes completely amorphous at the same temperature.

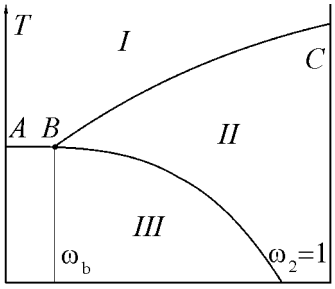
This viewpoint is supported by the differential scanning calorimetry data.

Melting points of polyolefins at various contents of a polymeric component in a system

LDP–toluene		PP-*o*-xylene	
ω_2, wt %	mp	ω_2, wt %	mp
0.5	66.7	–	–
1.0	67.2	–	–
3.2	66.6	4.1	102.7
4.3	67.0	9.2	105.2
8.8	67.7	10.5	103.3
15.0	70.4	17.3	104.9
19.4	70.8	24.4	104.4
32.6	78.1	30.5	108.9
46.4	84.5	52.6	130.0
77.6	98.2	77.4	148.1
100	110.6	100	168.7

EXPERIMENTAL

Subjects of the study were: low-density polyethylene (LDP) 15803-020-grade with melting point of 110.6 ± 0.5°C, density of 0.920 g cm^{-3} at 25°C (determined by the floatation method), and melt index of 1.32 ± 0.05 g/10 min; polypropylene (PP) (technical specifications 2211-015-00203521-99) with melting point of 168.7 ± 0.5°C, density of 0.906 ± 0.001 g cm^{-3} at 25°C, and melt index of 1.29 g/10 min; chemically pure-grade toluene and *o*-xylene. The densities and refraction indexes of those latter estimated on a DMA-4500 densitometer and an IRF-454B2M refractometer corresponded to reference data.



Phase diagram of the system amorphous-crystalline polymer–liquid (scheme). Curves: *ABC*: melting of last crystallites of a polymer, *BD*: solubility of a liquid in a polymer. Areas: (*I*) single-phase system (molecular mixture of a liquid and a polymer free from net sites in the form of crystallites), (*II*) single-phase system–solution of a liquid in an amorphous-crystalline polymer (gel), (*III*) two-phase system (pure liquid + solution of a liquid in an amorphous-crystalline polymer). Explanations in the text.

Melting points of polymer systems in the presence of a liquid were determined on a Phoenix (NETZSCH) DSC 204 F1 differential scanning calorimeter. The calorimeter was calibrated by measuring temperatures and heat effects of phase transitions for 11 reference substances in the interval -86…476°C. A substance under study with a total weight up to 10 mg was placed in a molded aluminum crucible. The measurements were carried out in an argon flow with a heating rate of 10 deg min^{-1} relative to a base line recorded for two empty aluminum crucibles. The temperature corresponding to the melting peak maximum was accepted as a melting point of a polymer. The accuracy of the melting point determination was ±0.5°C.

The results of the fulfilled experiments for two investigated systems (LDP–toluene and PP–*o*-xylene) are given in the table. It is easy to see that in fact mp does not depend on the content of a polymeric component in a system in the region of mixtures enriched with a liquid, and the expansion of a section with mp = const is a function of the nature of a polymer and a solvent. So, mp constancy for the system LDP–toluene is retained up to a polymer content of about 5 wt % and for the system PP–*o*-xylene, approximately up to 25 wt %.

CONCLUSION

It was found that polyethylene and polypropylene become completely amorphous at the same temperature if certain amount of an organic liquid is contained in the initial heterogeneous mixtures.

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