European Polymer Journal

Volume 49, Issue 6, June 2013, Pages 1146–1150

http://dx.doi.org/10.1016/j.eurpolymj.2013.04.009

http://www.sciencedirect.com/science/article/pii/S001430571300178X

Recent advances in bio-based polymers and composites

Preface to the BiPoCo 2012 Special Section

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1. Introduction

The increasing environmental awareness of the society has become an important factor in recent decades affecting legislation, commerce and industry as well as research and development to a great extent [1-7]. This tendency has also been recognized by the European Community, which supports numerous projects in order to promote innovative solutions leading to a sustainable economy. Three such projects of the Seventh Framework Programme with overlapping scopes, Biostruct [8], Forbioplast [9] and Woody [10], focused on the valorization of forest-derived resources for the production of various bio-based products, including polymers, additives, and composites with natural reinforcements. The leaders of these projects decided to join forces to organize a conference in order to create a possibility to disseminate their results as well as to increase the efficiency of their research and development by exchanging ideas with leading experts in the field. The International Conference on Bio-based Polymers and Composites (BiPoCo 2012) was organized for the first time in Siófok, Hungary, between May 27th and 31th, 2012, with 234 registered participants delivering more than 90 oral and 110 poster presentations. Scientific and technological lectures focused on the theory and practice of biopolymers, renewable-based monomers, fillers and additives as well as sustainable polymer blends and composites with possible application in packaging, agriculture, automotive or biomedicine. In the following sections we provide a short overview of the main research areas and presentations related to the event, and by doing so, continue the line set by Filip Du Prez, Jean-Marie Raquez and Philippe Dubois as Editors of the recent Biobased Polymers and Related Materials special issue of the European Polymer Journal [11]. Below we introduce to the reader the BiPoCo 2012 Special Section containing four feature articles and several research papers.

2. Natural building blocks

Nature offers an extremely wide range of macromolecules and small molecular weight compounds in abundance. Quite a few of these materials might be valuable resources for the chemical industry, if appropriate and cost-effective techniques can be developed for their extraction, characterization and conversion. Biomass, however, generally consist of a very complex mixture of organic compounds, the separation of which is a rather challenging task. Another difficulty is that it is very difficult to define and maintain constant composition and quality of the raw materials, because several environmental factors affect these characteristics, e.g. species of the source, geographical region, climate, weather, etc. In some cases, even describing the exact chemical structure of natural macromolecules proved to be difficult; one of the most abundant biopolymers, lignin is an excellent example. However, a profound knowledge of the structure of lignin and other complex natural compounds is a crucial requirement for their successful valorization.

The ability of natural systems to fulfill a certain function, on the other hand, lies in their complexity, thus virgin, extracted natural compounds can rarely be applied without modification. Lignin, for instance, represents a renewable source of aromatic compounds being able to provide a wide range of chemicals. In their feature article, Lange et al. [12] give a state-of-the-art review of the structural aspects of lignin including its isolation, characterization and modification, focusing on the oxidative upgrade of this polymer. The authors emphasize that the variable complex structure of lignin (see Fig. 1) requires the development of modification strategies aimed at controlling and tailoring its multi-functionality, i.e. selective oxidation, reactive groups protection and functionalization. The reactive free hydroxyl groups of lignin make this material an ideal structural base for the synthesis of complex polymeric systems, e.g. polyurethanes (PU), as Cinelli et al. suggest [13]. In their paper, the authors report the production of partially renewable-based PU soft foams with possible applications in

the packaging and automotive industries. Other natural phenolic compounds can also provide important complex building blocks, among which the significance of tannins should be emphasized, because of their abundance in nature. Gallic acid (Fig. 1), one of the main components of hydrolyzable tannins, can be used as a renewable monomer for thermosetting applications. Aouf et al. [14] describe the production of a bio-based epoxy resin using a novel glycidyl derivative of gallic acid, which demonstrates the feasibility of formulating epoxy thermosets based completely on a natural phenolic compound.

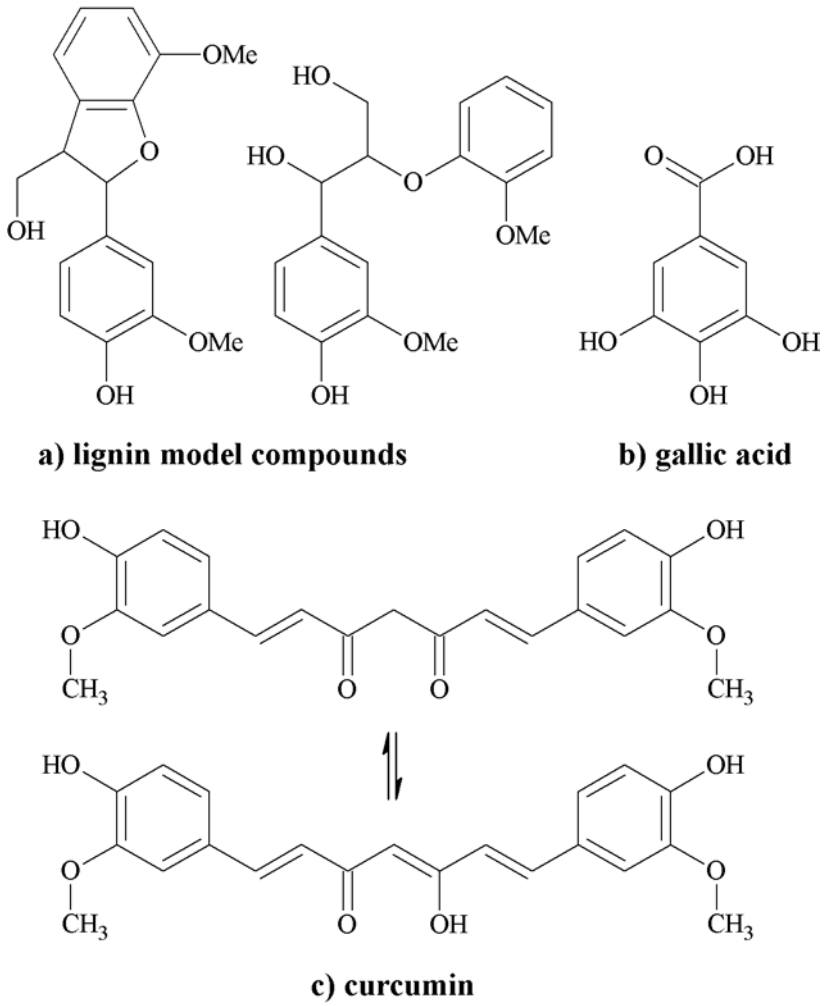

Fig. 1 *Natural phenolic compounds (a) lignin model compounds [12], b) gallic acid [14], c) curcumin [16]*

Synthetic phenolic antioxidants are widely applied as stabilizers for polyolefins and many other polymers to protect them during processing and application. The possible effect of the reaction products of these compounds on the environment as well as on human health, however, raised several questions recently, thus their substitution with environmentally friendly alternatives would be highly desirable. Several natural antioxidants, and many phenolic compounds among them, might be ideal candidates for this purpose [15,16]. The effect of one of such materials, curcumin (Fig. 1), on the melt stability of polyethylene was investigated for the first time by Tátraaljai et al. [16]. The authors found in their study that curcumin is more efficient than the synthetic antioxidant applied routinely in practice, while they also suggested a possible stabilizing mechanism, the knowledge of which is an important condition for the development of suitable stabilizer packages.

Besides natural phenolic compounds, the main constituents of plant oils, such as triglycerides, also represent a major potential alternative feedstock for the polymer industry [17, 18]. They are available in large quantities at low price, while their chemical modification might lead to a large variety of monomers [19] and polymers [20, 21]. Although in many cases plant oils do not require extensive modification before their application, a wide range of techniques are available for the synthesis of valuable, bio-based derivatives. For their renewability and interesting properties, a growing interest can be observed in the use of triglycerides and fatty acids as precursors of monomers for various polymers, e.g. thermosets [22] and elastomeric compounds [23]. Hydroxylated plant oils are of high importance in polyurethane production, as they might replace conventional fossil-based polyols [24, 25]. Since a wide range of neat or modified triglycerides can be used for this purpose, describing the correlation between their chemical structure and the macroscopic properties of the resulting polymer is of large importance. Fridrihsone et al. [25] studied the impact of molecular weight between

cross-links, urethane group concentration and dangling chain concentration on structure, physical, mechanical and thermal properties of PU networks.

3. Biopolymers and their modification

The generally accepted definition of biopolymers covers polymers that are bio-based, biodegradable or both [26]. The substitution of conventional raw materials with renewable feedstocks and the application of biodegradable and compostable plastics can be advantageous in many areas. Nevertheless, besides their obvious benefits, these materials also possess several drawbacks. The abundance of natural polymers results in low price, but their properties do not come even close to those of commodity plastics. While synthetic biopolymers, i.e. polymers based on renewable monomers are more expensive, their properties are also often inferior compared to fossil-based alternatives, or at least do not correspond to the expectations of converters or users. As a consequence, biopolymers generally are not applied without modification. In their feature article, Imre and Pukánszky [27] give an overview of the various physical (plasticizing, blending [28], composite preparation) and chemical (copolymerization [29], grafting [30]) modification approaches, focusing on structure (the typical morphology of bi-component polymer blends can be observed on Fig. 2), interfacial interactions, macroscopic properties and compatibilization in biopolymer-based blends. Since the structure of bio-based and biodegradable polymers generally favors their chemical modification, special emphasis was placed on reactive compatibilization techniques and reactive processing. The application of biopolymer blends is reviewed in the paper including advanced biomedical applications as well as other commercial areas.

Various applications require considerably differing properties; bio-based grades are mostly used in automotive and electronics, while biodegradability is particularly advantageous in agriculture and packaging. A biopolymer blend consisting of starch,

polycaprolactone and chitosan was studied by Alix et al. [31], in order to obtain an active food packaging material with water scavenging effect. The lack of a plasticizer in the blend decreases the risk of migration of low molecular weight compounds into the product, while chitosan acts as antimicrobial agent increasing shelf-life.

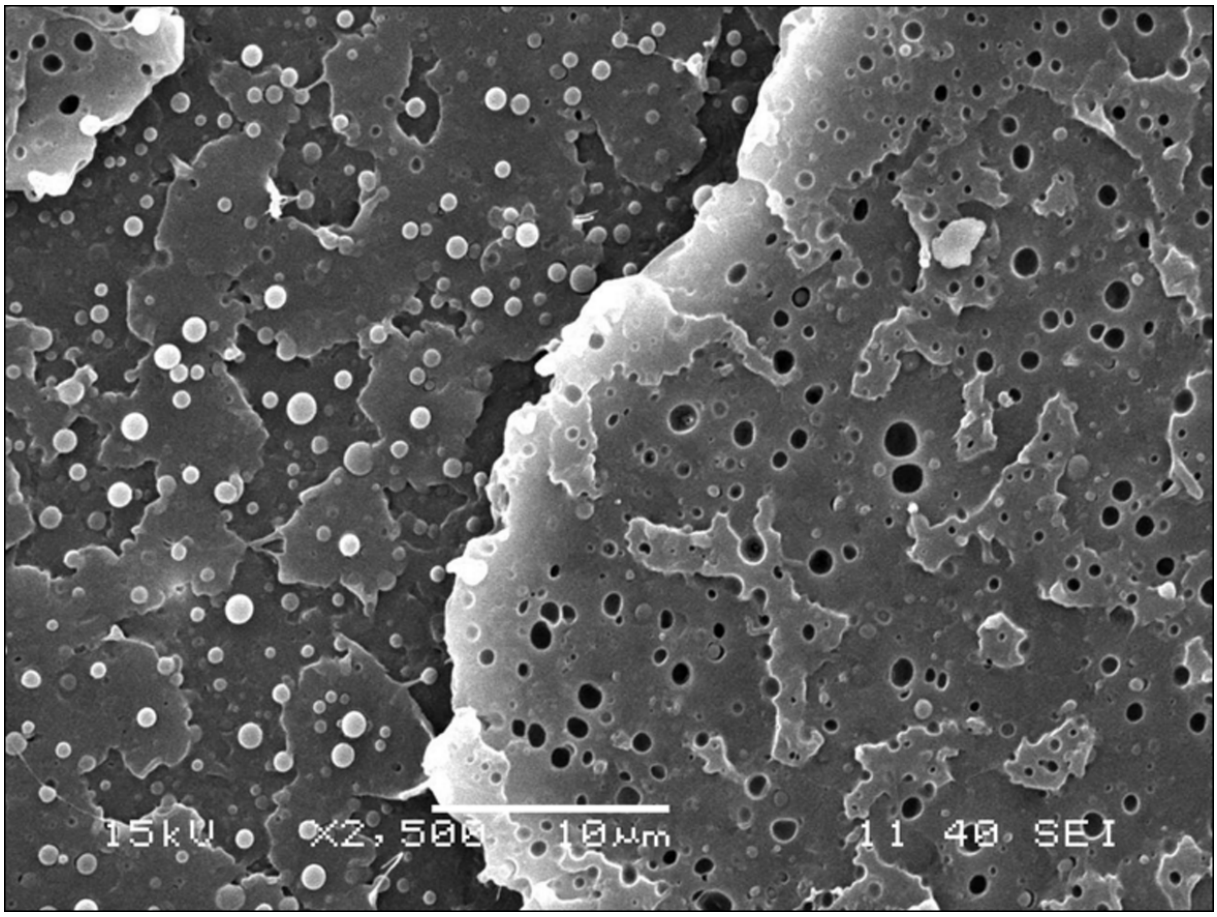

Fig. 2 *Morphology of a poly(lactic acid)/poly(butylene adipate-co-terephtalate) (PBAT) blend (10 v/v% PBAT, fracture surface, SEM, 2500x magnification)*

Biopolymers can also be modified by the incorporation of fillers and reinforcements, thus providing various biocomposites. Although conventional, mineral fillers might also be applied [32], most studies focus on the potential use of natural lignocellulosic fibers, i.e. wood flour, sisal, flax, etc. into both conventional and biopolymers [6]. These biocomposite materials predominantly find applications in the building and automotive industry. Recently, environmental concerns lead to a considerable spread of renewable-based and biodegradable ma-

trices, many of these based on plant oils, e.g epoxy, alkydic and polyurethane thermosets, as well as PU elastomers, as Mosiewicki and Aranguren [33] emphasize in their feature article. The authors review the effect of different particles, synthetic and natural fibers as well as nanosized inclusions in triglycerides based polymeric systems. Lignocellulosic reinforcements might present a viable alternative to glass fibers applied traditionally, while biopolymer systems containing particles with one or more dimensions in the nanometer scale, i.e. bionanocomposites, form a special class of materials possessing a range of unique characteristics with respect to gas and water vapor permeability, thermal stability, fire resistance, mechanical and optical properties, etc. The characteristics of biopolymers can be altered using either natural nanofibers (cellulose nanofibers and nanowhiskers) [34], as in the case of a bacterial cellulose reinforced chitosan film shown in Fig. 3 [35], or inorganic nanofillers (silica, layered silicates) [36], providing different combinations of properties [37]. In order to achieve nanoscale dispersion, i.e. intercalated or exfoliated structure resulting in superior properties, nanoclays must be modified with suitable organic compounds in order to promote the separation of the silicate layers. Fernández et al. [38] compare the effect of different surface modification strategies on the properties of poly(lactic acid) nanocomposites using various characterization techniques. A mixture of intercalated and exfoliated structure was confirmed in all cases.

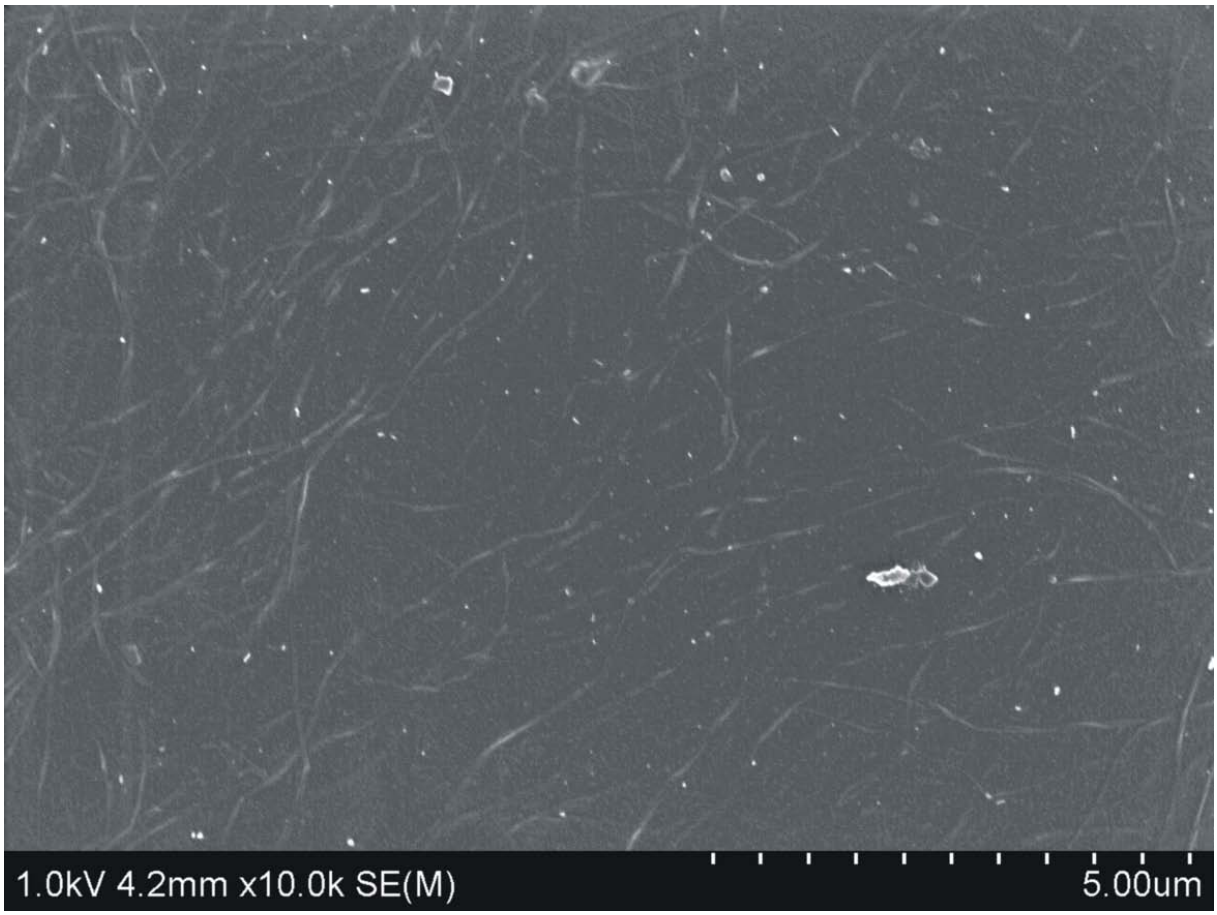

Fig. 3 *Morphology of a chitosan film reinforced with bacterial cellulose nanofibers (5 v/v% nanofibers, SEM, 10000x magnification) [35]*

4. Advanced biomedical applications

Bio-based and biodegradable polymeric materials are applied in many fields ranging from packaging and agriculture to applications with higher added value, i.e. electronics and automotive. Advanced biomaterials are also being used in increasing quantities in biomedical applications in various forms [39]. One of the main functions of these materials is to bridge the interface between artificial and biological systems, i.e. they must be biocompatible. Biodegradability is also favorable in most cases, but a long list of other important and specific requirements can also be provided. Using appropriate modification techniques, natural and synthetic biopolymers are able to meet these requirements, while the biomedical field tolerates the rather high price of these materials much better than other application areas, thus

novel ideas find their way to everyday practice on a shorter time scale in this field. Examples include nano- and microparticles for drug delivery and controlled release, membranes for wound dressing or porous matrices (scaffolds) [40, 41] for tissue engineering purposes.

Responsive materials in general, and responsive hydrogels in particular, have been in the focus of recent scientific interest. Hydrogels [7, 42, 43] are cross-linked three-dimensional hydrophilic polymer networks, thus they are highly swellable in aqueous fluids, as Fig. 4 illustrates. Their structural similarity to body tissues makes them ideal biomaterials. Responsive hydrogels are able to produce a pre-determined response to certain environmental stimuli. Gyarmati et al. [44] review redox-sensitive systems in their feature article focusing on thiol-disulphide exchange reactions, which have large biological relevance. Besides the incorporation of thiol or disulphide functional groups into polymer networks, the authors also discuss possible applications of such materials.

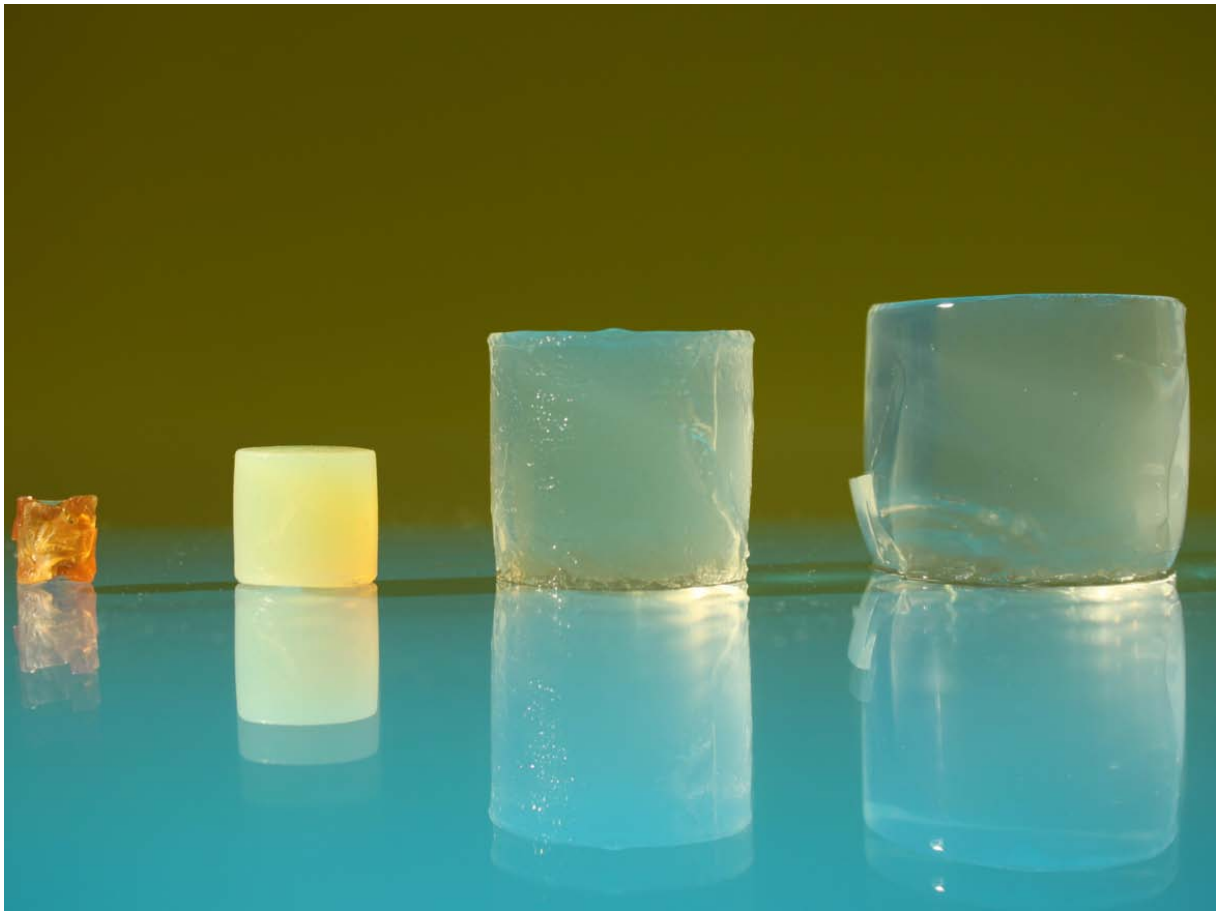

Fig. 4 *pH-sensitive poly(aspartic acid–gelatin) co-network hydrogels in a dry state and swollen in different water based buffer solutions*

5. Conclusions

In the near future the role of both renewable-based materials and biodegradability is expected to grow in the polymer industry, thus scientific research and development must pay more attention to these areas. With the articles collected in the BiPoCo 2012 Special Section of the European Polymer Journal, we offer an overview of recent developments in the field of biopolymer science to the reader, with an outlook for future developments. The interest in the materials discussed in this contribution, the success of BiPoCo 2012 related to them, and the very positive response of the participants encouraged our group to organize the second conference with an extended scope including advanced biomaterials. BiPoCo 2014 will take place in Visegrád, Hungary, from August 24 to 28 in 2014.

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