Making polymers colored and stiffer by dyed regenerated cellulose employing Pickering emulsions

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GRAPHICAL ABSTRACT

This work presents the preparation of well-defined composites of polymethyl methacrylate and dyed regenerated cellulose *via* a Pickering emulsion approach. The Pickering emulsion-based composition procedure is simple and cost effectively, and could be easily adopted to the preparation of similar polymer-nanocomposites.
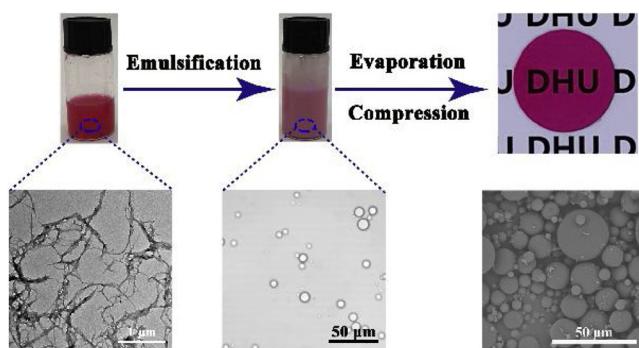
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ABSTRACT

We demonstrate the successful use of Pickering emulsions utilizing regenerated cellulose that carry covalently immobilized dye molecules as emulsifiers to color PMMA and enhance its mechanical performance. Due to the use of this biobased dye carrier, the materials we describe exhibit enhanced "green" character. First we show that oil-in-water Pickering emulsions of PMMA can be effectively stabilized by dyed regenerated cellulose. We describe how uniformly colored PMMA-cellulose composites with high transparency in the visible range can be obtained. We provide detailed characterization of the resulting composites. Thermogravimetric analysis shows an increase of onset of degradation temperature, thus indicates improved thermal stability. Also the mechanical properties become improved, as indicated by flexural strength enhancement. The Pickering emulsion-based procedure is simple and cost effective, and could be easily adopted to prepare other polymer-nanocomposite systems.

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1. Introduction

The use of pigments in polymers (plastics, coatings and bulk products) is as old as the polymer industry [1]. Pigments have been used for decorative, as well as functional purposes. Recent progress in high value added applications, like security printing or angle-dependent automotive decorative paints, have added further interest in the continuing development of this field [2].

However, due to the often different chemical nature of the pigment and the polymer matrix to be colored, molecular incompatibility and immiscibility effects often make it difficult to obtain well dispersed and stable pigments for a given polymer. To tackle this challenge, surfactants or encapsulation can be used. For example, miniemulsion polymerization can provide designer "pigment containers", and surface functionalization of the solid particle can be tuned to achieve compatibilization with the matrix [3].

Another way to obtain color in polymers is related to coupling of dye molecules to suitable carriers. Here we describe a strategy to use environmentally friendly dyed regenerated cellulose (DRC) as dye carrier in Pickering emulsions. Regenerated cellulose (RC) not only provides a surface active component as emulsifier and as carrier of dye molecules, but also adds strength (improves mechanical performance) to the polymer when it is used in composite systems following solvent removal. As active agent, we chose a DRC, which is a promising environmentally friendly, coloring material [4,5]. As matrix we chose polymethyl methacrylate (PMMA), which is a glassy polymer with excellent transparency and good processing ability, and is commonly used in the transportation sectors, and as building materials, special application windows and body implants [6–8]. Our primary objective is not to offer a new type of PMMA, but demonstrate the use of Pickering emulsions in nanocomposite preparations for simultaneous mechanical performance improvement and coloring.

The combination of PMMA with nanocellulose [9,10] has been discussed in the literature. Results demonstrate increase of mechanical strength and stiffness of PMMA composites while still retaining good optical transparency [11]. The optical properties of PMMA/nanocellulose composites are greatly influenced by the quality of the dispersion of nanocellulose in the matrix. Poor dispersion will severely compromise the transparency and mechanical properties of the composite even at very low loadings [12]. Previously, we have shown that cellulose nanofibers [13], RC [14], and lignin nanoparticle [15] could be evenly dispersed into polylactic acid (PLA) *via* a Pickering emulsion approach, where the cellulose nanoparticles served as the solid emulsifiers for O/W emulsions. Upon slow evaporation of CH_2Cl_2, microspheres of PLA composites could be obtained, which were then hot pressed at 180 °C to yield composite PLA films with enhanced mechanical and thermal properties.

As mentioned, here we present the preparation of composites of PMMA and DRC with high transmittance (60 %), different color and good mechanical properties *via* the Pickering emulsion route as a case study to demonstrate the feasibility of our successful "dual approach" (enhancing mechanical performance, and uniformly dispersing a pigment). DRC acted as the stabilizer and dye carrier in the oil-in-water Pickering emulsion featuring PMMA in the hydrophobic phase. Evenly colored composite PMMA/DRC microspheres obtained after solvent evaporation were further converted to films by compression molding. Thermal and mechanical characterization of these nanocomposites were performed. In comparison with common coloration methods of melt blending in colorants [16], this approach could add bright color and mechanical strength to PMMA without compromising its transparency.

2. Experimental section

2.1. Materials

Polymethyl methacrylate (PMMA) with a number-average molecular weight (M_n) of ~ 46,000 Da and weight-average (Mw) of ~ 110,000 Da, was supplied by Energy Chemical, China.

Wood Pulp was obtained from the Xinxiang Natural Chemical Co., Ltd. The viscosity-average degree of polymerization measured in a cupric ethylene diamine hydroxide (CUEN) solution was 870. Solution viscosity measurements were performed using an Ubbelohde viscometer.

Colour Index (C.I.) Reactive Red 24 (RR24) pigments were supplied by Taoyuan Dyestuff Co., Ltd, Wujiang, China. Phosphoric acid (85 %) was received from Titan Scientific Co., Ltd, Shanghai, China. Sodium chloride (NaCl), sodium carbonate (Na_2CO_3), sodium hydroxide (NaOH) and Dichloromethane (CH_2Cl_2) were supplied by Sinopharm Chemical Reagent CO., Ltd. All chemicals were used as received.

2.2. Preparation of RC suspensions

RC suspensions were prepared by a previously reported procedure [14]. In short, phosphoric acid and deionized water were pre-cooled to 4 °C. Wood pulp (2 g) was pre-wetted with 6 ml of deionized water and 200 ml of 85 % phosphoric acid was added thereto. The mixture was stirred at 5 °C for 24 h to obtain a clear solution. Subsequently, 1 L of deionized water was used to regenerate the cellulose. The dispersion was centrifuged at 12,000 rpm Thermo, USA until a constant pH was reached. Prior to use, the RC was re-dispersed twice at 800 bar using a high-pressure homogenizer (APV-2000 Homogenizer, Germany).

2.3. Preparation of DRC suspensions

The DRC suspension was prepared by a method previously reported by our group [4]. RC suspension and RR24 dye were added into a three-necked flask at room temperature. A predetermined amount of aqueous NaCl (20 g/L) was added after 15 min. Following this step, the mixture was heated to and maintained at 70 °C. Na_2CO_3 (15 g/L) was added into the mixture 30 min later. The mixture was allowed to react for 1 h. Finally, the dye bath was subsequently cooled to room temperature and the DRC was washed with D.I. water by centrifugation until the supernatant became colorless.

2.4. Preparation of PMMA/DRC composites

A DRC dispersion was diluted with deionized water to obtain cellulose dispersions of concentrations at 0.05, 0.1, 0.15 and 0.2 % w/v. The DRC to PMMA ratio was adjusted (1, 2, 3 and 4 wt. %) to deliver the targeted DRC composition of the composites. A solution of PMMA in CH_2Cl_2 (10 ml, 100 mg/ml) was added to the DRC aqueous dispersion (50 ml). The mixture was homogenized (IKA T18 homogenizer, Germany) at 12,000 rpm for 3 min followed by ultrasonication (SCIENTZ, JY 92-IIDN, China) for 3 min to obtain Pickering emulsions. CH_2Cl_2 was evaporated at ambient temperature over the course of 24 h. The precipitates were vacuum filtered using a 500-mesh filter screen. The paste collected on the filter screen was vacuum dried at 60 °C for 24 h. The PMMA/DRC composite films were prepared by hot-pressing of the dried paste employing a Carver Laboratory Press (Carver Inc., USA) at 170 °C and 1500 Kg for 5 min.

2.5. Characterization

The morphologies of RC and DRC were characterized using transmission electron microscopy (TEM, JEM-2100, JEOL, Japan) operated at 100 kV. TEM observations were performed on one dried drop of a 0.05 % aqueous suspension of RC and DRC, respectively on a carbon

coated grid (200 mesh).

Freeze-dried RC samples were analyzed by using a Rigaku X-ray diffractor (D/max 2550PC, Japan). The samples were exposed for 1.5 s for each angle of incidence (θ) using a Cu Kα X-ray source with a wavelength of 1.541 Å. The angle of incidence is varied from 4 to 50 by steps of 0.02 s.

Percentage dye fixation was measured according to the procedure previously reported [17]. 0.1 g of DRC was dissolved into 5 mL of 70 % H_2SO_4. The amount of fixed dyes on RC was determined spectroscopically using a Shimadzu UV-1800 spectrophotometer.

The solid state ^{13}C NMR spectra of DRC was recorded on a Bruker AVANCE 400 spectrometer (Switzerland).

The emulsion obtained was observed using an optical microscope (Eclipse E100, Nikon, Japan). After filtration, PMMA/DRC composite microspheres were observed with scanning electron microscopy (SEM, TM-1000, Hitchi, Japan) at 2 kV and 6–8 A. The samples were dried at 40 °C for overnight. Then they were coated with a gold-palladium alloy.

The conductivity of the Pickering emulsions was measured using a DDSJ-308 F conductivity meter (leici, Shanghai, China).

Transmittance UV-VIS spectra of the neat PMMA and PMMA/DRC composite films were obtained using an optical spectrophotometer (UV-3600, Shimadzu).

Thermal properties of neat PMMA and PMMA/DRC composites were characterized by differential scanning calorimetry (DSC, 214, Netzsch, Germany) equipped with a cooling system, under a nitrogen atmosphere. The samples (5–10 mg) were loaded and sealed in aluminum pans. The samples were heated from 25 to 200 °C at a ramp speed of 10 °C/min, isothermed for 5 min to eliminate thermal history, cooled to 25 °C at 2 °C/min, and heated again to 200 °C at 10 °C/min under nitrogen purge. The glass transition temperature (T_g) was determined from the second heating scan.

The thermal decomposition of neat PMMA and PMMA/DRC composites were characterized to determine their thermal stability using thermogravimetric analysis (TG, Netzsch 209F3, Germany). The specimens were scanned from 30 °C to 600 °C at the rate of 10 °C/min and analyses were performed under a nitrogen gas flow.

The tensile properties of neat PMMA and the PMMA/DRC composites were obtained using a universal testing machine (UH6502, Youhong, China). The experiments were carried out at a gauge length of 30 mm and a crosshead speed of 10 mm/min. The samples were thin rectangular plates with dimensions of $100 \times 20 \times 0.5$ mm³. Flexural testing was conducted using a universal testing machine (UH6502, Youhong, China) on rectangular specimens ($50.8 \times 12.7 \times 0.5$ mm³) at a support span of 25.4 mm and a crosshead speed of 5 mm/min according to the procedure described in ASTM D 790-2007.

3. Results and discussion

3.1. PMMA/DRC composites

An XRD pattern of RC is shown in Fig. S1 (in the Supplementary Information Section). The crystalline form of RC is cellulose II. DRC suspensions were prepared by reacting RC with reactive dyes (RR24) in deionized water. The dyeing mechanism is the same as that of reactive dyeing of cotton fabrics. The coupling chemistry to covalently attach the dye to cellulose is shown in Fig. 1(a). The solid-state ^{13}C NMR spectra of RC and DRC shown in Fig. S2 (in the Supplementary Information Section). Compared with RC, the chemical shift of the amorphous region (59.92 ppm) of C6 in DRC was obvious, increasing by 0.64 ppm, which was caused by the resonance up-shift effect of adjacent carbon during the hydroxyl modification, indicating that the dye was grafted on the RC. Similar observations upon chemical modification of cellulose were reported previously [18]. The dye fixation is 16.6 %. TEM images of RC and DRC are shown in Fig. 1. The fibrillar diameter of the RC and DRC (bearing covalently coupled dye) were in the nanometer range. The morphology of RC and DRC were similar, both of

which exhibited a networked structure. Therefore, the morphology of RC was not changed by the dyeing process. DRC has good dispersion stability in water due to the hydrophilicity of cellulose. The DRC suspension could be stored over prolonged periods without precipitation as reported previously [4,5].

RC acts as the stabilizer in Pickering emulsions via a combination of Pickering and networking mechanisms [19,20]. DRC used in this study performed also very well as stabilizer to prepare colored Pickering emulsions. When the content of DRC was below 1%, Pickering emulsions were not formed due to the insufficient quantity of DRC. The conductivity of the Pickering emulsions of dyed cellulose and undyed cellulose is showed in Table S1 (in the Supplementary Information Section). All of them had conductivity over 10 us/cm, affirming the oil-in-water nature of the emulsions [21]. The emulsions stabilized by DRC had higher conductivity due to the negative charges of ionized dyes on its surface.

Optical micrographs of Pickering emulsions stabilized by varying DRC content are displayed in Fig. 2. It can be seen that the oil droplets containing PMMA were well dispersed in the aqueous phase and the diameter values of the oil droplets were less than 50 μm for all emulsions. Optical images of the emulsions as prepared and after 24 h of standing showed no noticable difference in droplet size, which is showed in Fig. S3 (in the Supplementary Information Section), indicating the effective stabilizing ability of DRC. We note that this procedure is not limited to PMMA; other emulsions with DRC could also be similarly obtained when needed.

Colored PMMA microspheres were prepared during slowly evaporating the DCM solution from the emulsion at room temperature. SEM images of the resulting PMMA/DRC composite microspheres with different DRC contents are presented in Fig. 3. The microspheres have diameters below 50 μm, which were similar in size to the oil droplets in the corresponding emulsions (see Fig. 2(a–d)). When the content of DRC was low, the microspheres had a relatively smooth surface. As more DRC was used, the surface roughness appeared to increase, likely due to the surface deposition of excess DRC.

Colored PMMA/DRC composite films were obtained by hot-pressing and thus fusing these colored composite microspheres. Fig. 4(a) show the images of neat compressed PMMA, and the colored PMMA/DRC composite films with different DRC (and thus dye) loadings. The printed letters in the background can be seen through, indicating that all composites prepared here were visibly transparent. (We note that later we show, the optical transmittance values in the visible spectrum decreased with increasing dye content.) Visual inspection of the photographs in Fig. 4(a) confirm that the color of the composite film was even and uniform without noticeable DRC aggregates, indicating that DRC was uniformly dispersed in the PMMA matrix throughout the concentration range studied. Obviously, darker color tones could be achieved as more DRC was incorporated into the PMMA matrix, showing the color depth of the composites are tunable by adjusting the DRC (and thus the dye) contents.

Fig. 4(b) shows the quantitatively measured profiles of light transmittance versus the wavelength of visible light for the neat PMMA matrix and color PMMA/DRC composites examined by a UV–vis spectrometer at a visible wavelength range between 400–800 nm. As expected, the neat PMMA showed the highest transmission (about 90 %). The transmittance spectra of the composite exhibited reduced values with increasing DRC (dye) loading due to structural heterogeneity (scattering) in line with earlier reports [22,23]. Fig. 4(c) shows the difference of transmittance in the spectral absorption wavelength at 550 nm, which indicated the increasing color depth of the composites with increased DRC loading. The color fastness of the PMMA/DRC film against solvent leaching was tested in water and ethanol. As shown in Fig. S4 (in the Supplementary Information Section), no leaching of color was detected after 24 h of immersion in either solvent.
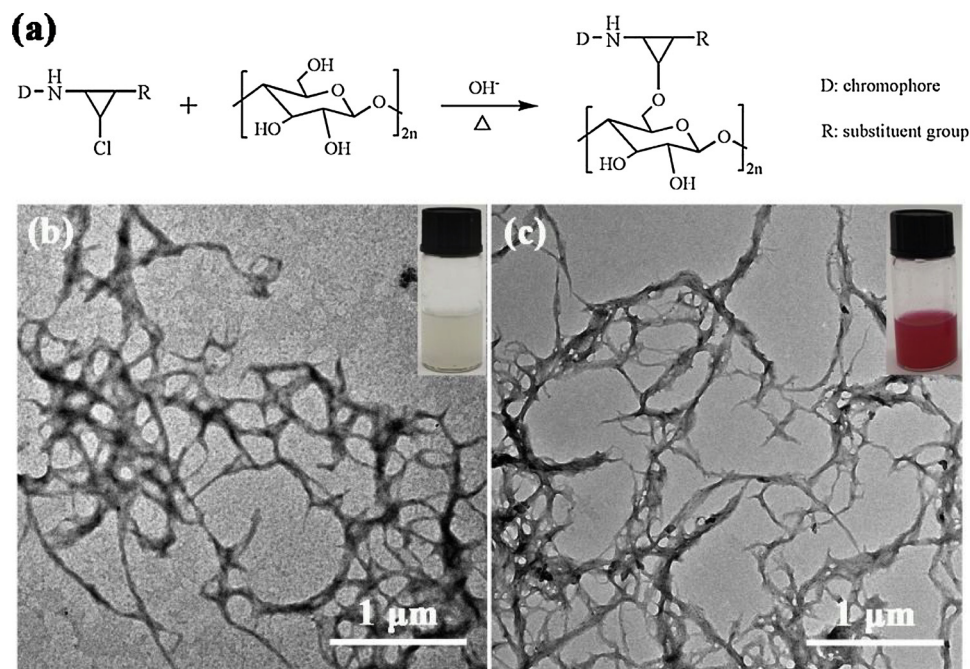
Fig. 1. (a) The process of DRC dyeing, TEM images of (b) RC and (c) DRC.
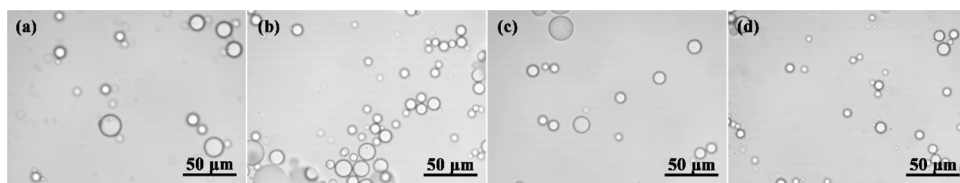

Fig. 2. The optical microscope images of Pickering emulsion stabilized by (a) 1% DRC, (b) 2% DRC, (c) 3% DRC and (d) 4% DRC.

3.2. Thermal properties of PMMA/DRC composites

The thermal decomposition of PMMA/DRC composites was monitored by thermogravimetric analysis (TGA) in nitrogen atmosphere. The resulted TG and DTG thermograms are presented in Fig. S5 (in the Supplementary Information Section). The onset of thermal decomposition (T_{onset}) and the maximum of thermal decomposition (T_{max}) of the composites were summarized in Table 1. T_{onset} and T_{max} shifted to higher temperatures as more DRC were incorporated into PMMA demonstrating enhanced thermal stability of the colored PMMA composites. As is shown in the Fig. S5, the thermal decomposition temperature of DRC was around 330 °C, which had a lower value than the thermal decomposition temperature of the PMMA matrix. The enhancement of thermal stability is assumed to be due to the DRC preventing outward diffusion of the volatile decomposition production [24]. There was no residual mass obtained for neat PMMA and the composites, which was attributed to the degradation of PMMA starting slowly at 220 °C and reached completion at a temperature higher than 360 °C [25].

The DSC thermograms of neat PMMA and PMMA/DRC composites with different DRC contents were shown in Fig. S6 (in the Supplementary Information Section). No obvious crystallization of any of the constituents was observed, which is consistent with the previous

work [26]. Glass transition temperature values (T_g) were taken as the midpoint of the endothermic transition. The T_g of neat PMMA was 101.1 °C while the T_g of PMMA-1%-DRC, PMMA-2%-DRC, PMMA-3%-DRC and PMMA-4%-DRC were 99.7 °C, 100.3 °C, 99.3 °C and 100.1 °C, respectively. The T_g values of the PMMA composites change very little in comparison with the neat PMMA. Although a slight increase of the mobility of polymer chains upon introducing the Pickering surfactant particles has been reported [27], we could not see a trend in our data beyond the experimental error.

3.3. Mechanical properties of PMMA/DRC composites

The mechanical properties of the PMMA and the PMMA/DRC composites were determined and compared with that of neat PMMA to examine the influence of DRC on the deformation behavior of the nanocomposites. The results are shown in Fig. 5. The flexural modulus increased compared to that of neat PMMA for all composites with different DRC contents, which indicated that DRC acted as reinforcement in the PMMA matrix by transferring load from the PMMA to the DRC [28]. In the Fig. 5(b), PMMA-1%-DRC has the highest flexural modulus of 80.5 MPa, enhancements of 10.0 % compared with neat PMMA. Interestingly, flexural strength values do not increase significantly with
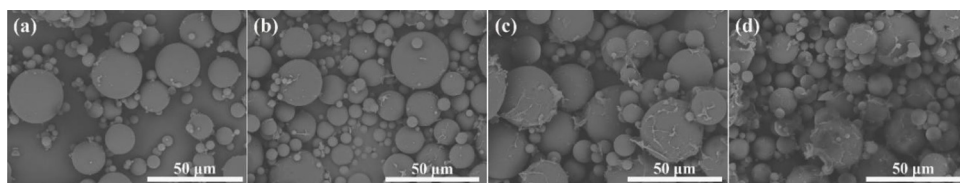

Fig. 3. SEM images of PMMA microspheres with (a) 1% DRC, (b) 2% DRC, (c) 3% DRC and (d) 4% DRC.
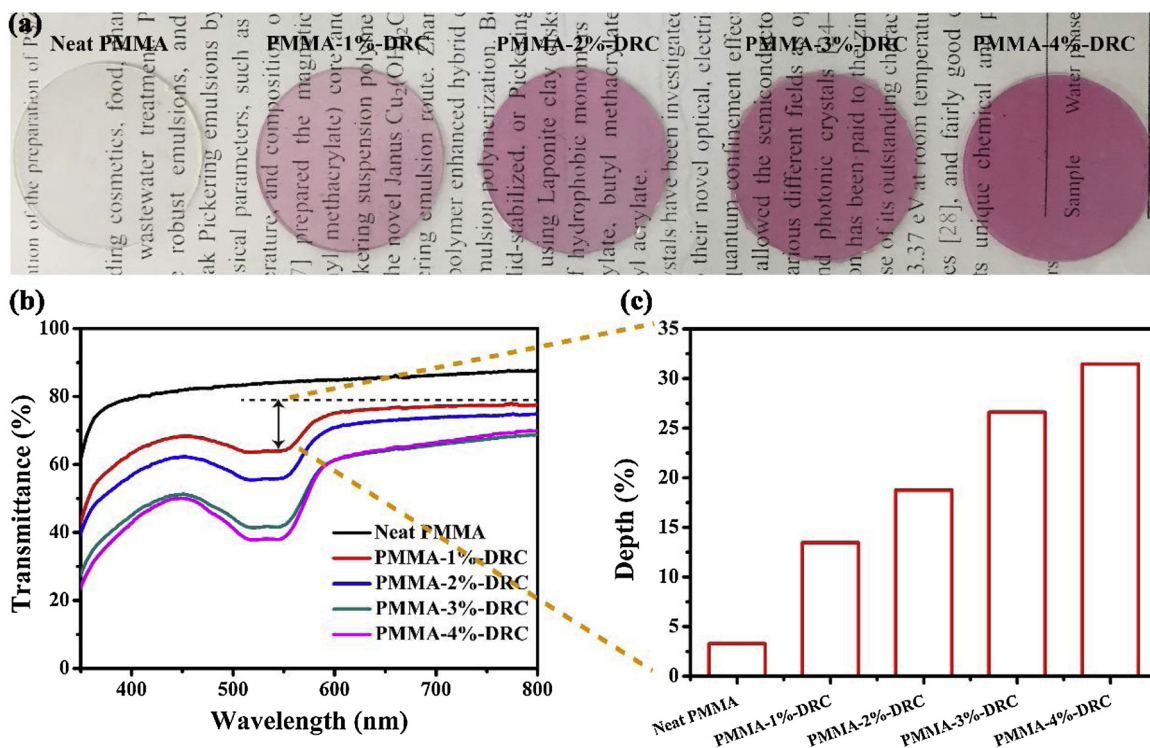
Fig. 4. (a) Photograph of compressed PMMA nanocomposites with different DRC loading, (b) UV–Vis spectra and (c) color depth (from 550 nm to 800 nm) of the colored PMMA/DRC composites with different DRC contents.

Table 1
T_{onset} and T_{max} of the neat PMMA and PMMA/DRC composites.

Sample	T_{onset} (°C)	T_{max} (°C)
Neat PMMA	366.8	389.4
PMMA-1%-DRC	373.2	391.6
PMMA-2%-DRC	384.7	390.6
PMMA-3%-DRC	386.2	391.1
PMMA-4%-DRC	390.7	395.3

increasing DRC content within the experimental error, probably due to the conflicting effect of filler content and the association of DRC [29]. This might be attributed to the network formation of DRC in the PMMA matrix following compression [30]. The tensile strength of PMMA/DRC composites is shown in Fig. S7 (in the Supplementary Information Section). The tensile strength of composites decreased with increasing DRC concentration in PMMA matrix due to the poor compatibility between DRC and PMMA. The changing trends of mechanical properties of the PMMA/DRC composites are similar to those of PLA/CNC composites prepared by Pickering emulsion approach [29].
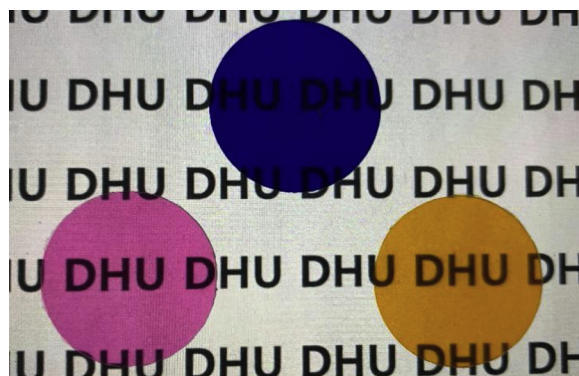

Fig. 6. Optical image of colored PMMA/DRC composites with different color.

3.4. Differently colored PMMA/DRC composites

As is shown in Fig. 6, PMMA/DRC composites with different color can be prepared by using RC dyed with blue, red and yellow dyes as the
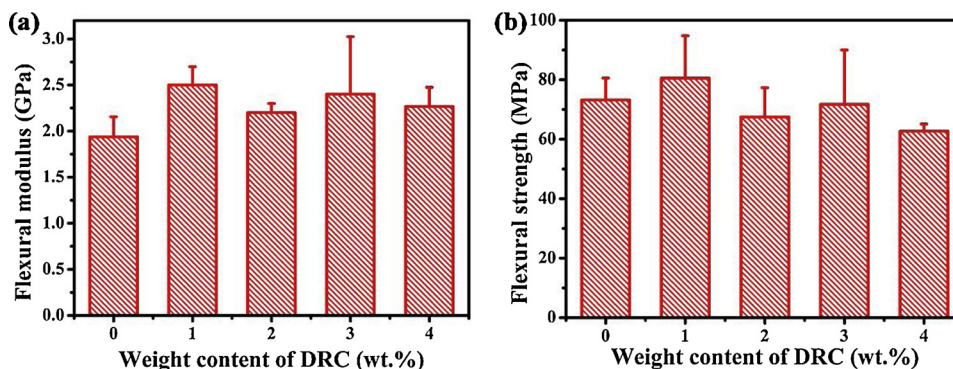

Fig. 5. (a) flexural modulus and (b) strength of neat PMMA and PMMA/DRC composites.

Pickering stabilizer. According to our previous research, any desirable color shade could be produced by blending DRCs of the three prime colors, namely red, blue, and yellow. Therefore, the procedure reported herein is generic to making colored PMMA/RC composites of any color. The wasted and dyed PMMA film can be reused by thermal processing. Transmittance and color intensity were maintained in the reprocessed film as shown in Fig. S8. (in the Supplementary Information Section).

4. Conclusions

Colored polymer/DRC composites prepared via Pickering emulsion approach are reported with PMMA as matrix material chosen to demonstrate the approach. Color was achieved by grafting dye molecules to cellulose. The colored Pickering emulsion containing oily PMMA phase could be efficiently stabilized by DRC. Composite microspheres were prepared by removing the solvent DCM and water. The color of the composites is uniform in the PMMA matrix and no DRC aggregate is observed. The color depth of the composites could be tuned via adjusting the DRC contents in the PMMA matrix. An increase of the thermal stability was observed for the nanocomposites when compared with the neat polymer. The flexural modulus of PMMA composites was enhanced for all DRC contents. The Pickering emulsion procedure used in this work can be applied to obtain composites exhibiting other colors, reinforced by the environmental friendly DRC, as well as to other polymers, thus providing a generic platform.

CRediT authorship contribution statement

Yunchong Zhang: Conceptualization, Data curation, Formal analysis, Investigation, Writing - original draft. **Lei Ding:** Formal analysis, Investigation. **Binbin Ming:** Formal analysis, Investigation. **Bijia Wang:** Conceptualization, Supervision, Writing - review & editing. **Xueling Feng:** Supervision, Writing - review & editing. **G. Julius Vancso:** Supervision, Funding acquisition. **Xiaofeng Sui:** Conceptualization, Funding acquisition, Resources, Supervision.

Declaration of Competing Interest

The authors declare no competing financial interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.colsurfa.2020.124601.

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