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Synthesis of Acrylic Copolymer for Spray Plastic*

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Abstract

Properties of industrial copolymers were determined and the optimum ratios of monomers to obtain similar acrylic polymers were found. The effect of the composition of monomers on characteristic viscosity and relative hardness of acrylic copolymers based on methyl methacrylate and butyl methacrylate was studied. The optimum conditions for the synthesis of acrylic copolymer with required properties were defined. Spray plastic with good performance properties was developed

Keywords: butyl methacrylate, methyl methacrylate, bead copolymers, acrylic coatings, spray plastic

INTRODUCTION

One of the basic tools to ensure road traffic safety is road marking, *i.e.* lines, labels, and other markings on the roadway, elements of road facilities and furnishing of roads establishing the order of traffic showing the dimensions of road construction or indicate road directions made in accordance with GOST R 51256–99 and GOST R 52575–2006 requirements. Markings are accepted efficient, if they have the following properties: are well visible in any time of a day and under different weather conditions, stable to temperature changes, chemical and meteorological impacts, ensure vehicle wheel clutch to the road required for safe traffic; are quickly formed after application; have the required durability, *i.e.* have the required operation life.

Special paints, ceramic and clinker paving stones, porcelain chips, white polymer or cement concrete, coloured asphalt concrete, marking blocks and plates, metal buttons, thermoplastic, and other materials are currently used as marking materials. Road paints, thermoplastics, and spray plastics are most widely used. Service time of road marking is mainly determined by surface carry-over of solid species of composition materials due to weak interphase interaction. Furthermore, marking compositions are overfilled composition materials, therefore properties of a polymer matrix play a substantial part in ensuring the required durability.

Thermoplastic acrylic copolymers with a minor content of elementary units based on acrylic or methacrylic acid (Degalan, NeoCryl, *etc.*) are

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TABLE 1

Physical and chemical properties of NeoCryl-B-725 and Degalan LP 64/12 copolymers

Indicators	NeoCryl-B-725	Degalan LP 64/12
Molecular mass, g/mol	55 000	60 000
Melting point, °C	63	64
Softening point, °C	155	–
Relatve density,g/cm^3 at 20 °C	1.11	1.08
Solubility	Water-insoluble. Soluble in esters, ketones, aromatic and chlorinated solvents	Water-insoluble. Soluble in esters, ketones, aromatic and chlorinated solvents
Brookfield viscosity at 25 °C, mPa·s:		
– for 40 % solution in toluene	375	–
– for 40 % solution in methyl ethyl ketone	–	180
Acid number, mg KOH/g	8.0	6.0

increasingly used as such polymers in the production of road paints [1–3]. In this regard, it is advisable to establish the composition of monomers forming acrylic copolymers comparable to industrial ones by their properties.

EXPERIMENTAL

Acrylic copolymers were synthesized in solution. A specified amount of an appropriate monomer, benzoyl peroxide, and a solvent (butyl acetate) are placed into a three-neck flask equipped with a hermetically sealed stirrer, a reflux condenser, and a thermometer. Afterwards, flask content is heated in a water bath at 80 °C for 4–6 h until preparation of a syrupy product [4, 5]. The resulting copolymers were isolated by precipitation from solutions into heptane and dried to a constant mass. The IR spectra of acrylic copolymers were registered in the 4000–400 cm using Specord 75 IR spectrometer at room temperature by the procedures described in [6]. The content of volatile and nonvolatile compounds in the synthesized lacquers was determined by heating of a sample of the synthesized lacquer at a specified temperature to a constant mass [4]. The characteristic viscosity [η] was determined in toluene at 30 °C using the Ubbelohde viscometer [4].

Coatings from the synthesized lacquers were obtained by pouring in one layer followed by solidification at room temperature. Plates made of 08KP steel with a thickness of 0.2-2 mm were used as substrates for obtaining coatings. Metal surfaces were treated by the abrasive cloth N6 followed by rinsing with toluene. The relative hardness was determined by means of a pendulum device of Kening type [7].

The DSK curves of the synthesized copolymers were removed using DSC Q-200 TA device in the temperature range from −30 to 150 °C with a rise of the sample temperature at a rate of 5 °C [8].

RESULTS AND DISCUSSION

One of the main requirements for road marking paints is the drying time of the paint. According to the GOST R 51256–99 and GOST R 52575–2006, it should not exceed 30 min, therefore the initial condition of the acrylic copolymer used in paints plays an important role. Acrylic copolymers, such as NeoCryl-B-725 (Neoresins, Netherlands) and Degalan LP 64/12 (Degussa, Germany) are widely used in the composition of road marking paints. The NeoCryl-B-725 co-

TABLE 2

Additional properties of industrial acrylic copolymers

Samples	Characteristic viscosity	Relative hardness
NeoCryl-B-725	0.18	0.54
Degalan LP 64/12	0.20	0.51

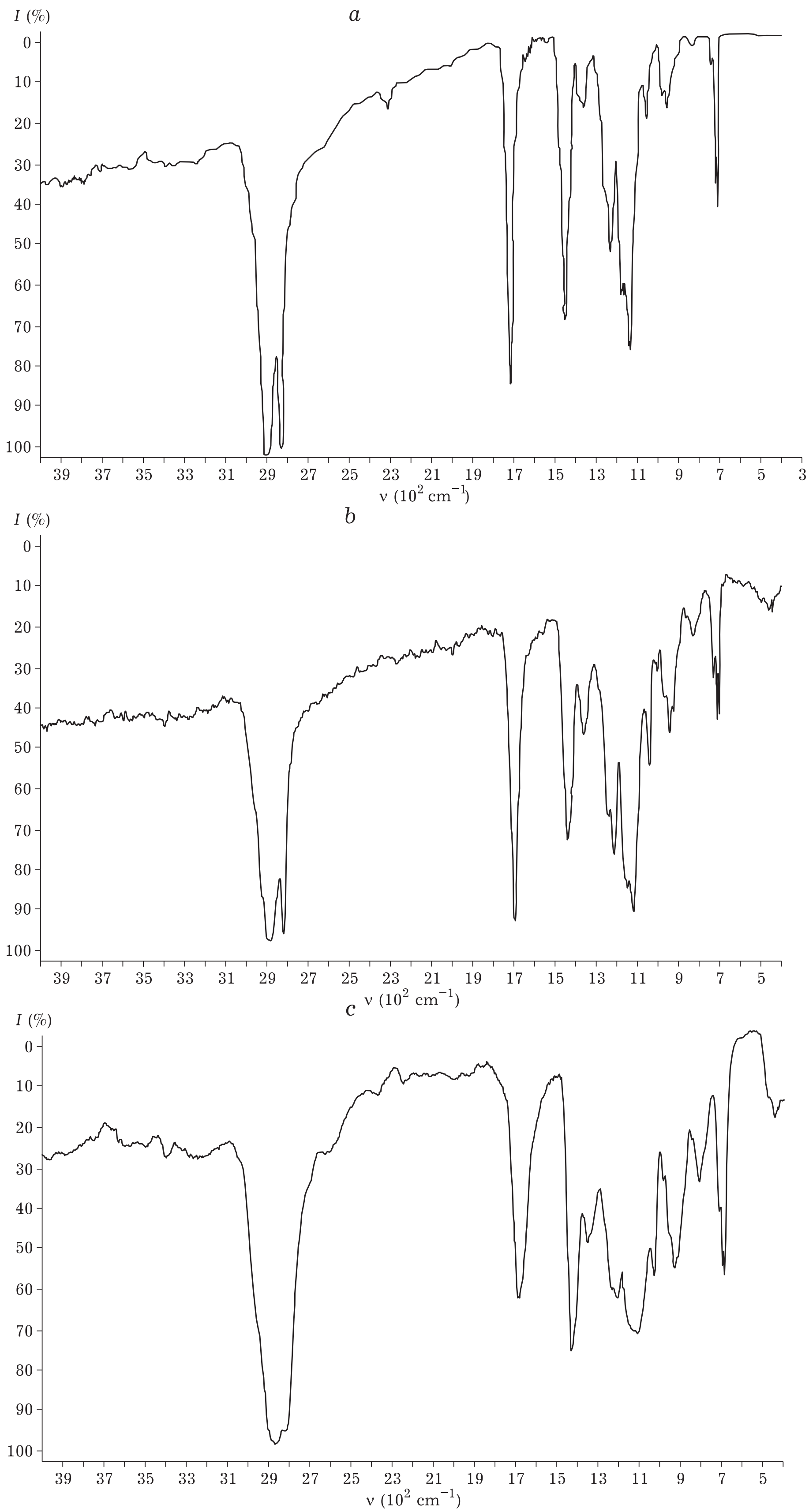

Fig. 1. IR spectra: *a* − synthesized copolymer (monomer ratio of 60 mass % of MMA, 40 mass % of BMA); *b* −Neocryl-B-725, and *c* − Degalan LP 64/12 copolymers.

TABLE 3

Properties of synthesized coatings and isolated copolymers

Monomer ratio, mass %	Initiator content, mass %	Dry varnish residue, mass %	Characteristic viscosity	Relative hardness
50 : 50	0.2	42.0	0.26	0.55
50 : 50	0.4	55.0	0.25	0.50
50 : 50	0.6	63.0	0.19	0.49
50 : 50	0.75	53.0	0.15	0.57

polymer is a readily soluble solid polymer based on methacrylic monomers (methyl methacrylate (MMA) and butyl methacrylate (BMA)). It is readily compatible with other polymers [9]. The Degalan LP 64/12 copolymer is a fine low-disperse low-dust white powder obtained on the basis of the same monomers. The Degalan LP 64/12 copolymer ensures good thermal stability, high weather resistance, and resistant original colour. Its good compatibility with many film-forming substances has been noted [10].

Table 1 gives physicochemical properties of NeoCryl-B-725 and Degalan LP 64/12 copolymers described in [9] and [10].

To obtain copolymers similar to NeoCryl-B-725 и Degalan LP 64/12, MMA/BMA ratio should be clarified to ensure properties analogous to the data of Table 1.

Figure 1 gives IR spectra of the copolymer synthesized by us, and also those of NeoCryl-B-725 and Degalan LP 64/12 copolymers. The infrared spectra were removed from samples prepared by lacquer application onto thin polyethylene films followed by solvent evaporation. It can be seen that all three IR spectra are almost identical.

As reference points, Table 2 gives additional characteristics of industrial acrylic copolymers (characteristic viscosity [η] at 30 °C and a relative hardness of lacquer coatings).

Thus, there had been determined a property set that the acrylic copolymer synthesized by us should have.

The optimum benzoyl peroxide content during synthesis was determined according to characteristic viscosity value that should be close to the data of Table 2. The MMA/BMA ratio was 50 : 50 mass parts. The content of benzoyl peroxide varied within 0.2–0.75 mass parts.

As can be seen from the data in Table 3, the characteristic viscosity of the polymer obtained with a content of benzoyl peroxide of 0.6 mass % is most close to that of industrial copolymers. Herewith, relative hardness does not depend heavily on initiator content. Therefore to obtain the acrylic copolymer with similar hardness, syntheses of copolymers with different monomer ratios are given. Figure 2 gives characteristic viscosity and relative hardness versus MMA content in the composition of monomers.

It can be seen that a coating based on the synthesised copolymer with a monomer ratio of 60 mass % MMA and 40 mass % of BMA with a content of benzoyl peroxide of 0.6 mass parts to 100 mass parts of monomers has the relative hardness most close to industrial analogues. The acrylic copolymer with a characteristic viscosity of 0.19 and a relative hardness of 0.56 was obtained under these conditions.

Figure 3 gives DSK curve for the resulting monomer; the melting point acquired according to DSC data is 60.64 °C, which is almost identical

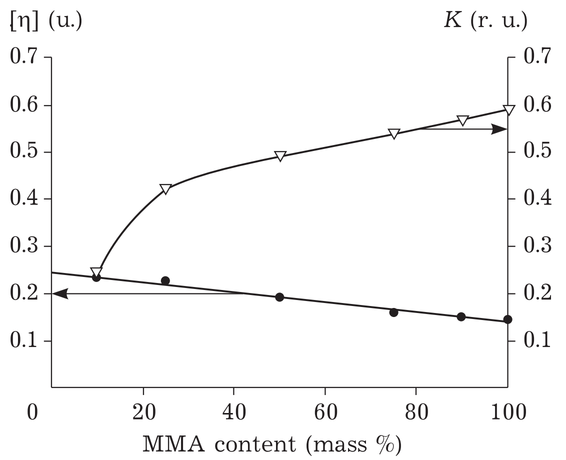

Fig. 2. Characteristic viscosity [η] and relative hardness *versus* MMA content in the composition of the monomers.

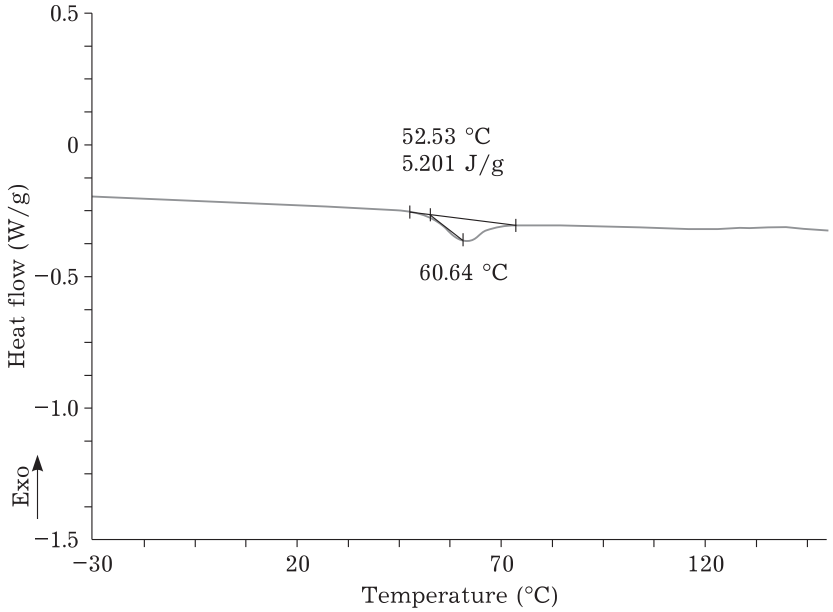

Fig. 3. DSC curve of polymer synthesized with monomer ratio of 60 mass % of MMA and 40 mass % of BMA.

TABLE 4

Characteristics of cold spray plastic RoadStreet-CP (TU 5217-010-83458073−2012)

Indicators	Requirements of GOST R 52575−2006	Test results
Coating colour	White, yellow. It should be within accepted deviations determined by reference samples of colour	Respond
Coating appearance	Smooth, uniform, opaque structure (without pockmarks, drips, wrinkles, and foreign inclusions)	Respond
Coating density, g/cm^3	1.9−2.1 ((Subsection 2)	1.9
Condotional viscosity at (20.0+0.5) °C, according to VZ-246 viscometer with a nozzle diameter of 4 mm, s	80−200	115
Rubbing degree by wedge method, μm, no more than	40	30
Mass fraction of non-volatile matter, %, no less than	75−95	78.2
Water adsorption, %, ±0.002	Not normalized	0.005
Coating resistance to static action:		
− of water at (20±2) °C, no less than	72	Respond
− saturated aqueous solution NaCl при температуре (0±2)°C, no less than	72	Respond
− 3 % NaCl at (0±2) °C, no less than	72	Respond

to the data for industrial samples (see Table 1).

Research results were used in the development of cold spray plastic RoadStreet-CP (TU 5217-010-83458073–2012), characteristics of which are given in Table 4.

CONCLUSION

Thus, research results in the area of synthesis of acrylic copolymers led to the development of industrial grades of marking materials. For example, cold spray plastic RoadStreet-CP (TU 5217-010-83458073–2012) was developed; its performance properties correspond to requirements of GOST R 52575–2006.

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