The formation of microscopic pores and fibrils in polymers under stress — a process called crazing — often preludes material failure. Controlled crazing has now been used to produce an array of colours in polymer films. See LETTER P.363

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When a typical transparent, glassy polymer is bent or stretched, partial whitening of the material often occurs just before it cracks or fractures. This unpredictable phenomenon is called crazing, and has generally been seen as something to be avoided. But on page 363, Ito et al. report that crazing can be fully controlled, and can be used to endow transparent polymers with colour. Controlled crazing could therefore be developed as the basis of an inkless, high-resolution method for printing colour on various flexible and transparent polymer materials.

Transparent polymers have conventionally been colorized by mixing them with pigments, or by printing pigment-containing ink on polymer surfaces. However, transparent polymers can also be colorized by producing microscopic structures within the materials — an effect known as structural coloration. Structural colours are frequently observed in nature, for example in butterfly wings. Ito and co-workers use crazing as the basis for structural colour.

Crazing patterns in polymers form in a direction perpendicular to the applied stress, and consist of interpenetrating, micrometre-scale voids bridged by highly oriented polymer
Figure 1 | Inkless colour printing in polymers. a, Ito et al. 2 have produced colour images in transparent polymers by shining standing waves of light through masks on polymer films. The light generates alternating layers of crosslinked and non-crosslinked polymers, which causes stress to build in the non-crosslinked layers. b, When treated with solvent, the non-crosslinked layers undergo crazing—microscopic pores and fibrils form, releasing the stress. This produces alternating dense and porous polymer layers, which cause the refractive index of the film to vary periodically. White light striking the layered parts of the film therefore reflects in such a way that a particular colour is produced. In principle, any colour can be generated.

microfibrils. The microvoids and microfibrils in uncontrolled crazes vary widely in size, and reflect a broad range of wavelengths of light—which explains why crazes usually look white. Ito and colleagues have demonstrated that, if crazing is controlled to generate porous layers that alternate with compact, non-porous layers, this can reinforce interference of the light reflected from the different layers, thereby producing specific colours.

The authors take advantage of a phenomenon 4 that controls a polymer’s stress field (the distribution of forces within it that balances external forces), and so controls craze generation. When a ‘standing wave’ light pattern is formed in a light-sensitive polymer film, crosslinks between the polymer molecules form selectively in layers, which are separated by other layers in which no crosslinking has occurred (Fig. 1); this causes tensile stress to build across the non-crosslinked layers. The authors exposed such layered films to a solvent, which releases the stress by causing crazes to form in the non-crosslinked layers. The resulting films therefore contained alternating dense and porous layers, generating periodic variations in the refractive index of the material. Light shining on the films is reflected at successive craze layers, leading to interference effects that cause structural coloration.

Ito et al. carried out a series of experiments to investigate the physical mechanism of, and the optimum conditions for, periodic craze formation in various transparent polymer films. The microvoids in crazes are, effectively, tiny cracks, and the authors conclude that the formation of the cracks must be controlled to control the crazing process. Their method is therefore a real triumph: crack-formation processes are much more complex and difficult to manage in amorphous materials (such as polymer films) than in crystalline ones 5, because the microscopic structures of amorphous materials are more random.

The authors report the production of only a few colours in their work, but a wide range should, in principle, be generated by carefully adjusting the spacing of the alternating layers. The spacing can, in turn, be controlled by altering several factors: the wavelength of light used to produce the layers and the amount of time used to irradiate the films; the type and molecular weight of the polymer; the initial thickness of the film; the type and temperature of the solvent used to produce crazing; and the period of time for which the film is immersed in the solvent.

The authors are not the first to observe this kind of structural coloration in a multilayered transparent film. However, most research in this area has involved complex and expensive methods in which alternating layers of films are deposited on a substrate in a vacuum (see ref. 7, for example). By contrast, Ito and co-workers have developed a simple, inexpensive method based on a phenomenon that was previously regarded as useless. Indeed, previous studies of crazing have concentrated mostly on finding ways to inhibit or prevent it 6,9, rather than to control it.

The authors demonstrate that craze control can be used for inkless colour printing at incredibly high resolution (up to 14,000 dots per inch). The resolution of conventional colour-printing methods, such as inkjet printing, is generally just 600–1,200 dots per inch because of limitations associated with the size of the ink droplets that can be generated and the effects of ink spreading. Another advantage of Ito and colleagues’ technique is that the printing time will not depend strongly on the size of the substrate, because it is a parallel process (the whole pattern is printed into the film at the same time), whereas conventional inkjet printing is a serial writing process that takes considerably longer to print large areas.

The impact of this work is not limited to the coloration of transparent polymer materials—it will also enhance our understanding of crazing more generally. For example, the crazing described by Ito et al. occurs in the out-of-plane direction (the layers stack up in the direction of the film’s thickness), rather than in the plane of the film, as is normally observed in polymers under stress. It is thus an intriguing phenomenon that deserves further study. It will also be interesting to explore the mechanical and electrical properties of controlled crazing.

The surprisingly simple nature of the authors’ method means that it could easily be adapted for use by currently available technology for colorizing polymers. However, as with any new technology, several hurdles will need to be overcome. The authors’ process is largely limited to a narrow set of operating conditions and certain material combinations, so its general applicability to other materials remains to be seen. Further work exploring the physical mechanism involved in detail might reveal how the method could be applied to any polymer material. In the meantime, craze control will probably find exciting applications beyond inkless colour printing in a transparent polymer, such as in electronic devices and sensors.

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