EFFECT OF IONIZING RADIATION ON PROPERTIES OF ACRYLIC PRESSURE SENSITIVE ADHESIVES

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Abstract

Pressure-sensitive adhesives for technical application are widely produced. The biological properties of adhesive depend on the type of monomers used. The available literature date as experience of the authors of this study in the area of pressure-sensitive acrylic adhesive, polymers used in medicine, polymerisation in aqueous media, radiation sterilization, permit to make an assumption that it is possible to elaborate the technology of production of pressure-sensitive adhesives in aqueous emulsion, for medical application[1]. Identification of phenomena influencing the adhesive properties, especially its adhesion, cohesion, tack and durability is of great importance. The control of polymers structure is performed by means of adequate selection of conditions of synthesis and parameters of radiation processing. The authors investigate the influence on the final products of such factors as the type and amount of monomers used, their mutual ratio as well as the ratio monomers and as the dose of ionising radiation. There is no available literature information concerning the investigation of resistance of acrylic emulsion adhesive to sterilisation by electron beam. It is know from unpublished research that some adhesive are resistant to radiation, while others undergo destruction. It depends probably on the composition of emulsion specifically on the additives which modify adhesives. Simultaneous *achievement of good cohesion and adhesion in the case of such type pressure sensitive* adhesives is very difficult.

PRESSURE SENSITIVE ADHESIVES FOR MEDICAL APPLICATION

Pressure sensitive adhesives for medical application (sticking plaster) should be resistant to radiation sterilization. Both the pressure sensitive adhesive and its substrate would be unaffected by sterilization doses of fast electron. The existing technologies of manufacturing of pressure-sensitive adhesives with improved properties consist in the synthesis in organic solvents. Copolymers of acrylic acid and 2-ethylhexyl acrylate is

following glues utilized in medical peoducts. The control of the polymer structure is possible by means of adequate selection of conditions of synthesis: temperature, amount of initiator and the type and amount of the cross-linking agent). The radiation resistant glue should hold its adhesive properties, such as: adhesion, tack and cohesion. These properties depend on fine polymer structure. The glue parameters are examined as follows:

- adhesion - by measuring of force needed to failure the glue joint between smoothed chromium steel plate and adhesive plaster of 25 mm width. Adhesive plasters for medical applications should have the adhesion within the range 3 to 7 N/25 mm - peel adhesion;
- cohesion - by measurement of the time of deglutination of the adhesive plaster (glued to glass inside a thermostat at 70°C, and o.5 kg loading). The cohesion of medical use of adhesive plaster should be greater than one hour.
- tack - by measurement of the path length of roll of the steel ball accelerated from the inclined plane with a slope of 45 °. The steel ball should roll from 3 to 15 cm - along the glue surface of adhesive plaster - the tack rolling ball method.

Above the mentioned properties of the depends on many various factors. The adhesion and tack are connected with the diffusion of free polymer chains, Van der Waals interaction and an electrostatic attraction (of functional groups generated at the surface of glue layer). The cohesion depends on the molecular mass of the polymer. Assuming normalized measurements and the application of identical recipes, that the obtained parameters are a function of the averaged molecular mass of its statistical distribution. The adhesion and tack are larger at lower masses, and the cohesion is higher at larger masses.

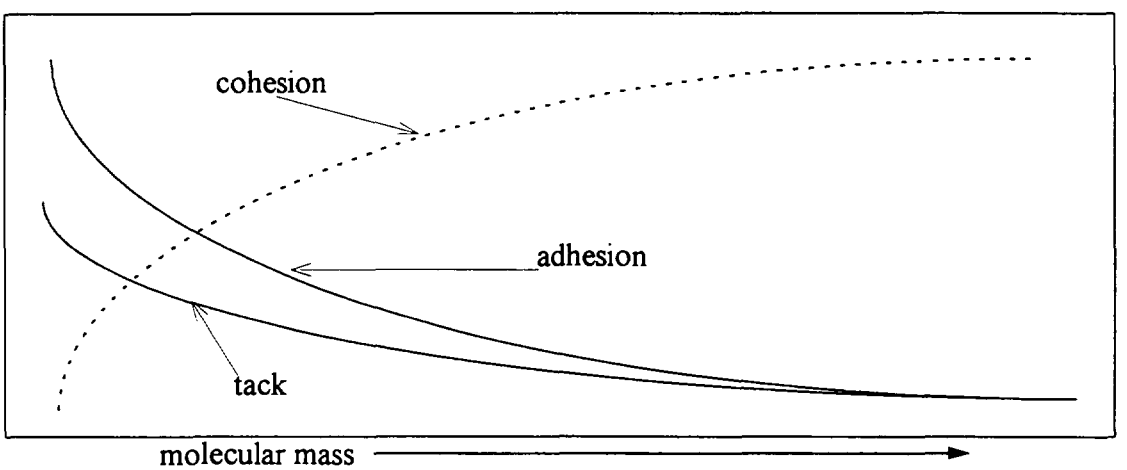

Fig.1. The main properties of pressure sensitive adhesive vs. molecular mass of used polymer, after [2]

Date in Fig.1. suggest that the glue having good properties should be characterised by a certain optimum molecular mass and its statistical distribution. The similar dependencies of glue properties as a function of molecular masses with more detailed data are presented in Fig.2.

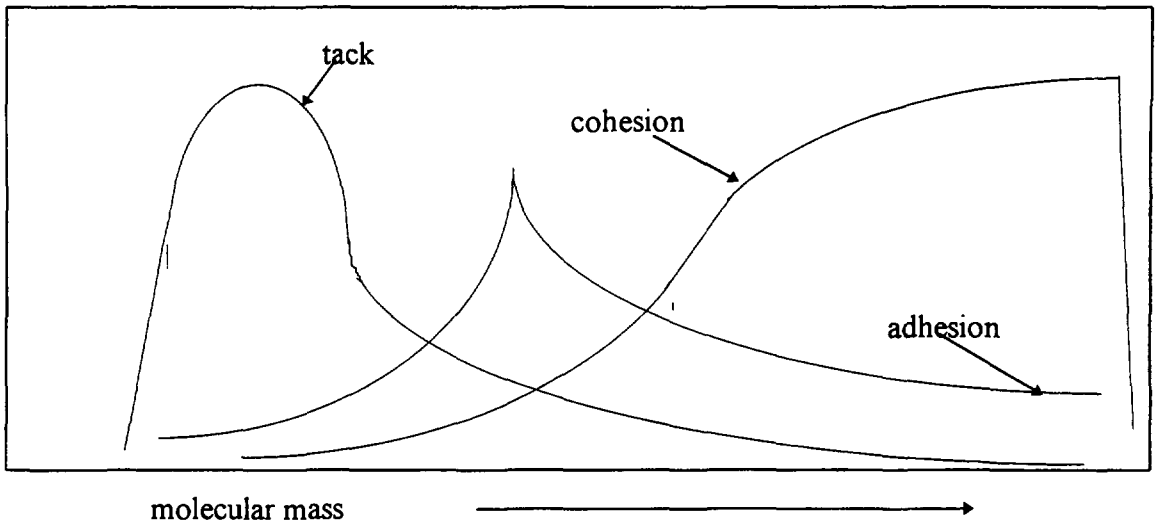

Fig.2. Relationship between the properties of self adhesive glue and the polymer molecular mass for wide range of change of molecular masses

RADIATION-INDUCED EMULSION COPOLYMERIZATION

The motivation for the work on the radiation-induced copolimerization was the considerable industrial interest in emulsion polymerisation and the high yield of free radicals from the radiolysis of water. The radical produced by the radiolysis of water are hydrogen atoms and, mainly, hydroxyl radicals. In addition, however radiation can attack the surfactant, the monomers and the polymer being produced causing some addition differences.

Initiation with radiation is essentially temperature independent. This leads to comparatively low temperature dependencies for the overall reaction, the activation energy dropping from about 20 for chemical initiation to any about 7 kcal/mol. This also means that copolimerization can be conducted at will at any temperature and at any initiation rate. Comparative studies of chemical and radiation polymerization of styrene in emulsion indicated that the molecular weight distribution was somewhat sharper with potassium persulfate initiation [3].

SAMPLES PREPARATION

The glue coats were prepared of various values of adhesion from 1 to 15 N/25 mm, and the cohesion test results within the range of 2 min up to above 1 hour. These samples were irradiated with a recommended dose of 25 kGy. Firstly the sample with worse properties was used for preparation of coat on the surface of polyester foil. Then the sample obtained by this way were irradiated with various doses from 20 to 40 kGy. All samples before and after irradiation were examined for the determination of: adhesion, cohesion and tack.

IRRADIATION PROCEDURE

The irradiations were conducted in a new electron beam facility for radiation sterilization of medical devices for single use (installed in INCT), applying an electron linacs LAE-13/9 and UELV-10-10-S-70-1 (Table 1). Both research and commercial irradiations were made by linear electron accelerator LAE 13/9 with electron energy of 10 MeV and approximate capacity of 10 million pieces of sterile products per year. New electron beam facility for radiation sterilization of single use medical devices was designed and build in 1992. 50-100 million pieces of sterilized devices per year is estimated capacity of this facility[4].

Table 1. Main technical characteristics of the UELV-10-10-S-70-1 electron linear accelerator, produced by the Research Production Association, TORIY, Russia.

Electron nominal energy	10 MeV
Electron energy instability	5%
EB current instability	5%
Average beam power	up to 10 kW
Pulse duration	4.5 μs
Repetition rate	25 to 400 Hz
Scan frequency	1, 2, 5 Hz
Scan line length	65 cm

Some sample were irradiated with increasing doses: of 20, 25, 30 and 35 kGy at conveyor velocities of: 53, 42, 36 and 30 cm/min respectively.

THE ACCELERATOR PROCESSING DOSIMETRY.

Calibrations of electron beam (EB) of linacs: LAE-13/9 and UELV 10-10-70-1 using calorimeters and routine dosimeters to be used in large scale sterilization and polymer cross-liking has been carried out. A series of graphite calorimeters Fig. 3. (equipped with thermistor detection of radiation-induced temperature rise) have been designed and manufactured for accurata dosimetric control:

- calorimetric bodies made of nuclear purity graphite have been manufactured,
- Styrofoam casings (thermal insulation) have been produced,
- thermometric thermistors have been calibrated,
- and a simple computer code for fast calculation of dose has been elaborated.

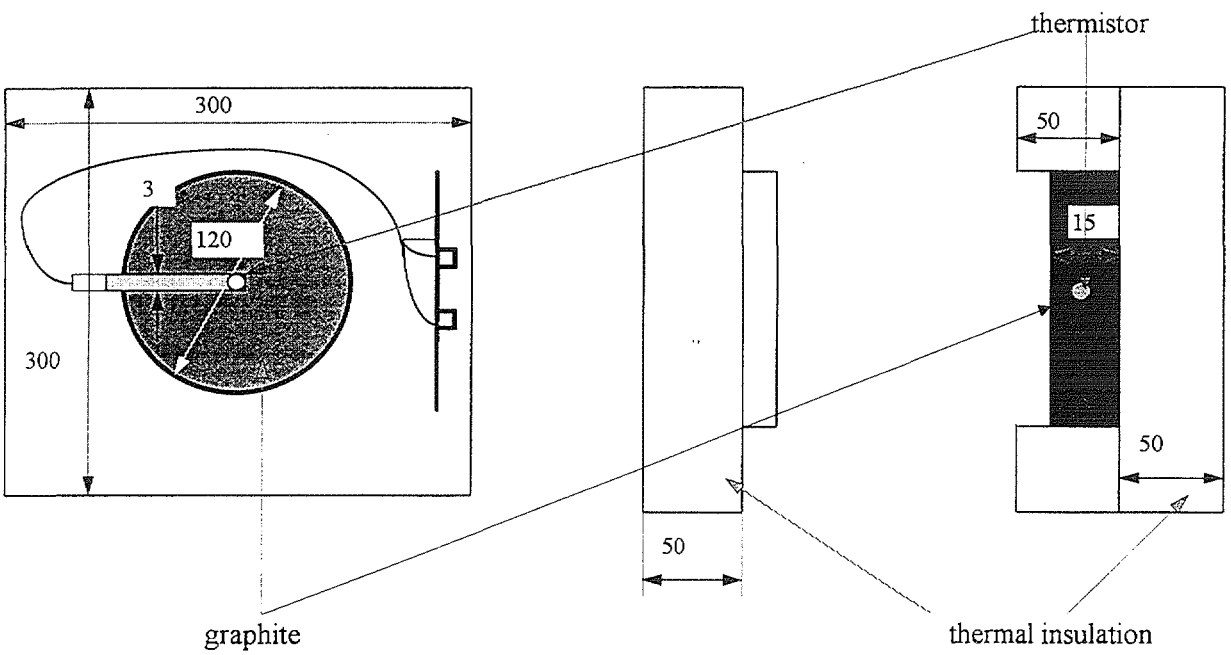

Fig.3. The graphite calorimeter

Using the above mentioned calorimeters measurements were performed of electron dose of the linacs LAE-13/9 and UELV-10-10-70-1 at a nominal energy of 10 MeV at a velocity of conveyors of about 42 cm/min. Parallel to calorimetric measurements routine evaluations of dose were performed in the range 10-40 kGy the typical doses for sterilization of disposable devices. For this purpose stripes on unplasticized PVC films were employed (spectrophotometric measurement of radiation-induced absorbancy at 395 nm).

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Irradiation results are shown in Tables 2 and 3.

Table2. Properties of glued coats for various samples of the glue, irradiated with dose of 25 kGy.

Run no.	***Before irradiated***		***After irradiated***	
	adhesion N/2.5 cm	cohesion (time)	adhesion N/2.5 cm	cohesion (time)
1	3.5-10	2 min	3.5-6.5	>1h
2	3.0-5.8	3h	3.6-4.8	3h
3	3.3-6.2	1h	3.6-4.8	1h
4	7.0-10	3h	7.3-9.0	.3h
5	3.0-5.8	7min	3.0-4.7	12h

Table 3. Properties of glued coats manufactured with a choose glue bath after the absorption of various doses.

Dose [kGy]	Adhesion N/2.5 cm	Cohesion (time)
0	3.5	33 min
22.9	3.5-6.2	>1h
26.1	3.5-5.7	>1h
31.1	5.0-7.2	>1h
38.5	3.0-4.5	>1h

Primary radical products products of radiation-induced, effects of acrylic copolimers can be studied by EPR spectroscopy. One of such effects is the creation of stable paramagnetic centers, whose nature and concentration can be analyzed by the electron spin resonance (ESR) method. Paramagnetic signal (Fig.4) observed in irradiated copolimer is ascribed to the radicals originated from the acrylic copolimes. Copolymer attacked by the radiation may changes structures leading to branching, cross- linking and other. Using radiolysis with spektrophotometrical detection some spacies were observed at about 300 nm. The mechanism of this reaction is still on progress.

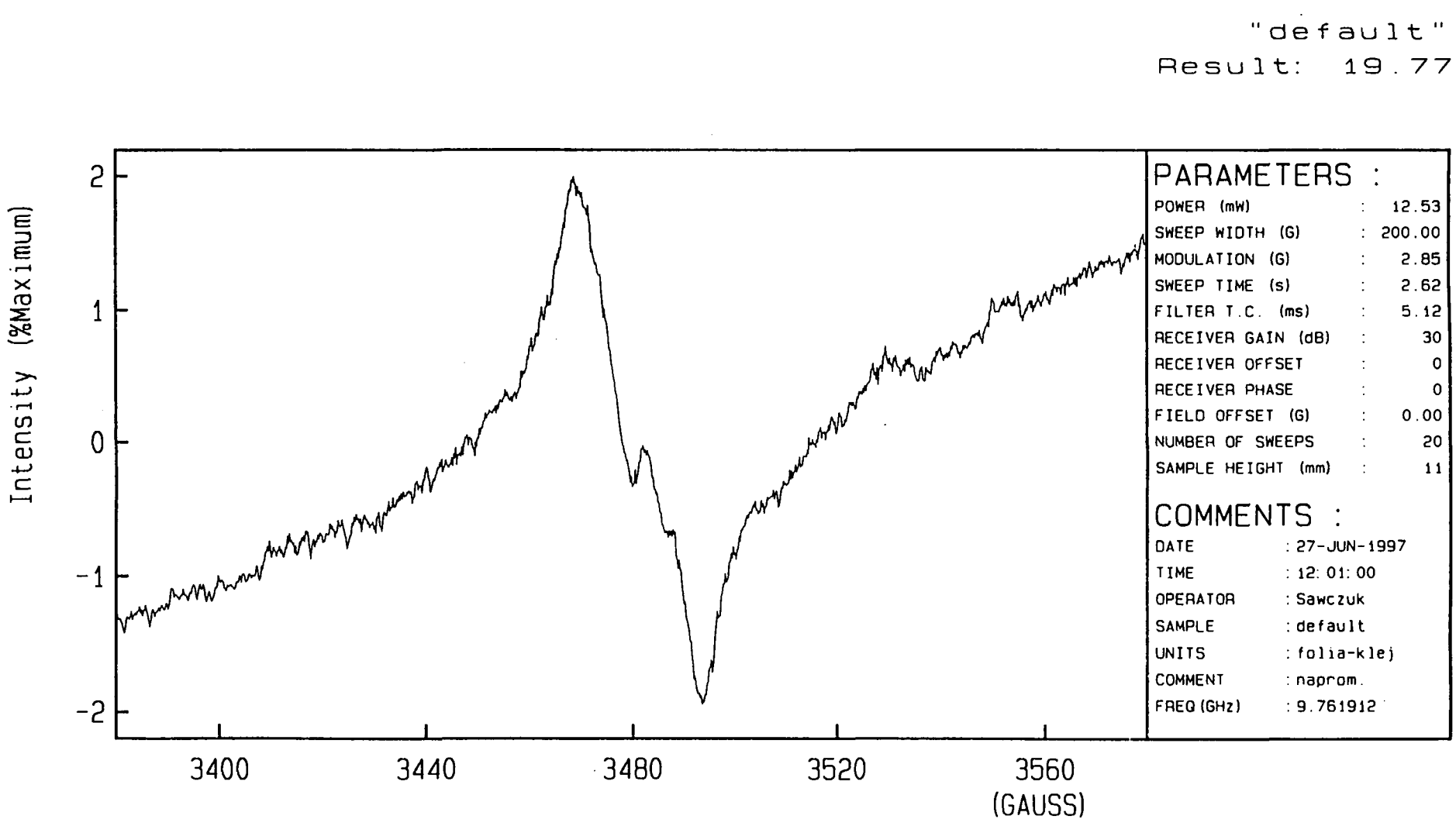

FIG.4. Paramagnetic signal observed in irradiated acrylic copolimer (dose 25 kGy)

CONCLUSIONS

- sticking plasters for medical applications prepared on the basic of the acrylic emulsion radiation are resistant up to a dose level of 40 kGy.
- properties of the irradiated glue are improved, the adhesive dose is not changing and the cohesion increases. The elaborated glue is suitable for sticking plasters or self adhesive tapes contacting with living human tissues.
- there are a number practical advantages associated with the use radiation - emulsion polymerization in comparison to traditional chemical initiation system:
  - high yield of free radicals from radiolysis of water,
  - the lack of any activation energy with the initiation reaction,
  - excellent distribution of free radicals in bath.

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