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UHU® adhesive holograms replication

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Abstract

It is possible to apply a new recording material with high diffraction efficiency (of the order of 82.3%) to replicate computer phase or analogical holograms. This material is the all purpose adhesive UHU®. It is constituted by some components of polyvinyl, nitrates and some solvent agents; it is easily applied to any substrate. We record this material with heat generation by hand rubbing, using a mask (Kodalith® films) manufactured with lithographic techniques. The holographic replication is excellent on the new material UHU® adhesive, showing a phase modulation for refraction index and relief. This modulation is determined by the cured polymers process induced by friction, as pressure and temperature, with an anaerobic reaction.

For copy of conventional holograms at high frequencies (holographic ranges), the diffraction efficiency parameter is in the neighborhood of 19.1% at first order or more, depending on diffraction efficiency of the pattern of the hologram. The hologram is elaborated in the absence of any development process and does not need to have carefully controlled conditions of the environment. Following this process, the hologram is obtained at standard atmospheric conditions of pressure and temperature.

Keywords: Holography; Replication holograms; Adhesives holograms point

1. Introduction

The decisive breakthrough occurred in 1932, when August Fischer succeeded in developing the first ready to use clear-crystal synthetic adhesive resin in the world. It was able to stick together all known materials of the time, including the first plastics such as Bakelite®. It was customary for the office and writing sectors to name their products according to the names of the birds, and it took the name of a Black Forest bird, which was at that time still to be found: the UHU universal adhesive.

Germany Bolton groups, which possess, UHU® (owl in German), offer a comprehensive range of all-purpose adhesives, indispensable for basic requirements in glueing. UHU's "Alleskleber", invented in 1932, was the very first synthetic resin all-purpose glue. Due to its new formula, it is excellent also for styropor and more particularly for PVAc [1].

Reaction adhesives are those that harden due to a chemical, physical or catalytic reaction. These products are single- or two-component adhesives, depending on the type of reaction. Single-component reaction adhesives are those that, depending on their type, react to ambient humidity, UV radiation or ambient oxygen (aerobic adhesives), or to the exclusion of air, i.e., using

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metal ions (anaerobic adhesives). When using single-component adhesives as all purpose UHU®, the product is applied to one of the parts, in order for it to be stuck to the other. The reaction is triggered immediately by a second component reaction, present in the surrounding area or on the surface being stuck.

UHU® adhesive shows a quality similar to those that are pressure sensitive adhesives, which remain permanently adhesive. They are used wherever the assembly is only temporary and a subsequent separation is required. In our case, the mask is used as micro-photography holographic pattern. Pressure-sensitive adhesives are usually applied in the form of adhesive films [1,2].

UHU® adhesive has an excellent behavior in environment temperatures and shows excellent thermo-sensitive response, which is activated only with heat induced by a rubbing process. With this material, computer phase holograms are recorded, with high diffraction efficiency (around 82.3%) measured with the red light from He–Ne laser.

The replication of analogical or display holograms with high frequencies is possible with this material, the diffraction efficiency parameter is in the neighborhood of 22%, at first order or more, depending on diffraction efficiency of the pattern of the hologram. In our case, we use gratings made with fotoresist Sipley 1350J®. The hologram copy is elaborated in the absence of any development process and does not need to have carefully controlled conditions of the environment.

This modulation is determined by the cured polymers process induced by rubbing. We see that in the modulation of the adhesive to record images or holograms, there are involved some events at the same time, such as pressure, temperature, and electric charges. The more significant parameter is the temperature; due to this reason, we characterize the material according to this dominant parameter. For future works we will, consider, in a more detailed form the other involucrate parameters.

2. Theory

Organic materials, such as the polyvinyl acetate (PVAc) (contained in UHU® adhesive), are the most commonly used thermoplastic polymer resins. Thermoplastic resins are polymers in which the monomeric units are linked together and form two-dimensional linear chains, soluble in a certain range of concentration of solvents. They remain permanently fusible and soluble. Some thermoplastic resins form insoluble, infusible ones after long exposure to light or heat. Such exposure may cause chemical bonds or links, referred to as cross linking. They establish themselves as linear chains and form three-dimensional networks characteristic of thermosetting resins [2].

UHU® adhesive is activated by events at the same time, as the electrical charges produced by: ribbing process, starting an anaerobic reaction, recording a latent image or image with low diffraction efficiency. The pressure and rubbing friction applies to mask, producing a thermal induction too. With this event, the image is amplified, obtaining high diffraction efficiency and good quality of replication. These processes are manifested in the replication phenomena.

Anaerobic (without oxygen) induction corresponds to the process of removing the oxygen molecules when the electrical charge is induced by rubbing friction on the surface of a soft hologram substrate made with acetate base assembled on the mixed polymer material. The metallic ions necessary to start the cure process are obtained from silver ionized Ag^+. After the developed process, the silver becomes an Ag^0 metal; this ionizes again for the action of the nitrate molecule, contained in the compound of cellulose nitrate [3].

Bonded in the molecule R–O–NO_2 (nitrate group linked to radical carbonyl) where R has the structure $R = (C_{24}H_{40-n}O_{20-n})$ together with the group $(NO_3)_n$,

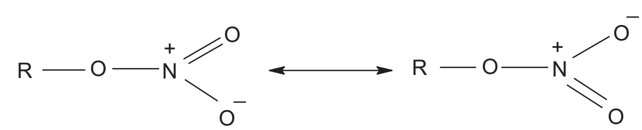


Fig. 1. Dipolar resonance derived from cellulose nitrate, which is stabilized by the presence on metallic ion supply for the mask (hologram) Ag^+. It probably represents the recording image.

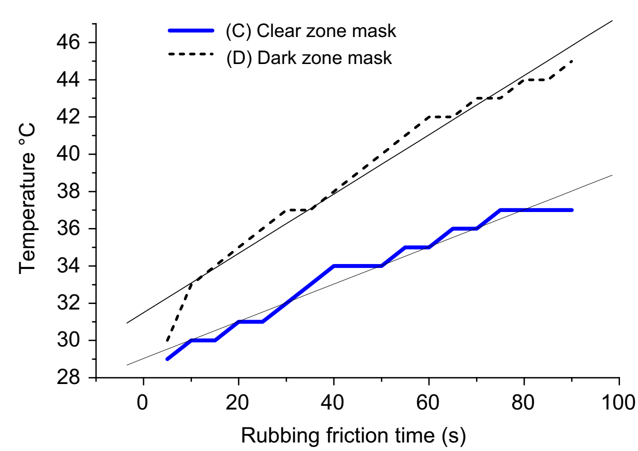


Fig. 2. Thermo modulation as a function of rubbing friction times from the mask (Kodalith® negative film) used to modulate the UHU® all purpose adhesive.

where n is the nitration degree, normally between 1 and 11. Furthermore, we must consider the way for dipolar generation.

When there is heat on the film, induced by rubbing through the mask film, some dipoles are generated as a result of resonance presented in the cellulose nitrate molecule, specifically in the carbonyl region, and it can be presented in the following way (see Fig. 1) [4].

Holograms are recorded in a high contrast commercial Kodalith® negative film (mask) that contains halogens $Ag^{+}Br$ from the Kodak company [5]. Thermal processes were apparent when we applied heat induced by friction on the material that was recording a hologram. Pressure parameter is essential to start the thermal and anaerobic reaction, which in turn will modulate the material by zones with more or less located densities [6].

3. Results

3.1. Thermo modulation

With UHU® adhesive we apply gel–liquid, as a polymer, on glass substrate. It has shown high thermal sensitivity, see Fig. 3. This property was determined by the nitrate contained in UHU® adhesive: the basic characteristic of the nitrate films is its inflammability [7,8]. To verify the thermo-sensitive properties of the films, an analysis of their thermo-response behavior was carried out. After applying the friction process to induce heat through the negative film as mask, some changes of temperature were presented Fig. 2.

Fig. 2 shows graphically the dark (D) and clear (C) areas of the mask. It shows some changes of temperature as a result of the friction process through our mask (hologram). The graphic shows that the black zones absorb more heat than the clear zones; both plots represented by continued and dotted lines can be represented by linear behavior that is directly proportional to the relationship between friction time and temperature, that is, while we increase the friction time, the temperature also increases.

3.2. Refraction index modulation

Table 1 shows the refraction index modulation values from UHU® all purpose adhesive as a film layer on a glass substrate measuring 2 × 2 in. The modulations between clear zones and dark zones are manifested at a hundredth of a fraction, see Table 1; we measured with an Abbe refractometer model *Vista C10* from *R.L. Instruments*.

Table 1. Refraction index values of glass substrate; UHU® all purpose adhesive at different processes

Sodium line n_d = 5875.618 nm. Yellow He	Refractive index
Substratum (glass)	1.5156
UHU® film without heat applied	1.5185
UHU® film after we applied heat by friction process through clear zones mask	1.446
UHU® film after we applied heat by friction process through dark zones mask	1.468

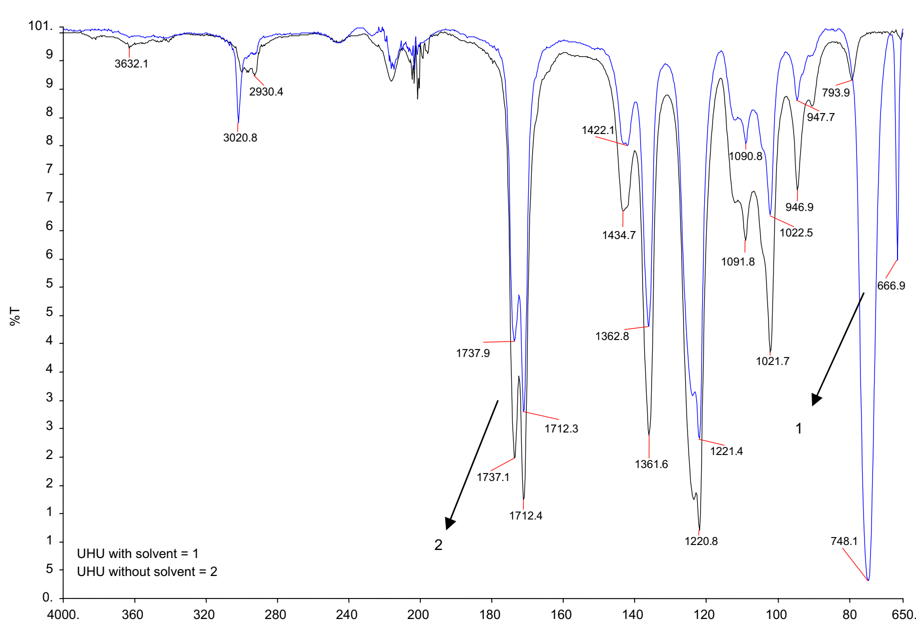


Fig. 3. Transmittance difference between the adhesive UHU doped (1) and not doped (2); in our case, the doped agent is a solvent.

3.3. IR absorbance spectrum

All-purpose adhesive UHU® shows the IR absorbance spectrum of adhesive polymer film after heat is induced by a rubbing process.

Fig. 3 shows the transmittance profile of IR between UHU® adhesive all purpose (in liquid) without doped and UHU® adhesive all purpose with acetone and chloroform solvents doped (in liquid).

In both IR spectrum the carbonyl has a stretching strong absorption, which occurs at about 1735–1750 cm^{-1} and C–O stretching absorption in the range from 1300 to 1100 cm^{-1} which corresponds to most features of an ester [9].

The nitro group **(NO_2)** gives two strong bands in the infrared spectrum. Conjugation of the nitro group with an aromatic ring shifts the bands to the lower frequencies: 1355–1315 cm^{-1}.

Strong bands at 1236.51, 1220.87 from –O–NO_2 stretching asymmetry and cis vibration occur at 666.93; nitrous group **(R–NO)** appear at 1434.79, 1422.10 cm^{-1}.

At 1220.87, 1221.45 cm^{-1}, it has stretch vibrations from C–C(=O)–O acetate. When the adhesive is doped with solvents, these appear in the IR spectrum with new strong band at 750 [9].

Fig. 4 shows the transmittance difference of IR from the doped adhesive UHU after applying rubbing process through a binary mask (dark D and clear C zones).

Adhesive IR spectrum (Fig. 4) shows the graphic that corresponds to the behavior modulation of UHU® all purpose adhesive, when heat is applied through the mask (hologram) in the dark areas (D). Localized regions in the dark and clear areas (C) are the extreme modulation values of holographic code mapped to polymer adhesive.

Dark zones (D) contain a higher concentration of metallic silver Ag^0 than the clear zones (C). Nitrate group activates again the silver Ag^+, starting the thermal anaerobic polymerization process in our emulsion.

Fig. 4 shows an important response at $\lambda = 8.087\,\mu m$, that corresponds to 1236.51 cm^{-1}, which determines an event of vibrations that stretch itself between ring and the nitrate group nitro **–O–NO_2–** [9]. These events start the process of polymerization of our emulsion (UHU® all purpose adhesive) recording a phase image.

Table 2 shows the main involucrate resonant molecular groups in the register of the image or hologram, coded with dark and clear zones on our mask (soft hologram).

Table 2 corresponds to UHU as a coating film after heating through clear (C) and dark (D) areas from the negative Kodalith.

The strong absorption at 1731.70 and 1730.08, which correspond to the carbonyl group **(C=O)**, in 1225.49, 1226.47 cm^{-1}, have stretch vibration from C–C(=O)–O acetate; the band 1370 cm^{-1} [9].

Of the intensity mean is of the methyl together with the carbonyl group CH_3–C=O, in the region 2920.79, 2926.58 cm^{-1} appear asymmetry tension vibration of the bond C–H and methyl and methylene, respectively [9].

The nitrous group in the range of the nitro group **(NO_2)** gives two strong bands in the infrared spectrum. Conjugation of nitro group with an aromatic ring shifts the bands to lower frequencies: 1355–1315 cm^{-1} and cis

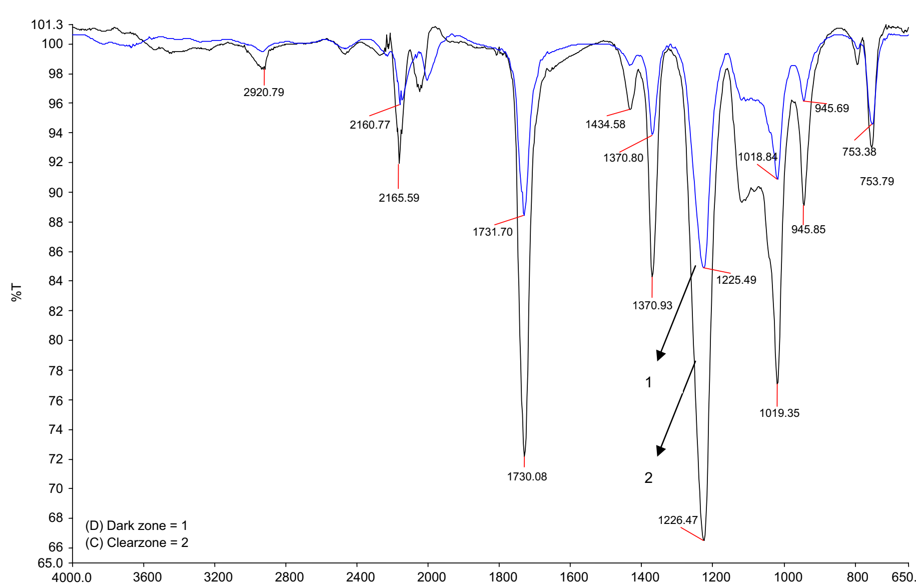


Fig. 4. IR profile of the UHU adhesive after friction a process for clear (C) and dark (D) zones.

Table 2. Principal resonant molecular structures of Fig. 4

Functional group	v (cm^{-1}) reported	v (cm^{-1}) result from (C)	v (cm^{-1}) result from (D)	λ(μm) (C) result	λ(μm) (D) result
C=O	1750–1735	1731.70	1730.08	5.7	5.8
C–H	2926	2926.58	2920.79	3.4	3.4
C–C(=O)–O	1140–1210	1225.49	1226.47	8.2	8.1
CH3–C=O	1175–1375	1226	1225	8.1	8.2
		1374	1370	7.3	7.3

vibration occur at 666.93 and the nitrous group **(R–NO)** appear in 1434.79, 1422.10.

In 1220.87, 1221.45 cm^{-1}, have stretch vibration from C–C(=O)–O acetate. Strong bands at 1236.51, from –O–NO_2 asymmetry stretching and cis vibration occur at 666.93 and both disappear [9].

3.4. Diffraction efficiency

When it comes to the application of techniques [10], in order to get high quality thin layers of UHU® all purpose adhesive on glasses as substrates, Fig. 5 shows that the energy distributed does not have a linear behavior. Each point in the plot is obtained measuring diffraction efficiency parameter from nine gratings including the dispersion date from standard deviation of all the points. The maximum diffraction efficiency is obtained as 82.3% when we applied heat induced by hand rubbing friction process during 35 s, which corresponds to 35 °C of temperature. Consequently, Fig. 5 shows the nonlinear behavior modulation from our emulsion. Another important point is applying rubbing when we reach 21 s; at this point, the diffraction efficiency is of the order of 62.5%, which corresponds to a temperature of 32.4 °C. If we have fast replication after approximately one second applying friction only, it is possible to obtain a hologram with 47.71% diffraction efficiency, with this polymeric matrix.

The recording time increases with energy exposure; if the diffraction efficiency declines, the films show a diffuse degradation after 60 s, producing poor computer holograms replication. All measurements were made at a 45% humidity environment.

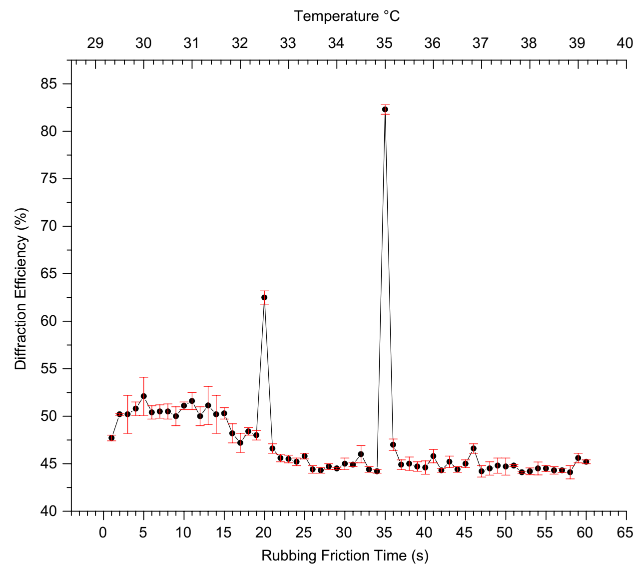
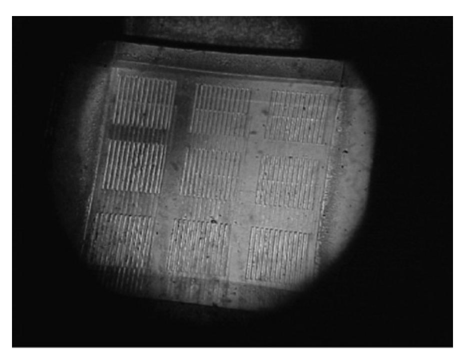


Fig. 5. Diffraction efficiency of the grating, made with UHU® all purpose adhesive.

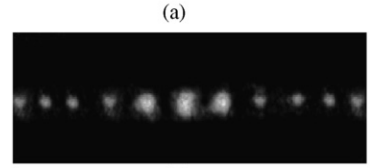
3.5. Recording computer holograms

Recording a computer hologram [11,12] using adhesives as matrix for replication by contact or with light radiation [13,14], we have new alternatives of replication and store information.

In Fig. 6a we could observe a microphotograph of nine sinusoidal gratings in the material (UHU® all purpose adhesive) with a magnification of 25 times. We



(a)



(b)

Fig. 6. (a) Microphotography of nine sinusoidal gratings, recorded in UHU® all purpose adhesive applying rubbing. (b) Grating diffraction pattern of one sample from (a).

recorded nine gratings to obtain the average diffraction efficiency. It is possible to observe in Fig. 6b a diffraction pattern showing many diffracted orders; this response is only caused by a phase grating (Fig. 6a), since the material is not revealed for watery chemical agents and it is not a removed material since we assumed that the modulation is to ascertain refraction index. For reflection, the diffraction pattern is manifested deducing that the material shows ascertained relief modulation too.

Fig. 7a shows the computer UHU® icon binary image created by 300×300 pixels, Fig. 7b shows a computer Fourier hologram with 256 gray levels, and Fig. 7c shows a numeric reconstruction of a computer hologram image.

Fig. 8a represents an image that shows the microphotograph of the holographic code from Fig. 7b, with a magnification as high as 100 times; this recording was generated by applying friction between our mask (hologram) and the glass substrate with a film of UHU® all purpose adhesive, registering a Fourier hologram generated by a computer. The circular aperture is produced by the eyepiece of the microscope; Fig. 8b shows a photography of the optical reconstruction, which in turn shows a diffracted image of a Fourier hologram, projected on a dark paper at a distance of 2 m from the hologram, where two UHU® icons images present themselves, with high diffraction efficiency and low noise. This reconstruction was obtained using He–Ne laser.

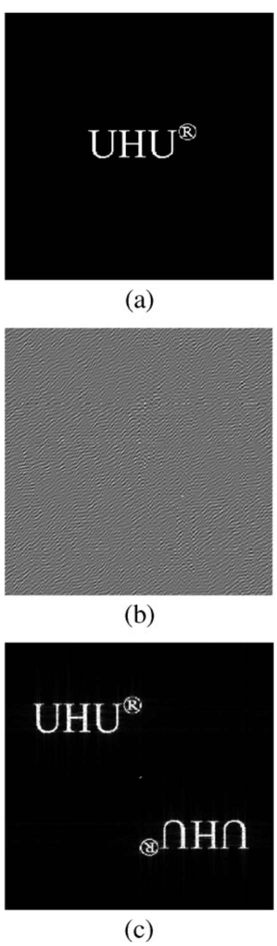


Fig. 7. (a) Binary image, (b) computer Fourier hologram with 256 gray levels, (c) computer reconstruction.

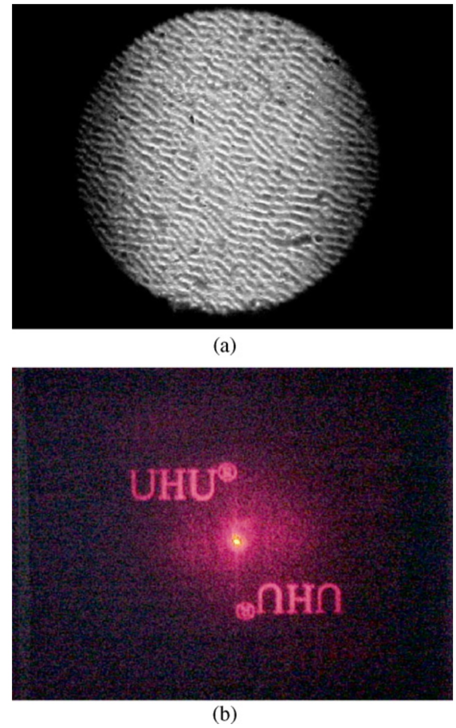


Fig. 8. (a) Computer Fourier hologram microphotography made with UHU® all purpose adhesive. (b) Optical reconstruction of the computer hologram with He–Ne laser.

In Fig. 9, we duplicated photoresist gratings to obtain a MTF response with adhesive UHU® all purpose. In Fig. 9a a response's behavior MTF, of photoresist Sipley of diffraction efficiency, at first order vs. spatial frequency (dotted line) can be observed, and in Fig. 9b the replication response MTF of adhesive UHU® all purpose material obtaining very good replication profile from photoresists grating (continuous line). It is interesting to observe that the diffraction is slightly more high in the adhesive UHU® all purpose copy than photoresists. This response is due to the fact that absorbance profile of photoresists is more than that of adhesive UHU® all purpose. This is the reason for which it presents itself the small difference, the order of which lies between 1% and 4%, with respect to the original diffraction efficiency of the hologram pattern.

Adhesive UHU® all purpose is very able to duplicate holograms reliefs with high frequency to embossing holograms, becoming a very interesting procedure from the commercial point of view.

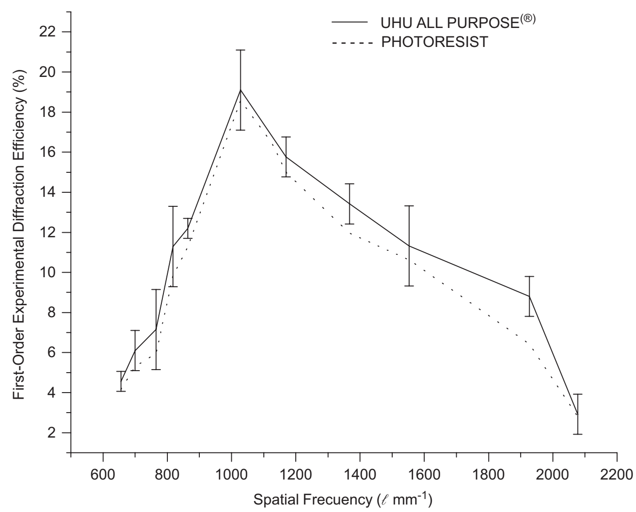


Fig. 9. The MTF diffraction grating (a) made with photoresist Shipley 1350J® (dotted line). (b) Replication grating applying the all purpose adhesive UHU® (continuous line).

4. Conclusions

UHU® all purpose adhesive, has an excellent behavior at environment temperatures and shows an excellent thermo-sensitive response, which is activated only by applying heat, induced by a rubbing process. An anaerobic induction is produced with metallic ions obtained from silver ionized Ag^{+}, and maybe produced by electrical charges by a rubbing process. The hologram substrate is recorded with a high contrast commercial Kodalith® negative film (our mask), that contains halogens $Ag^{+}Br$, obtained from Kodak company.

The diffraction efficiency with this adhesive is high, around 82.3%, with low noise. This can be used to copy or replicate holograms or images, applying lithographic techniques. Furthermore, the adhesive material opens the possibility to design elements of phase diffraction. One of the advantages of using this material is that it does not require some techniques developed to get a phase hologram modulated by refraction index and relief.

For copy holograms with high frequencies (holographic ranges), the diffraction efficiency parameter is in the neighborhood of 19.1% at first order or more, depending on diffraction efficiency of the pattern of the hologram. The hologram is elaborated in the absence of the development of any process and does not need to have carefully controlled conditions of the environment.

This hologram is possibly implicated in all the physical and chemical processes between the electrostatic charges induced by rubbing technique, that helps the recording information to describe all the components involucrated in this cured process.

The more significant event is the temperature. For this reason we characterize the material according to the dominant parameter. In future works we will consider with more detail the other involucrated parameters.

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