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Studies on organic binders with high infrared transparency*

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This paper reports that two kinds of polymers with high infrared transparency and good mechanical and physical properties have been prepared. An internal standard method is used to evaluate the infrared transparency of the binders. The physical and mechanical properties of the binders are measured according to corresponding standards. The results show the absorbance of polymer A in 8–14 μm range is 26% that of the ethylene-vinyl acetate copolymer (EVA), and polymer B is 9% that of the EVA correspondingly. The film of polymer A shows good flexibility of above 1 mm, a hardness of grade 1, and adhesion of grade 2. The film of polymer B shows good flexibility of above 1 mm, a hardness of grade 1, and adhesion of grade 1.

Keywords: infrared transparency, adhesion, hardness, internal standard
PACC: 7800, 7830, 8190

1. Introduction

As technology becomes available to give high-quality images in real time, the threat of surveillance in thermal infrared (IR) wavebands is of increasing concern.[1] There are two thermal IR "windows' where radiation from objects can be transmitted through the atmosphere, at wavelengths of 3 to 5 and 8 to 14 microns.[2] The former waveband is known as the 'intermediate IR' and the latter as 'far IR'. The far IR enables much clearer imaging of objects whose temperature is close to the ambient background, whereas the intermediate IR region is used when the object is much hotter than the surroundings, such as with hot exhaust pipes. For the targets without a power source, the waveband of IR camouflaging is focused on 8 to 14 μm wavebands.[3]

Thermal radiation is emitted by a target as a result of its temperature, and as the temperature increases, the target emits energy at a shorter wavelength. There are differences of thermal radiation between army targets and the natural background. Detection of a target by IR detectors depends on the difference of thermal infrared signatures between the target and background. Therefore, IR camouflage is mainly to suppress the thermal infrared signatures of targets to an ambient clutter level. Research efforts are underway to develop two suppression techniques: one is to control the radiation temperature of a target by thermal isolation materials such as foamed polyurethane or phase-change material. Alternatively, the emissivity of coatings covered on the surface of a target is controlled to approach that of the surroundings. Now researchers all over the world are focusing on patches with high, middle and low emissivities. These patches show varied thermal patterns even though their temperature is uniform. Therefore the shape and profile of the target is distorted and broken up when observed by the infrared imager.

Coatings of paints comprise of pigments, binders, solvents, and fillers, etc. The coatings would give high camouflage efficiency both in the IR and the visual regions. In order to fulfill this goal, different pigments and binders are characterized, both individually and mixed together as paint.[4] The paint should also undergo different trials in order to determine the effects of weather, how cleaning will affect the IR and visual reflectance properties, and mechanical and physical properties of coatings.

Binders not only impart the film forming property, but also control to a great extent many of the fundamental properties of the coating. The hardness, adhesion of the film, flexibility, oil resistance, chemical resistance, solvent resistance, weatherability, aging and performance under various conditions are all largely dependent on the type of binders used. But for the binders used in low emissivity coatings, another

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important requirement is the absorption property of the binder material in 8 to 14 μm. The absorption of the binder has to be as low as possible, otherwise the radiation that enters the paint layer will be absorbed by the binder. Therefore emissivity of the whole coating is increased. Most importantly, the binder absorption has to be low in the two atmospheric transmission windows at 3–5 and 8–14 μm, where military and other surveillance IR sensors systems operate. Thus, outside of these windows the emissivity of the paint does not have to be low. In fact, having a high emissivity (i.e. low reflectance) outside the transmission windows, allows the cooling of a surface by radiation without the risk of being detected, at least not at a longer range.

In the thermal IR region, almost all of the polymers used in the coatings industry have various degrees of absorbance and resulting emissivity. The standard practice of attaching side groups to the polymer backbone to impart specific properties of hardness, adhesiveness, solubility and cross-linked densities usually lowers the transparency to an unacceptable value. Some organic resins such as polyethylene, though highly transparent in the region of 8 to 14 μm, is very difficult to dissolve into the solvent below room temperature. Various types of polymer-based binders (such as polyurethanes, vinyl polymers, silicone polymers, epoxy resins, polyethylene, chlorinated polyolefine) are characterized in order to find one with good transmission properties. Some of these results were presented in Ref.[5]. In 3–5 μm there will in most cases be absorption bands due to C–H vibrations, but sometimes also due to O–H. In 8–12 μm there exist typically more and stronger bands, due to vibrations from C–H, C–N, C–O, Cl–C, C–C and Si–O (for silicone polymers). While Ethylene-Vinyl acetate copolymer (EVA), despite having high transparency, has some drawbacks, such as low glass transition temperature, low hardness etc. when utilized as binders. Therefore binders with high transparency in 8 to 14 μm and good mechanical properties are much needed for low infrared emissivity coatings.

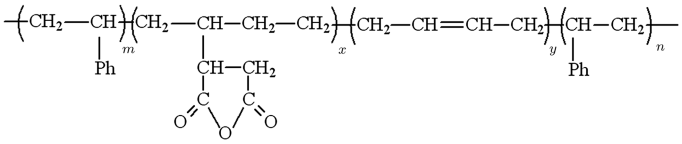
There are many factors which could influence the binders' infrared transparency. How to objectively evaluate the thermal infrared transparency of binders is very important. Applying infrared spectroscopy to evaluate binders' infrared transparency is a new research field. Infrared spectroscopy is a tool which could give information about the overall composition of any unknown material in terms of its functional groups. Every characteristic absorbance peak corresponds to its chemical composition in the IR spectrum, and the absorbance intensity is related to the film thickness and sampling amount. Therefore it is difficult to judge the IR thermal transparency of different binders without the influence of such factors as film thickness, sampling amount, etc.

Given the problem as stated above, in this paper, polymers with high transparency and good mechanical properties are fabricated. An internal standard method (ISM) is proposed to measure the IR transparency of polymers, and the physical and mechanical properties are measured according to corresponding standards.

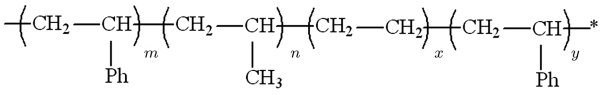
2. Experimental sections

2.1. Polymer synthesis

A styrene butadiene styrene block polymer (SBS) was synthesized by using a known anionic polymerization technique.[6] There are many unsaturated double bonds presented in SBS, which makes the weatherability of SBS poor. Therefore a hydrogen addition reaction was carried out to improve the weatherability of the SBS polymer, and graft modification was underway by means of Maleated rosin.[7] Therefore product *A* was obtained and its chemical structure formula was as follows:



Also, the styrene Isoprene copolymer is synthesized by an anionic polymerization technique.[6] A Hydrogen addition reaction is carried out and product B is obtained. Chemical equation is:



2.2. Characterization methods

2.2.1. Infrared spectroscopy measurement

A Nicolet Magana 550 Fourier transform infrared spectrometer (FT-IR) was used to measure the infrared spectroscopy of the synthesized polymers. The integrating sphere was equipped in the spectrometer.

2.2.2. Evaluation of infrared transparency

The ISM was used to evaluate the infrared transparency of binders. Briefly, the ISM consists of a known amount of the sample and a known amount of a material which is not already presented in the sample. The material being added to the sample is referred to as the internal standard. The infrared spectrum of the mixture is then obtained by using an infrared spectroscopy measurement. The absorbance for a band of the internal standard and a band of the component being quantified are determined.

According to Lambert–Beer law, absorbance is related to the thickness and concentration of a sample by the following equation:

$$A = abc,$$

where A = absorption intensity; a = absorptivity of sample at a specific wavenumber or wavelength; b = the thickness of sample; c = concentration (grams/liter).

Because it is the infrared transparency of binders in 8 to 14 μm wavebands which are concerned in this paper, integrated intensities within the 8 to 14 μm range are calculated by the following equation:

$$A = b * c \int_{v_1}^{v_2} a\mathrm{d}v = bcS.$$

Thus, for sample 1 consisting of binder 1 and internal standard, it meets the following equation:

$$A_{1u} = b_{1u}c_{1u}S_{1u},$$

$$A_{1s} = b_{1s}c_{1s}S_{1s},$$

$$c_{1s} + c_{1u} = 1,$$

where u = the binder 1 in sample 1; s = the internal standard in sample 1.

Here, the integrated range for the binder and internal standard is different, and the former is 8 to 14 μm, the latter concentrates the featuring absorbance peak. Thus,

$$\frac{A_{1u}}{A_{1s}} = \frac{b_{1u}c_{1u}S_{1u}}{b_{1s}c_{1s}S_{1s}},$$

since b_{1u} and b_{1s} are equal, $\dfrac{A_{1u}}{A_{1s}} = \dfrac{c_{1u}S_{1u}}{c_{1s}S_{1s}}$.

Under the same conditions, for sample 2 consisting of binder 2 and the internal standard, it meets the following equation:

$$\frac{A_{2u}}{A_{2s}} = \frac{c_{2u}S_{2u}}{c_{2s}S_{2s}}.$$

If the internal standard is same, and the concentration of binder 1 in sample 1 and binder 2 in sample 2 are equal too, thus,

$$c_{1u} = c_{2u},$$

$$c_{1s} = c_{2s},$$

thus,

$$\frac{A_{1u}}{A_{2u}} = \frac{S_{1u}S_{2s}A_{1s}}{S_{2u}S_{1s}A_{2s}}.$$

Therefore, comparison of infrared transparency of different binders can be realized by comparing the integrated intensity in the range of 8 to 14 μm.

2.2.3. Glass transition temperature test

A differential scanning calorimeter was carried out on PE calorimeter at a heating rate of 10°C / min to measure the glass transition temperature (T_g) of polymers.

2.2.4. Mechanical and physical property test

Polymers were dissolved thoroughly in the mixed solvents consisting of methylbenzene, xylene, and acetone, and the nonvolatile weight percent was 20%. A portion of the samples was charged into a wide-mouth glass container equipped with a high speed air-driven stirrer with a turbine propeller. Films were applied on steel panels. Afterwards, the panels were thoroughly dried and then tested. The thickness of the dry films was 20–30 μm.

An adhesion test was carried out according to ASTM D-3002 and ASTM D-3359. The pencil hardness was measured according to ASTM D-3363-92a. The flexibility is determined over a 6.35 mm mandrel in accordance with method 6221 of FED-STD-141.

3. Results and discussion

3.1. Infrared spectroscopy

Figures 1 and 2 were the FTIR spectrum of polymer A and B. The strong absorption peak in 3200–2800 cm^{-1} corresponded to the C–H stretching vibration; the absorption peak in 1600–1400 cm^{-1} corresponded to the characteristic absorbance of benzene, the strong single absorption peak around 770 cm^{-1} corresponded to the out-of-pland-bending vibration of C–H bond. Also it was shown that there were less absorption peaks in 8–14 μm, i.e. 700–1250 cm^{-1} for polymers A and B.

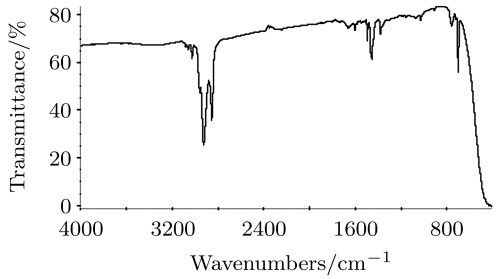


Fig.1. The FTIR spectrum of polymer A.

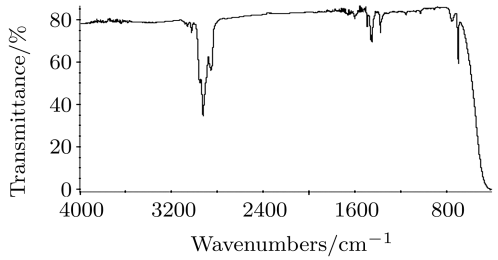


Fig.2. The FTIR spectrum of polymer B.

3.2. Evaluation of the infrared transparency of polymers

Acrylonitrile-butadiene rubber was selected as the internal standard to analyse the infrared transparency of different binders, and the characteristic absorption band is at 4.46 μm. With regard to EVA, which had high infrared transparency and was utilized as binders of infrared camouflage paints through lower glass transition temperature, EVA was used as a reference standard to evaluate the infrared transparency of the synthesized binders in this paper.

Table 1 shows the comparison of the infrared transparency of the synthesized binders with the EVA. It is shown that the IR transparency of polymers A and B was higher than the EVA. The absorption area in 8 to 14 μm for polymers A and B was only 26% and 12% of the EVA respectively.

Table 1. Comparison of the infrared transparency of synthesized binders with the EVA.

sample	EVA	A	B
absorption area of ABR at 4.46μm	2.1	1.2	3.3
absorption area of polymer at 8 to 14μm	37.5	5.5	7.0
ratio of absorption area of polymer with ABR	17.7	4.6	2.1
ratio of absorption area at 8 to 14μm of polymers with EVA/%	100	26	12

Table 2 shows the results of T_g, adhesion, hardness and flexibility test. All films had good flexibility; polymer B had good adhesion property; and polymer A had higher T_g and hardness. Comparing the chemical equation of polymers A and B, it can be seen that there were double bonds presented in polymer A, and thus the rigid chain was formed. Also the chemical structure of polymer A consisted of hard, phase-separated styrene domains tethered by soft, elastomeric poly(butadiene) segments,[3,4] the harder phase-separated styrene domains resulted in the improvement of T_g and hardness of polymer A. But with the graft of Maleated rosin, the steric hinderance of polymer B was increased, which reduced the adhesion property of polymer B.

Table 2. Mechanical test results of polymers A and B.

sample	T_g	adhesion	hardness	flexibility
A	93	grade 2	HB	1 mm
B	73	grade 1	B	1 mm

4. Conclusions

Two kinds of polymers with high transparency and good physical properties are prepared. The ISM

is proposed to measure the infrared transparency of polymers, and the physical and mechanical properties are measured according to corresponding standards. The results show that the absorbance of polymer A in 8–14 μm range is 26% that of the EVA and polymer B is 12% that of the EVA. The formed film with polymer A shows good flexibility of above 1 mm, hardness of grade 1, and adhesion of grade 2. The other formed film with polymer B shows good flexibility of above 1 mm, hardness of grade 2, and adhesion of grade 1. Both polymer A and polymer B can meet the elementary requirements for the infrared transparent binders.

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